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Helmut Bansa zum 65. Geburtstag

Seit 1985 ist Helmut Bansa Herausgeber der Zeitschrift RESTAURATOR. Seit dieser Zeit hat es noch nie einen Artikel, einen Beitrag oder auch nur eine Notiz in dieser Zeitschrift gegeben, die Helmut Bansa nicht kontrolliert, redigiert oder gar selbst geschrieben hätte. Es ist also eine Premiere, wenn dieses Prinzip heute zum ersten Mal durchbrochen wird.

Der Herausgeber wird gewissermaßen am Erscheinungstag von Heft 4 des Jahrganges 2001 65 Jahre alt. Alle, die ihn kennen, werden es nicht glauben – ich als sein Verleger seit 1997, sicherlich am allerwenigsten.

Es war im Jahr 1970, als ich zum ersten Mal einen Gastvortrag in der Bayerischen Bibliotheksschule halten durfte und zu den jungen Studenten, die meinen Ausführungen mehr oder weniger hingebungsvoll lauschten, gehörten Hermann Köstler, der heutige Direktor der Zentralbibliothek in Zürich, und Helmut Bansa. Daraus entwickelte sich ein außerordentlich sympathischer Kontakt, der nicht nur bis heute gehalten hat, sondern noch viele Jahre währen soll.

Helmut Bansa wurde am 18. Dezember 1936 in Berlin geboren, studierte Mediävistik und wurde 1965 promoviert. 1966 erhielt er ein Stipendium der Deutschen Forschungsgemeinschaft und war von 1968 bis 1972 wissenschaftlicher Mitarbeiter am Mittellateinischen Wörterbuch. Ab 1970 war er Bibliotheksreferendar an der Bayerischen Staatsbibliothek, legte die Fachprüfung erfolgreich 1972 ab und wurde im gleichen Jahr Bibliotheksrat zur Anwendung, 1974 offiziell Bibliotheksrat, 1976 gleich Oberbibliotheksrat und 1983 Bibliotheksdirektor. Seit den späten 70er Jahren war er der Direktor des Instituts für Buchrestauration der Bayerischen Staatsbibliothek. Hier hat er Maßgebliches und Wegweisendes geleistet, das weltweit Anerkennung gefunden hat.

Es war kein Zufall, daß er in die Gremien der IFLA berufen wurde, da auch die ausländischen Kollegen von seinen Erfahrungen profitieren wollten. Es war absolut folgerichtig, daß er auch noch nebenamtlich Leiter der Staatlichen Fachakademie zur Ausbildung von Restauratoren wurde. Die Geburt dieser Staatlichen Fachakademie war eine unendlich schwierige Angelegenheit und drohte immer wieder zu scheitern. Nur seinem Engagement, seinem Durchsetzungsvermögen, seiner berühmt-berüchtigten Hartnäckigkeit war es zu verdanken, daß dieses Experiment gelungen ist und wieder einmal maßstäblich wurde. Viele Jahre war er auch Schriftleiter der Mitteilungen der „Internationalen Arbeitsgemeinschaft der Archiv-, Bibliotheks- und Graphikrestauratoren“ (IADA) bzw. ab 1976 Redakteur der Zeitschrift „Restauro“ im Callwey Verlag, in die die Mitteilungen integriert wurden und die sich ebenfalls mit allen Fragen der Restaurierung von Bibliotheks-, Museums- und Archivmaterialien befaßte.

Es war ein ganz besonderer Glücksfall, daß der Verlag Munksgaard ihm 1985 die Herausgeberschaft ab Jahrgang 7 für die Zeitschrift RESTAURATOR übertrug. Es gehört zu den Glücksfällen für den K. G. Saur Verlag, daß es uns gelang, 12 Jahre später diese Zeitschrift zu übernehmen und mit Helmut Bansa fortzuführen und weiter auszubauen. Diese Zeitschrift ist das Werk von Helmut Bansa. Sie ist eine großartige Leistung, weltweit anerkannt, was auch dadurch bewiesen wird, daß es immer wieder gelingt, noch neue Abonnenten zu finden, und zwar mehr als Abbesteller.

Alle guten Wünsche begleiten Helmut Bansa auf seinem weiteren Lebensweg. Wir danken ihm und gratulieren ihm. Wir wünschen alles, alles Gute und wir sind glücklich darüber, daß dieser Geburtstag überhaupt keine Bedeutung für die Terminierung einer Herausgeberschaft hat.

Klaus G. Saur

Restaurator, 2001, 187–207
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A Method for the Non-Destructive Analysis of Paper Based on Reflectance and Viscosity

by JOSEP Mª GIBERT VIVES, JOAN RAMON MENDO ESCODA, ROGELIO AREAL GUERRA & LUÍS ALBERTO HERNÁNDEZ

INTRODUCTION

The most evident signs of paper ageing are yellowing and loss of mechanical strength. Essentially, these phenomena are linked with an increase in copper number and a decrease in degree of polymerization respectively.

It is usually accepted that the main cause of ageing is the acidity contained in the paper. This is why conservation processes are focused mostly on deacidification and the addition of an alkaline reserve. All deacidification processes, both in aqueous and non-aqueous media, succeed in inhibiting, to some extent, the main paper degradation reactions; therefore the tendency to embrittlement is slowed and the document can still be consulted.

Much effort is taken to solve the problem of strengthening already weakened paper. Yellowing is not considered such a severe problem as embrittlement, unless it interferes with the clarity of the writing. For this reason in mass deacidification processes simultaneous bleaching is not usually required, although changes in colour are included as side effects to be controlled for aesthetic reasons.

Degradation chemistry

To assess the effectiveness of a mass deacidification treatment it is necessary to compare the properties of paper over time of both treated and untreated samples. The property most often measured is folding endurance, since flexibility of the paper is necessary for the document to be useful. However, because of its great variability a large number of samples are needed to test this and, where papers are very brittle, it has only an indicative value. Chemical data such as pH, alkaline reserve and metal content, such as magnesium and/or calcium, ions present in most deacidification reagents and in an alkaline reserve, are the background on which the treatment efficacy and uniformity are established. Tests to assess the

cellulosic polymer chemical state, as degree of polymerization (viscosimetric), molecular weight distribution (gel permeation chromatography), estimation of reducing end groups (copper number), total carbonyls (derivatization) and carboxyls (methylene blue), as well as alkali soluble fraction are very useful to indicate degradation processes. These methods, however, are only applicable for pure cellulose paper that does not contain lignin and hydrophobic resins. Therefore, before these tests take place some charges and glues must be eliminated, otherwise high relative errors will occur.

Yellowing

Brightness loss, also called colour reversion, is one of the problems that paper producers, restorers, conservators and librarians face, because brightness range is not stable, even in chemically bleached paper. As the reason for this impairment is not really known, completely effective methods cannot be applied to avoid it. Yellowing hastens in light exposure, heat, under the influence of chemical agents and high humidity. A number of reasons for yellowing have been studied, i.e. residual lignin, hemicelluloses, pH, metallic catalysts, rosin, carbonyl groups, foxing, low bleaching, UV radiation, etc. Even chemical pulps completely free of lignin can turn yellow. In this case, the reasons for this phenomenon are assigned to polysaccharides themselves, especially if their polymeric chains are short (hydrocellulose) or oxidised (oxycellulose); this means that, the more olygomer and glucose, the higher the tendency to create coloured compounds. It has been said that a decrease in the degree of polymerization only does not directly lead to a significant discoloration of the cellulosic polymer.

The combined effect of oxidation on an already degraded material is the main cause of discoloration. This hypothesis is confirmed by the fact that a paper containing alkaline reserve, i.e. a paper not subjected to acid hydrolysis, turns less yellow than another sample of the same paper, without such reserve, under the same environmental conditions.

The reasons of cellulosic material yellowing have been widely reviewed[1]. Pure cellulose strongly absorbs UV radiation under 200 nm and absorbs UV less strongly between 200 and 300 nm, but the spectrum exceeds the UV limit of 400 nm, extending over the whole visible range. The main light absorbing species present in cellulosic materials are acetal, carbonyl and carboxyl functional groups. Lignin strongly absorbs violet light below 400 nm, gradually increasing the absorption to 200 nm, with a distinct peak at 280 nm (UV region). Rosin and other additives, removable or not, are clearly yellow, absorbing between 300 and 440 nm (violet-blue light).

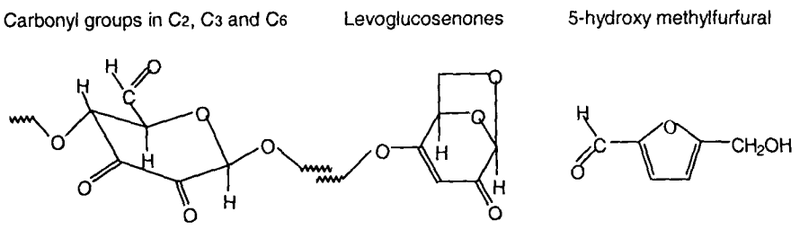

Fig. 1: Some structures responsible for aged paper coloration, free from lignin.

All chemical reactions causing paper degradation are also responsible for the creation of chromophores, especially thermal oxidations and photo-oxidations. Other reactions such as condensation, crosslinking and dehydration due to heat and strongly acid environment, also produce coloured chemical compounds[2, 6]. Metallic impurities play an important role as catalysts to oxidation processes[3, 4] (cf. Fig. 1).

In principle, simple acid hydrolysis does not affect colour, but low-molecular-weight products are more prone to oxidation and colour formation than cellulose chains.

Cellulose oxidation produces carbonyl groups (keto and aldehyde), especially at the carbons 2, 3 and 6, and carboxyl groups at carbons 6 and 1 of the anhydroglucose unit. Reducing end groups (aldehyde or hemiacetal), as well as carboxyl groups, are less important in yellowing than keto groups. However, the joined presence of carbonyl and carboxyl groups intensifies the colour. At high temperatures, oxidation reactions accelerate and chromophore group formation increases. In the aforementioned review[1], the following main factors of paper colour formation are cited:

- Carbonyl groups (keto) in carbons 2 and 3 of the anhydroglucose unit have an influence on colour. Carboxyl groups have ca. ten times less influence on colour creation than carbonyls during heating at 105°C.
- Ionic exchange of hydrogen ions caused by sodium ions in carboxyl groups at carbons 6 and 1 increases coloration, whereas exchange with calcium ions decreases.
- Secondary hydroxyl groups of carbons 2 and 3 do not have an influence on colour, even in cellulose widely hydrolysed with HCl.
- End and side chain aldehyde groups, and terminal hemiacetal groups of cellulose chains, do not cause coloration.
- It seems that the degree of polymerization has no effect on change in colour.

However, it is proved that partially oxidised cellulose is more vulnerable to acid hydrolysis; so there must be a relation between the number of chromophores and the degree of polymerization.

Measurement of yellowing

Paper colour is measured according to standard methods. The simplest one, which does not need a spectrophotometer, is the measurement of 457 nm reflectance, as at this wavelength a major change of the reflectance curve is observed during ageing. Kubelka-Munk law has also been applied, because it relates K/S parameter with chromophore concentration[5]. ISO-CIE whiteness should be applied only to papers qualified as "white", i.e. modern papers containing fluorescent whitening agents. Old papers usually are not white; so it is better to use standard colour coordinates, such as CIE coordinates L^*, a^*, b^*, C^*, h^*.

Purpose of this evaluation

The visual comparison of several tested papers showed a very different yellowing tendency, so that we supposed cellulose depolymerization might be related somehow to a change of colour. Moreover, some papers were too fragile and heterogeneous to give enough profitable results in such mechanical tests as tensile strength and folding endurance. This led us to focus only on the viscosimetric degree of polymerization and the colour. Colour measurement is a non-destructive, fast, easy to use, repeatable and reproducible method. Measuring the degree of polymerization of cellulose from the viscosity of its solutions in a standard solvent is also an accurate and reproducible method, practically non-destructive, because the samples necessary for this method are quite small, although it is more time-consuming. Both evaluations are independent from fibre morphologic characteristics and from the inner structure of a paper sheet. Mechanical properties, however, are highly dependent on this last quality; in addition, they are more random and destructive.

Many studies have showed that for a vast variety of pulps, the loss of mechanical properties during accelerated ageing do not statistically correlate well with coloration[7]. Some authors[8] had tried to substitute the viscosimetric method to determine the degree of polymerization with the colorimetric method, their aim being to make it easier to check the different kinds of papers selected for a comparative study on the effects of different deacidification methods. They considered that the correlation between colour difference (ΔE) and degree of polymerization

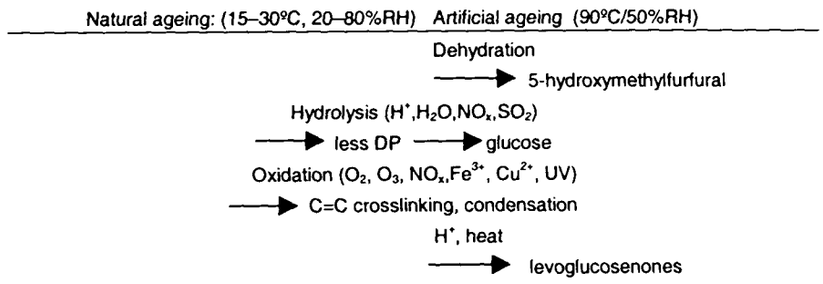

Fig. 2: Simplified scheme of paper degradation

(DPv) for nine papers from a same collection was not good enough (correlation coefficient r=0.76; full correlation being r=1); so they decided to continue their classification by using only the DPv data.

In the present study, the treatment of test data consisted primarily of graphic representation of each parameter (absolute or relative values) for all the papers, deacidified or not. The first result was that all samples tested positive for the Polytechnic University of Catalonia (UPC) deacidification treatment. A comprehensive study of degradation curves will allow all the kinetic equations to be adjusted, from which the permanence and efficiency factors will be calculated for each paper, but this is beyond the purpose of this study. Finally, for every kind of paper, the linear regression method between the viscosimetric degree of polymerization (DPv) and CIELAB colour difference (ΔE) was applied. For samples from the same paper, having a wide range of degradation levels, the regression method applied to ΔE versus DPv provided remarkably good results. The correlation coefficients run in the order of 0.9 and, consequently, viscosimetry may be used primarily and colorimetry a posteriori so that a non-destructive method giving an idea of paper permanence could be applied.

MATERIALS

Papers

- Paper made of cotton rags in 1683, without printed text or handwriting. Lignin test: negative. Prepared with starch. Slightly acid: cold extract pH 5.8. Octavo size sheets. Some leaves have borders degraded by mould, but in general they are kept in very good condition and are very white: Tappi whiteness 67.2, ISO 33.4.

- Craft-made papers in acidic medium in the Netherlands, from 1797, vergé, with water mark *Pieter De Vries & Co.*. Lignin free. Si: 0.92%; S: 0.56%; Ca: 0.28%. Cold extract: pH 5.7. Very homogeneous white folios without writing. Tappi whiteness 58.1, ISO 8.9.
- Machine-made papers of 1890, glossy, with printed lines. Slightly positive lignin test. Al: 1.10%; Si: 0.89%. Produced in acid medium, rosin-alum sized. Cold extract pH: 4.9. No alkaline reserve. Cream-coloured. Tappi whiteness 46.5.
- Current filter paper, trademark *Albet*. Tappi whiteness 86.9, ISO 74.5. It is used to detach leaves from other papers during accelerated ageing inside the climatic chamber. Not deacidified.

METHODS

Mass deacidification (UPC method)

The samples being treated were wrapped in filter paper, to avoid excessive amounts of the deacidification agent being deposited on the surface of the sample. Samples were treated with a deacidifying reagent solution at a liquor ratio 1/3 (v/v). The concentration of this solution is 8.8%, expressed as carbonated di-(1-propoxy)-magnesium, or 4% as magnesium carbonate.

Steps:

- Dehydration of books and stacks of leaves in a vacuum at a temperature not exceeding 50°C. Eight vacuum cycles from 1 bar to 30 mbar; each cycle ranging between 10–20 min. This operation is carried out to dehydrate papers from 6% moisture content to 2.5–3%, which is enough to apply the reagent.
- Addition of the reagent: $Mg(C_3H_8O)_2 . x\ CO_2$ solution ($x \approx 1$) in a 66% (w/w) concentration, corresponding to 30% of $MgCO_3$. After introducing the estimated quantity (66 g/kg paper), it is diluted with the hydrofluorocarbon solvent HFC 227 until it reaches the liquor ratio 1/3, with a reagent concentration of 4% for dry paper mass, expressed in magnesium carbonate.
- As the vessel is filled with HFC 227, the temperature spontaneously falls to 25°C and the impregnation phase begins; this is run for 2 h to ensure good penetration throughout the paper. The solution penetrates the paper quickly, but the deacidification reaction is quite slow, providing the advantage of a better distribution in the leaves, both at the borders and inside, as local pH measurements and alkaline reserve proved.
- Vacuum phase: the reaction vessel is drained off, moving the liquid solution (containing residual salts, excess of deacidification reagent, n-propanol and

HFC 227) into a collecting vessel located in the bottom of the deacidification autoclave. As the paper remains impregnated with n-propanol and HFC 227, a process of heating that lasts between 20 and 35 mins is started. The bottom container is cooled, thus bringing the reaction vessel to a pressure of 1.3 bar abs. The communication valve between both vessels closes automatically once the estimated drying time is reached. Simultaneously, the vessel is opened, the papers are taken out and exposed to air so that the reagent hydrolysis takes place while moisture equilibration occurs. At the same time, the recipient containing the used treatment solution is heated by inverting the cooling cycle, and distillation starts to recover HFC 227, which is collected into the first solvent vessel cooled at a temperature ranging between -25°C and -40°C. The existing temperature gradient between both vessels means that distillation is completed after ca. 2–3 h, with very little loss of HFC 227.

Conditioning of the samples

After airing the samples to eliminate every volatile remainder of the solvent, they were conditioned at 23°C and 50%RH. These conditions were maintained during all following tests.

Accelerated ageing

The samples for our tests were aged in a climatic chamber, trademark *Dycometal*, i.e. maintained constantly at 90±1°C 50±5% for 7, 14 and 21 days. The pages were positioned inside the climatic room separated from each other by filter paper sheets, forming three separate blocks lying on three separate grids.

Intrinsic viscosity

Intrinsic viscosity was determined according to the Spanish standard UNE 57.032-92 Part I[9]. Paper samples were dissolved in cupriethylenediamine (CED). The solution viscosity was measured using a Cannon-Fenske type viscometer immersed in a thermostatic bath Schott CT52 at a temperature of 25°C, with Schott AVS350 equipment. This automatically carries out viscosimeter filling and time of effusion measurements. From time ratios and solution concentration, the intrinsic viscosity or viscosity index limit [η] is determined.

In the deacidified papers, the introduced alkaline reserve might represent approximately 1–3% of the paper mass, which would interfere in the final test result

and later DPv determination. Therefore, an additional wash was given to keep the samples, deacidified or not, in appropriate condition so that they would be completely dissolved in the CED:

- Washing in acetic acid solution at 2%, liquor ratio 1/30 (mass/volume): 3 h
- Washing 3 times consecutively with distilled water, liquor ratio 1/30, 3 h each.
- Drying the samples between filter papers and conditioning.

Measuring CED paper solutions viscosity is not free from risks, since high solvent alkalinity and oxygen might provoke major degradation, especially in very weakened papers. To avoid this samples were dissolved without contact with the air, under a slow nitrogen stream. The viscosity measurement has to be carried out within 12 h after complete solution.

Colour measurement

Colour was measured using a reflection spectrophotometer *Spectraflash S300,* (Datacolor) according to the following conditions:

- Background: *Albet* filter paper. Folded in 8 layers for complete opacity.
- Sample: 2 layers placed on the background
- Number of readings for each sample: 3–6, for both sides
- Large area-of-view (LAV): 6 mm diameter
- Geometry: d/0 (integrating sphere), i.e. illumination: diffuse, viewing angle: 0–10°
- Conditioning time of background and samples: 23°C – 50% RH for 48 hours minimum. This is specifically important for samples coming directly from accelerated ageing; they must recover moisture and temperature equilibrium.

From the measured reflectance spectra the equipment calculates the tri-stimulus values $X\ Y\ Z$, for the CIE standard illuminant D65 and 10° standard observer, from which all relevant colorimetric parameters can be derived.

RESULTS

Degree of polymerization

Paper cellulose degree of polymerization was determined from intrinsic viscosity, a characteristic property of solute and solvent. This is related to the average viscosimetric molecular weight through Mark-Houwink equation:

$$\overline{Mv} = \exp\{(\ln[\eta] - \ln K)/a\}$$

Coefficients K and a are not universally accepted for the cellulose-CED system due to the complexity of cellulose macromolecular structure and its solutions. According to Goring, taken from Sjöström[6], for an average molecular weight of 50,000 cellulose intrinsic viscosity in CED is 181. Replacing these values in the last equation and taking 0.14 as the most accepted value for K, it results in an exponent a=0.6626. By dividing the molecular weight by the mass of the repeating unit, anhydroglucose, i.e. 162, we obtain the average viscosimetric degree of polymerization.

$$DPv = \overline{Mv}/162$$

From the individual values of intrinsic viscosities the corresponding values of degree of polymerization *DPv* were calculated. They are given in Table 1 and Fig. 3.

Table 1: Colorimetric values and degree of polymerization for the three papers, before and after treatment, before and after accelerated ageing.

Sample	De-acidification	Ageing (days)	L	a	b	C	H	ΔE	DPv
cellulose		0	96.69	-0.23	4.02	4.03	93.31	0.00	
1683		0	90.56	1.41	9.55	9.65	81.59	8.42	1257
1683		7	87.70	1.42	10.36	10.46	82.19	11.12	1139
1683		14	82.63	2.95	14.36	14.66	78.38	17.74	604.9
1683		21	81.64	3.07	14.28	14.61	77.88	18.51	579.4
1683	+	0	91.46	1.35	11.55	11.62	83.35	9.30	1257
1683	+	7	88.24	1.64	10.49	10.61	81.11	10.80	1100
1683	+	14	86.39	1.94	11.33	11.50	80.29	12.81	920.2
1683	+	21	86.31	2.08	11.73	11.91	79.95	13.13	755.3
1797		0	87.56	1.22	12.82	12.88	84.55	12.76	608.6
1797		7	82.89	2.28	14.95	15.12	81.32	17.78	573.5
1797		14	80.19	3.41	17.29	17.62	78.83	21.48	434.2
1797		21	78.47	3.68	17.33	17.72	78.02	22.90	426.3
1797	+	0	87.56	0.92	12.39	12.43	85.74	12.44	816.6
1797	+	7	84.95	1.73	14.22	14.33	83.07	15.67	683.9
1797	+	14	81.42	2.44	15.49	15.69	81.05	19.28	480
1797	+	21	80.10	2.73	16.21	16.44	80.43	20.79	463.4
1890		0	82.53	3.44	19.23	19.53	79.86	21.10	181.7
1890		7	75.49	4.93	20.73	21.31	76.62	27.48	140.6
1890		14	70.88	5.95	21.44	22.25	74.49	31.74	103.2
1890		21	66.71	6.52	21.04	22.03	72.79	35.13	92.8
1890	+	0	83.41	3.91	21.66	22.01	79.78	22.46	199.1
1890	+	7	77.71	4.46	21.84	22.29	78.46	26.46	177.4
1890	+	14	73.63	5.39	22.22	22.87	76.37	29.91	169
1890	+	21	72.71	5.38	21.01	21.69	75.64	29.92	119.6

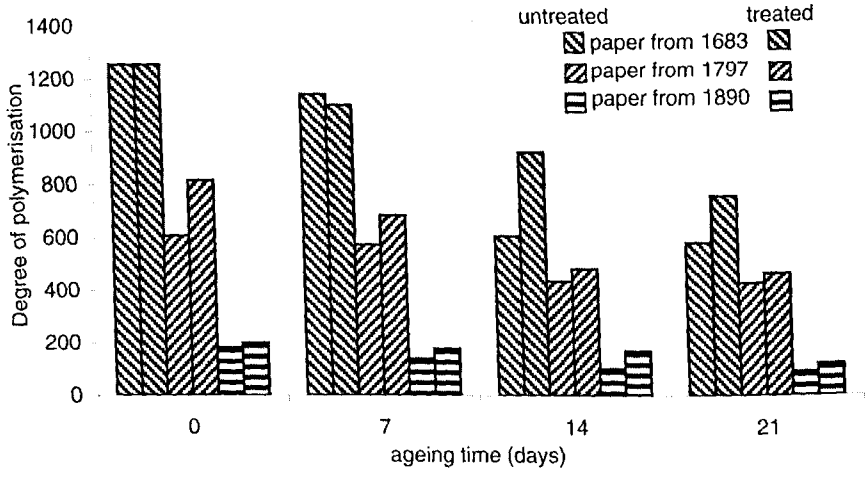

Fig. 3: Average degree of polymerization of historic papers before and after deacidification according to the UPC method during accelerated ageing (90°C 50%RH).

Colorimetric values

Table 1 gives the average values of CIE L^* a^* b^* C^* h^* for the three papers, before and after treatment, before and after accelerated ageing. The sixth column gives the total difference of colour (ΔE) between the samples and the filter paper (cellulose) taken as reference white.

Discussion

Study of changes in colour

We studied more deeply the significance of the colour change, by analysing the changes of the three components of colour $L^*a^*b^*$, or $L^*C^*h^*$ provoked on the paper by moist heat ageing.

Change in lightness L^* (Fig. 4) shows the darkening produced in the course of accelerated ageing. Comparing the values of treated and untreated samples, a positive effect of deacidification is observed in all the cases, the longer the ageing the more distinct it becomes distinct. It is very likely that as a result of the deacidification treatment, the thermal degradation rates are retarded, as this kind of degradation is one of the main causes of darkening.

Changes in chroma C^* (intensity of colour) as a result of both deacidification and of accelerated ageing are illustrated in Fig. 5. Papers from 17th and 18th centu-

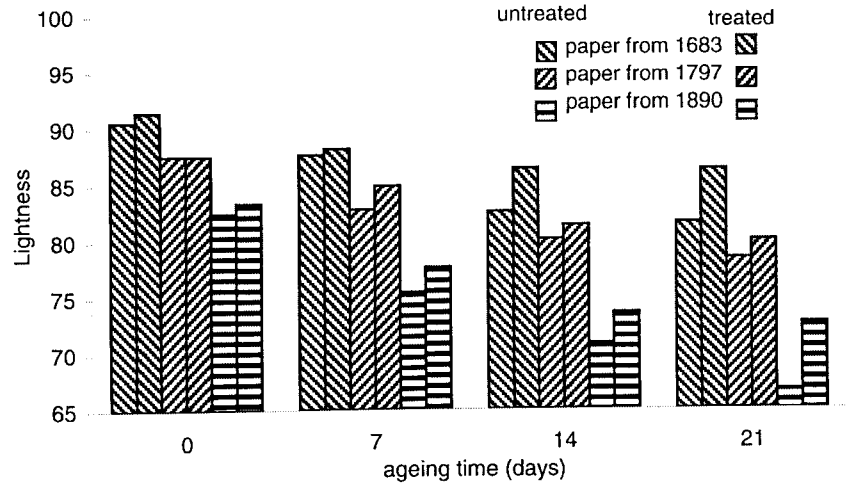

Fig. 4: Change of lightness of historic papers before and after deacidification according to the UPC method during accelerated ageing (90°C 50%RH).

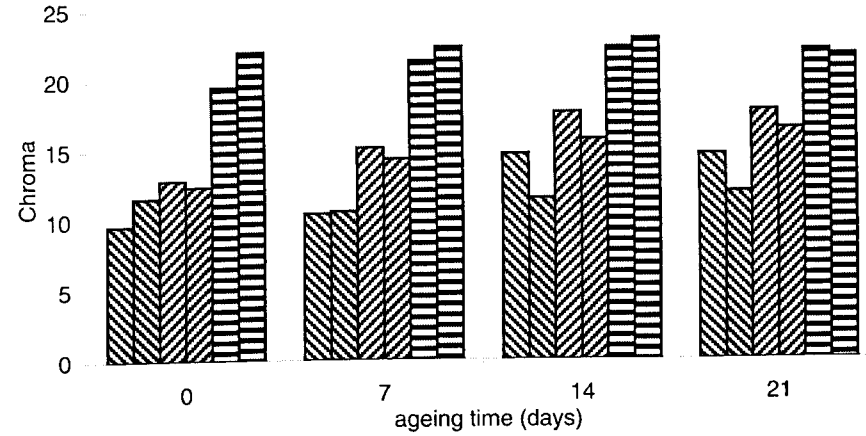

Fig. 5: Change of chroma of historic papers before and after deacidification according to the UPC method during accelerated ageing (90°C 50%RH). For key see Figs. 3 and 4.

ries, originally quite white, become gradually more coloured, and deacidification reduces these changes. In contrast paper from 1890, originally yellowish, shows very little change of chroma. In this particular case, it seems likely that ageing and deacidification provokes only darkening, that is, the formation of degradation products having dull, not saturated, colours.

Changes in hue and chroma are also illustrated in Fig. 6 and Fig. 7 (CIE a* vs CIE b*). It becomes evident that during accelerated ageing the hue changes towards yellow and, in less amount, towards red. The deacidification treatment shows different effects, not only on different kinds of paper, but also after different periods of ageing of one and the same paper. A uniform development can be seen with the paper from 1797: both the deacidified paper and the untreated one kept their hue value in the course of accelerated ageing. Deacidification only reduced the chroma, not the hue. The paper from 1683 behaved very similarly, with the exception that immediately after the deacidification process the paper was significantly more yellow and possibly also a little bit more red: an effect that was, as already said, not stable during accelerated ageing. On the other hand, the paper from 1890 became more yellow due to deacidification, but ageing only provoked a slight increase towards red, whereas the hue of the paper that had not been deacidified changed considerably towards yellow and also towards red after a long period of ageing.

Correlation between colour difference and degree of polymerization

Degradation kinetics can be studied by using different properties of paper. From Fig. 8 it becomes evident that the retention of DPv and the retention of CIE L^* (lightness) vary with time. The decrease is not linear, and fitting the curve to an ideal first order kinetics has gave poor results, this means that different laws will be required to explain the behaviour of specific papers. Changes in DPv were more pronounced than changes in L^*. There was always an improvement in the retention of DPv caused by deacidification; its minimum after the longest period of accelerated ageing was + 5%. The minimum retention of lightness caused by deacidification was +2%.

As it did not seem promising to search for different kinetic laws for the observed degradation, we preferred to look for a relationship between the changes in optical properties and chemical properties. We used a simple linear regression method. The degree of polymerization was taken as independent and the colorimetric data ΔE and CIE L^* as dependent variables. Fig. 9 gives the overall results, and Fig. 10 the results for the XIX century paper. Tables 2 and 3 show the numbers for the linear correlation equation, Yo being ΔEo in the case of total colour difference or Lo in the case of lightness:

$$Y = A^*x + Y_0$$

Those regression lines and their equations are also available via the computer for non-mathematicians.

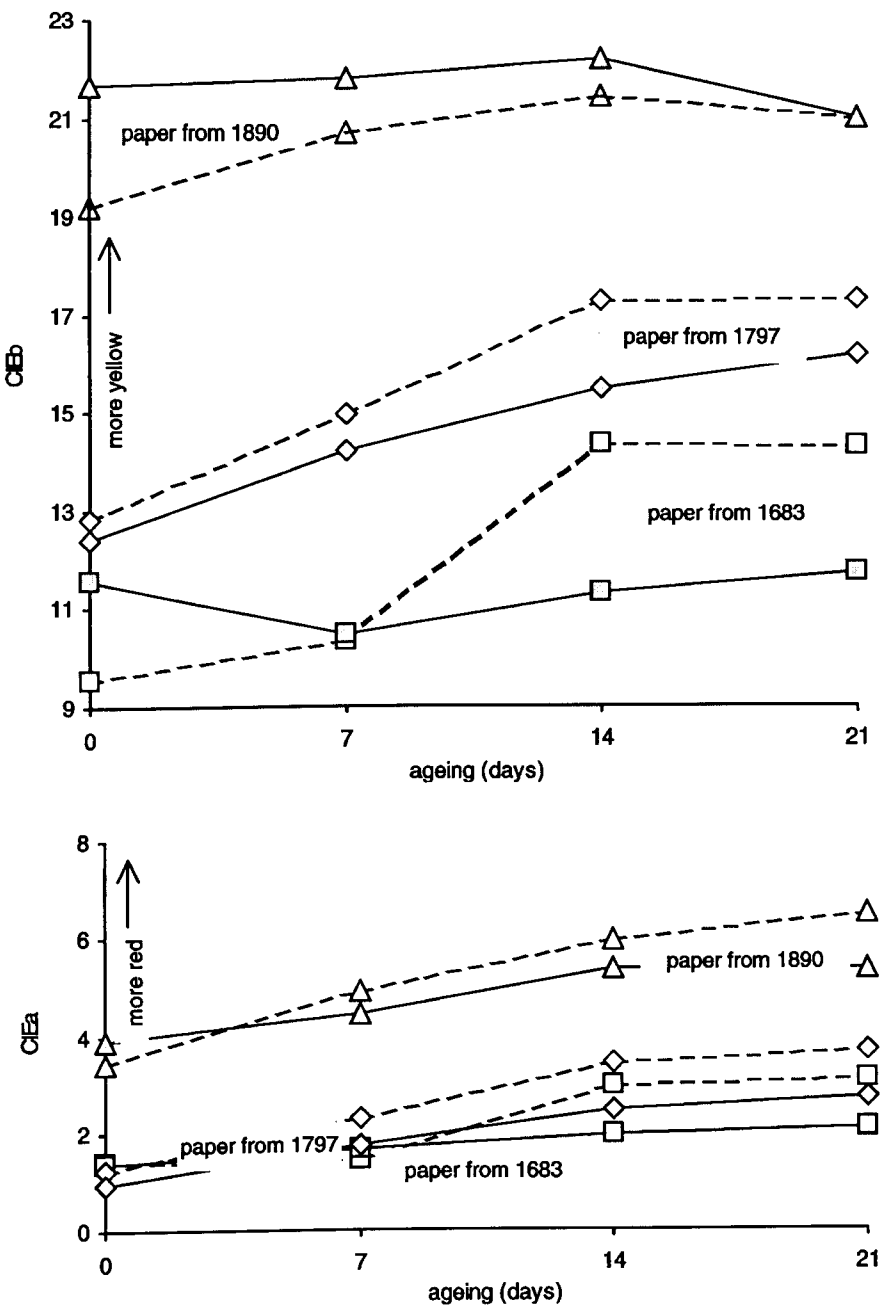

Fig. 6: Changes of chroma and hue of the three papers. – Outlined symbols: untreated; solid symbols: deacidified.

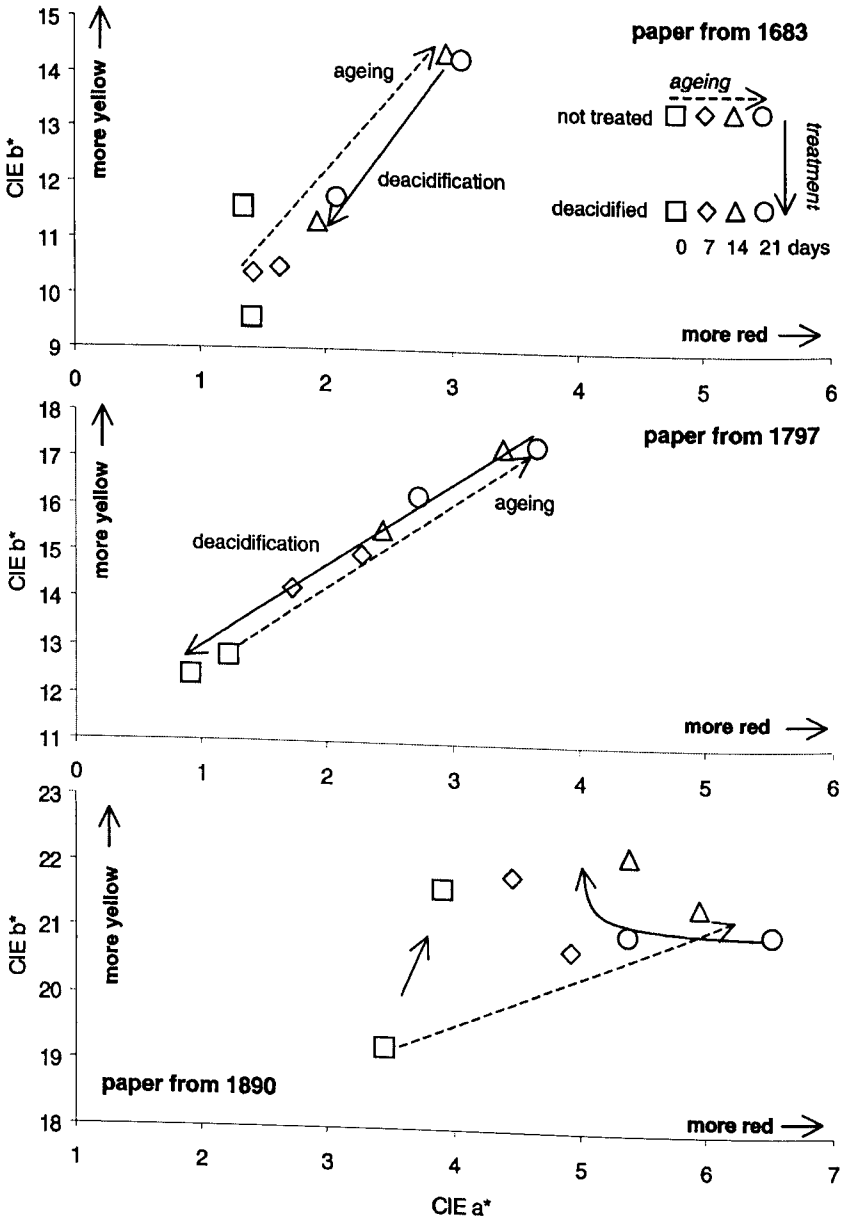

Fig. 7: Changes of chroma and hue of the three papers. Outlined symbols: untreated; solid symbols: deacidified.

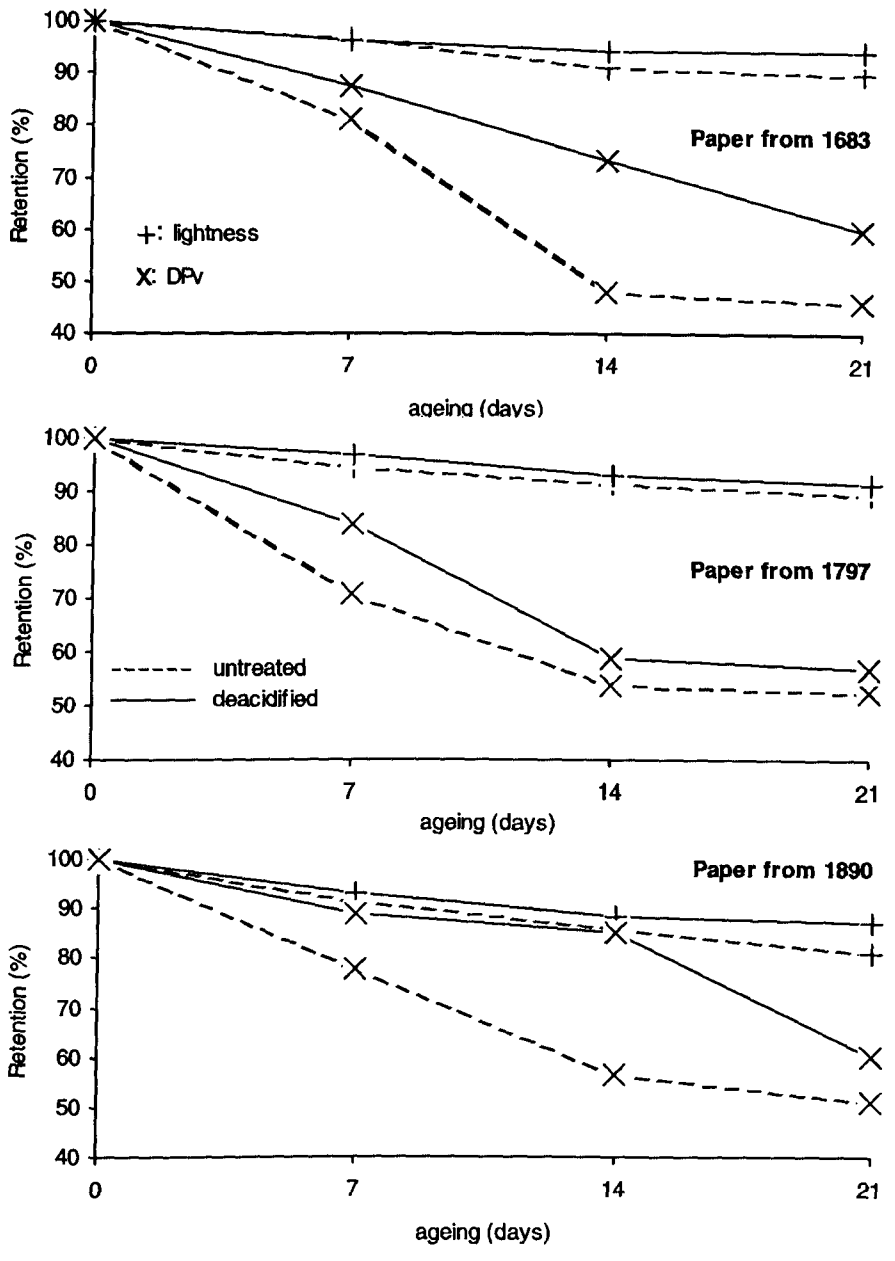

Fig. 8: Rate of degradation measured as retention of lightness (CIE L*) and degree of polymerization

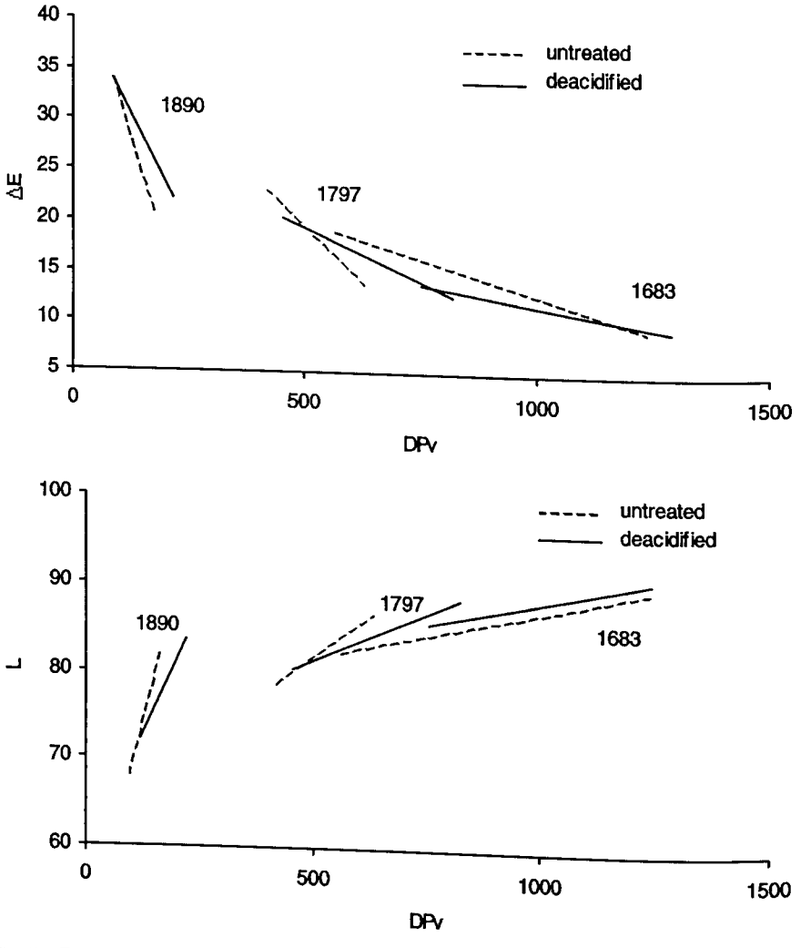

Fig. 9: Regression lines for the relation between colour change and degree of polymerization.

Each paper behaved differently, and covers a definite area of the diagram (see Fig. 9). The area where the oldest rag papers are located has no intersection with the area covered with the machine made 1890 paper.

Tables 2 and 3 also give the correlation coefficients of the linear trendlines. The nearer the number to 1, the better the correlation. The lowest (r = 0.7925) is found with ΔE vs DPv in the 1890 paper after deacidification. In all other

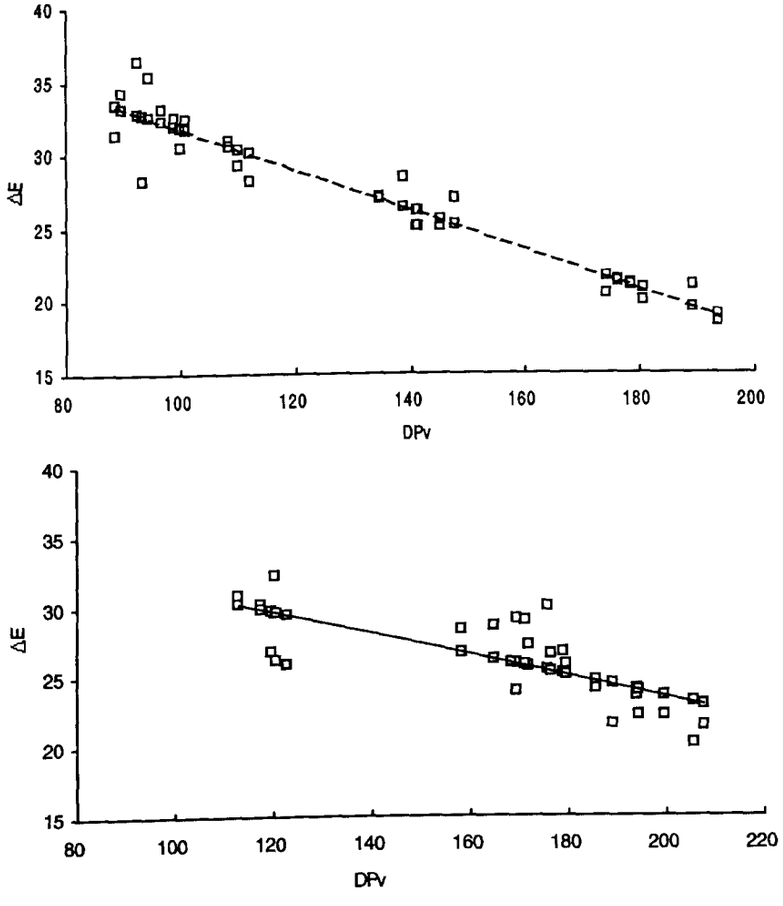

Fig. 10: Colour and degree of polymerization of the 1890 paper, untreated (above) and treated (below)

cases the correlation is quite good, which will allow the degree of polymerization to be calculated, at whatever ageing time, through a simple colour measurement.

We also studied the correlation of the colorimetric values ΔE and L^* of pure cellulose vs ΔE and L^* of the three historic papers and found a very good correlation, the lowest correlation coefficient being r = 0.95 (1683 untreated paper).

Table 2. Linear regression ΔE (y-coordinate) vs DPv (x-coordinate)

Paper	ΔEo	Slope (A)	Correlation coefficient (r)
1683	26.456	-0.014	0.9955
1683 deacidified	19.6	-0.008	0.9703
1797	41.975	-0.0455	0.9450
1797 deacidified	30.408	-0.0219	0.9914
1890	48.12	-0.1486	0.9918
1890 deacidified	41.099	-0.0837	0.7925

Table 3. Linear regression L (y-coordinate) vs DPv (x-coordinate)

Paper	Lo	Slope (A)	Correlation coefficient (r)
1683	75.066	0.0118	0.9873
1683 deacidified	77.788	0.0102	0.9227
1797	62.304	0.0391	0.9275
1797 deacidified	71.4	0.0198	0.9928
1890	52.386	0.1661	0.9887
1890 deacidified	56.77	0.1209	0.8331

CONCLUSION

The retention values of lightness and of degree of polymerization in the deacidified samples clearly show that the UPC mass deacidification treatment has a distinct, positive effect on the ageing behaviour of paper. The alkaline buffer that is brought into the paper by this process inhibits the degradation processes.

It has been demonstrated that the colour difference ΔE correlates well with the viscosimetric DPv, at least within ranges determined by the accelerated ageing test conditions (0–21 days at 90°C and 50% RH)

These and similar results can be used to define a method for non destructive analysis of papers, comprising the following steps:

- determinate the degree of polymerization of the paper by taking 5 or 6 small test specimens, weighing less than 200 mg at random. The paper sample should be washed previously in a diluted acidic bath in order to make the viscosimetric analysis more accurate. The results will be better in papers with the least amount of additives, sizings, coatings and lignin. Generally it may be enough to determine the DPv of a non-aged untreated paper only, but it would be more accurate to measure that of the most aged sample, too.

- obtain some different levels of paper degradation by means of different accelerated ageing periods.
- measure the colour of all the samples, aged and unaged.
- calculate the other degrees of polymerization, not determined by viscosity, by applying the regression equation DPv/ΔE previously found in a paper of similar characteristics.

ACKNOWLEDGEMENTS

We thank Mr. Antonio Clemente, (DETIP-UPC, Laboratorio de Química Papelera), for the intrinsic viscosity measurements and the company CSC, S.L. (Conservación de Sustratos Celulósicos) for financial support.

SUMMARIES

A Method for the Non-Destructive Analysis of Paper Based on Reflectance and Viscosity

During research to assess the effectiveness of the mass deacidification treatment developed at the Universitat Politècnica de Catalunya (UPC-ETSIIT-Spain), the changes produced in several chemical and physical properties of papers dating from the 17th, 18th and 19th centuries were compared, particularly the changes in viscosimetric degree of polymerization and colour parameters (lightness, chroma, and hue) caused by ageing and deacidification. A good statistical correlation between the colour differences of each sample versus a pure cellulose reference sample and the degree of polymerization for the same samples was observed. These findings will permit the use of the colorimetric method and the viscosimetric method for monitoring the conservation level of book and archival paper. It was also observed that •E and DPv ranges under determined ageing conditions depend on the type of paper and its composition; so these properties could be used for the characterisation of papers by their age and manufacturing system.

Une méthode non agressive d'analyse du papier basée sur la réflectance et la viscosité

Dans le cadre d'un travail de recherche ayant pour objectif d'évaluer l'efficacité du traitement de désacidification de masse développé à l'Université Polytechnique de Catalogne (UPC-ETSIIT) on a comparé les changements observés dans différentes propriétés chimiques et physiques de papiers datant des 17ème, 18ème et 19ème siècles, en particulier du degré viscosimétrique de polymérisation et des paramètres trichromatiques (clarté, intensité, nuance) causés par le vieillisse-

ment accéléré et la désacidification. On a observé une bonne corrélation statistique entre les différences chromatiques de chacun des échantillons par rapport à un échantillon de référence en cellulose pure et par rapport au degré de polymérisation de ces mêmes échantillons. Ces résultats permettent de préconiser l'utilisation de la méthode colorimétrique et de la méthode viscosimétrique pour contrôler le degré de conservation du papier des bibliothèques et des archives. On a également observé que les changements qui concernent les paramètres chromatiques (•E) et le degré de polymérisation, lors du vieillissement accéléré, sont liés au type du papier et à sa composition, ce qui signifie que ces propriétés pourraient être utilisées pour déterminer l'âge du papier et la méthode de sa fabrication.

Eine Methode der nicht-materialzerstörenden Papieranalyse, basierend auf Messung von Reflexion und Viscosität

Im Rahmen einer Untersuchung zur Einschätzung der Wirksamkeit des an der Polytechnischen Universität von Katalonien (UPC-ETSIIT) entwickelten Massenneutralisierungsverfahrens wurden die Veränderungen einiger chemischer und physikalischer Eigenschaften von Papieren des 17., 18. und 19. Jh. untersucht, insbesondere die Veränderungen, die der viskosimetrisch ermittelte Polymerisationsgrad und die Farbwerte (Weißgrad, Farbintensität, Farbton) durch das Neutralisieren und durch beschleunigte Alterung erfahren. Es zeigte sich eine statistische Korrelation zwischen den Farbveränderungen der einzelnen Proben gegenüber denen von reiner Cellulose und gegenüber dem Polymerisationsgrad der betreffenden Proben. Diese Feststellung ermöglicht es, mit Hilfe der Farb- und einer einzelnen Viskositätsmessung den Erhaltungsgrad von Papier in Archiv und Bibliothek zu erfassen. Es wurde auch beobachtet, daß die Veränderungen, die die Farbwerte (Gesamtfarbwert ΔE) und der Polyymerisationsgrad bei beschleunigter Alterung erfahren, von Typ und Zusammensetzung des Papiers abhängen, was bedeutet, daß diese zur Feststellung des Alters und der Herstellungsmethode verwendbar sind.

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The Influence of Mg on the Light Induced Oxidation of Newsprint

by VLADIMÍR BUKOVSKÝ & IVAN KUKA

INTRODUCTION

Different effective methods for the mass deacidification of paper use Mg; in most of them magnesium carbonate is the final alkaline reserve[1]. Undoubtedly, deacidification has a most favourable influence on woodfree papers[2, 3]. The lifetime of modern groundwood papers, too, is significantly increased by this process. On the other hand, alkalinity makes groundwood paper more sensitive to light, which can be observed even after a very short period of irradiation[2, 4, 5]. There are even post-radiation oxidation changes in newsprint paper which, after a deacidification treatment, has been exposed to light for a short time and has then been stored in the dark[6, 7].

YELLOWING

The understanding of the processes related to light induced oxidation degradation of groundwood papers is tightly bound to the processes of yellowing in connection with the content of lignin in paper. Existing knowledge about this process was summarized in 1994 by Leary[8]. Primary chromophores absorb the radiation in the wave-length range from 300 to 400 nm with the maximum between 310–320 nm[9]. Degradation products consisting of carbonyls (aldehydes and ketones), quinones, organic acids and other low-molecular substances are the result of the light induced oxidation processes[10, 11]. They are considered to be the secondary chromophores, which are able to absorb radiation even at longer wave-lenghts. The light induced oxidation degradation of lignin related to the creation of radicals can be described in three different model mechanisms[8, 12]:

- Phenoxy radical pathway. Free phenoxyl groups of lignin react with peroxide or hydroperoxide radicals; phenoxy radicals are formed and they produce yellow-coloured quinones. This pathway corresponds to approximately 33% of the light induced oxidation reactions of lignin.

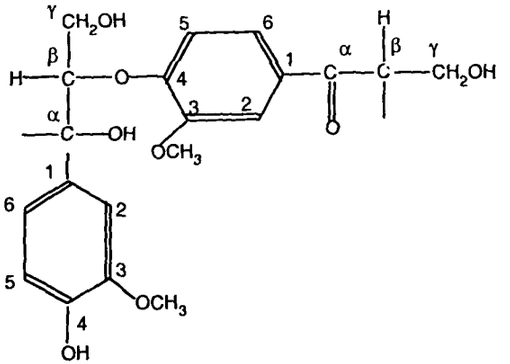

Fig. 1: Model of the lignin monomere

- Phenacyl pathway. β-C-O-4 linkages (cf. Fig. 1) are split in that part of the lignin molecule, where there is an α-C=O functional group; phenoxy radical and keton radicals are formed and the lignin molecule is split.
- Ketyl pathway. β-C-O-4 linkages are split in that part of the lignin molecule, where there is an α-C-OH group; phenoxy radicals and ketons are formed. The lignin molecule is split. Formed phenoxy radicals are changed into yellow-coloured quinones or other products.

INHIBITION OF YELLOWING

Two basic ways to inhibit light induced oxidation yellowing are focused on blocking the amount of free phenolic OH-groups, for instance by acetylation or methylation. Another one is adding radical blockers[8, 13]. In this context, we observed the influence of daylight with significantly reduced UVA radiation on the course of light induced oxidation of groundwood paper with a high lignin content (newsprint) independent of the amount of Mg in a newly formed alkaline reserve after deacidification with methanolic solution of methyl methoxymagnesium carbonate – MMMC [14, 15]. For comparison we used high quality, woodfree chromatographic paper W1. The effect of deacidification and alkalinisation of the treated paper depends on the concentration of the MMMC solution. Some of the substance changes to magnesium carbonate, which will act as an alkaline reserve in the future, some is bound to various structures present in the paper, mainly to the lignin[4]. The Mg bound to the lignin is very important for paper because it significantly inhibits the course of light induced oxidation reactions[2]. The aim of this work is to find answers to the following questions:

- What concentration of MMMC is necessary to achieve complete deacidification?
- What is the influence of an increased pH and alkaline reserve on the properties of groundwood newsprint?
- To what extent can the amount of Mg in paper inhibit the course of light induced oxidation reactions after irradiating by multivalent daylight?

MATERIALS AND METHODS

Paper samples

We used the same paper samples as in the preceding works[2, 16], in which the characteristics of these papers as well as the amount of lignin are given. There was not enough of sample No. 3 to be used, or, more correctly, the remaining amount (*Hlas našej dediny* newspaper) was significantly different from that used previously.

- No 1: newsprint made in Větrni, 1996, Czech Republic
- No 2: newsprint made in Štetí, 1996, Czech Republic
- No 4: newsprint made in Croatia, 1942
- No 5: newsprint made in Hungary, 1881
- W1 – chromatographic woodfree paper Whatman 1

Preparation of samples

Samples measuring 6cm MD x 1cm CD were weighed after having been conditioned for 2 days at 45% RH and 20°C±1. Then the samples were deacidified by soaking for 5 minutes in MMMC solution of different concentrations. The solutions were prepared by diluting the original 10% solution to weight concentrations of 1, 2, 4 and 6% active substance. A 1% solution contains 0.41 mol/l Mg or MMMC resp. After deacidification the samples were again air-conditioned in the same conditions as given above and again weighed. The alkaline reserve (AR) – we suppose it is magnesium carbonate – is recognizable in the increase of weight. The control samples were soaked for 5 minutes in pure methanol, i.e. not deacidified: 0% concentration of MMMC.

The alkaline reserve resulting from the treatment is given in Table 1, the MMMC concentration in Table 2 and Fig. 2.

Table 1: Alkaline reserve (%) after deacidification.

	Paper No				
MMMC solution	1	2	4	5	W1
0%	0	0	0	0	0
1%	1.03	0.77	0.92	0.34	0.82
2%	1.90	1.63	2.15	0.62	1.63
4%	4.06	3.31	4.43	1.73	3.70
6%	5.66	4.63	5.98	2.56	4.96

Table 2: Mg content* (weight %) before and after deacidification with various MMMC concentrations (%).

	Paper No				
MMMC solution	1	2	4	5	W1
0%	0.014	0.070	0.016	0.029	0.001
1%	0.590	0.530	0.470	0.290	0.271
2%	0.780	0.840	0.740	0.520	0.535
4%	1.580	1.520	1.090	0.890	1.020
6%	2.310	2.220	1.600	1.360	1.330

* Analysed by Ecochem analytical laboratories, Prague, Czech Republic, by means of ICP OES spectrophotometer Liberty 200 (Varian).

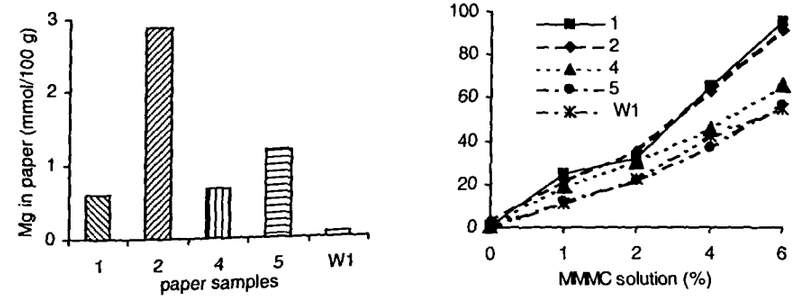

Fig. 2: Mg content in paper, *before treatment* and depending on MMMC concentration.

Sample exposure

Half of the samples were put into the dark immediately after treatment (D-samples). It can be assumed that changes observed in them result from the deacidification process only, mainly from a change in pH and the amount of alkaline reserve.

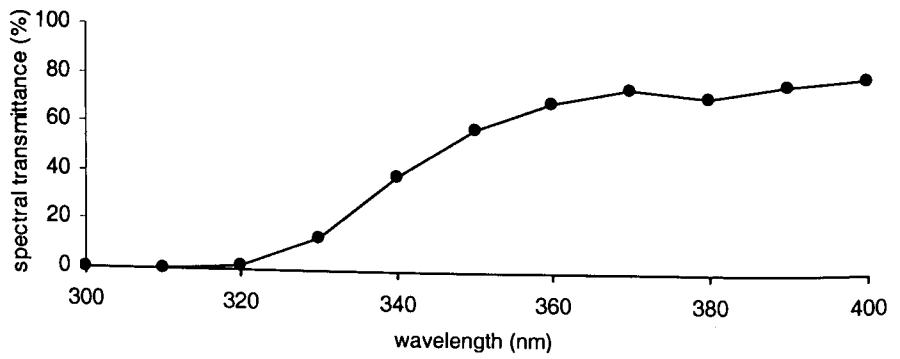

Fig. 3: The real spectral transmittance of two window panes ca. 5 cm apart from each other.

The other half of the samples were exposed to daylight by placing them on a window sill (L-samples). The daylight went through two glazed windows during the period August 13th to September 17th 2000, i.e. 35 days. This was the length of time necessary for the maximum of carbonyl formation, based on the conclusions of our previous work[2]. The intensity of the irradiation during the experiment was quite high: cloudless days 27%, almost cloudless 20%, partly cloudy 19%, almost cloudy 16%, overcast 18% and overcast-dark sky 0%. We assume that the temperature during irradiation was not high enough to influence on the ageing of the paper.

The spectral transmittance of light in the range between 300 and 400 nm going through the window, is given in Fig. 3. These data were given by the Slovak Institute of Metrology in Bratislava.

Measurements

After completion of the exposure time all samples, including those which had been stored in the dark, were air-conditioned for 2 days at 45% RH 20±1 °C and then tested for:

- Folding endurance according to Schopper[17]. The number of samples in the file after excluding both marginal values was 8.
- Brightness at 457 nm, L-samples both on irradiated and reverse side[4]. The number of samples was 7.
- Extractable agents and pH. The samples 6x1 cm were soaked for 1 h at 100°C in 2 ml deionized water. The resulting yellow water was measured for optical density (457 nm, Specol 11, Zeiss, Jena) and for pH (M-120 Mikrotechna, Czech Republic). The number of samples in the file was 7.

- Carbonyl content according to Albertsson and Samuelson[18]. The number of samples in the file was 3.

RESULTS AND DISCUSSION

Deacidification of samples and alkaline reserve

Gravimetric measuring of the alkaline reserve (AR) in paper gave comparatively rough results. Nevertheless, it can be seen from Tabs. 1 & 2 and Fig. 2 that there was a considerably increased amount of $MgCO_3$ present, corresponding to the MMMC concentration, as a result of the solution being absorbed by the paper. The smallest alkaline reserve was found in sample 5, i.e. a paper containing a high amount of mineral filler. The Mg content in paper consists of $MgCO_3$ and Mg chemically bound to lignin or cellulose; we do not know in what proportion.

Acidity and alkalinity (pH)

The initial acidity of the papers has a significant influence on the pH after deacidification (Fig. 4) and dark storage (D-samples). To significantly neutralize the more acidic papers (samples 1 and 5), a higher concentration of the MMMC solutions was necessary (sample 1: 2%, sample 5: 1.5%). The final pH of the groundwood papers did not exceed the values of 9.0–9.5 even after deacidification with more concentrated MMMC solutions. The highest pH was found after deacidification of the initially neutral paper W1. The acidity of non-deacidified groundwood papers after irradiation significantly increased; this is related to the formation of organic acids. pH decreases down to 2 (paper 1), and that is why a higher concentration of MMMC is necessary to deacidify these papers. In the lignin free paper W1 the pH was unchanged during irradiation.

Extractable degradation products

Yellow degradation products (Fig. 5) are formed in the groundwood papers during natural ageing, i.e. auto-oxidative disintegration of lignin. Alkalinity as a result of the deacidification treatment increases the degradation of lignin and has little influence on the oxidative degradation of cellulose[19, 20]. The tendency of lignin to oxidize in an alkaline environment becomes obvious by the formation of water extractable agents in the D-samples. Their amount increases together with

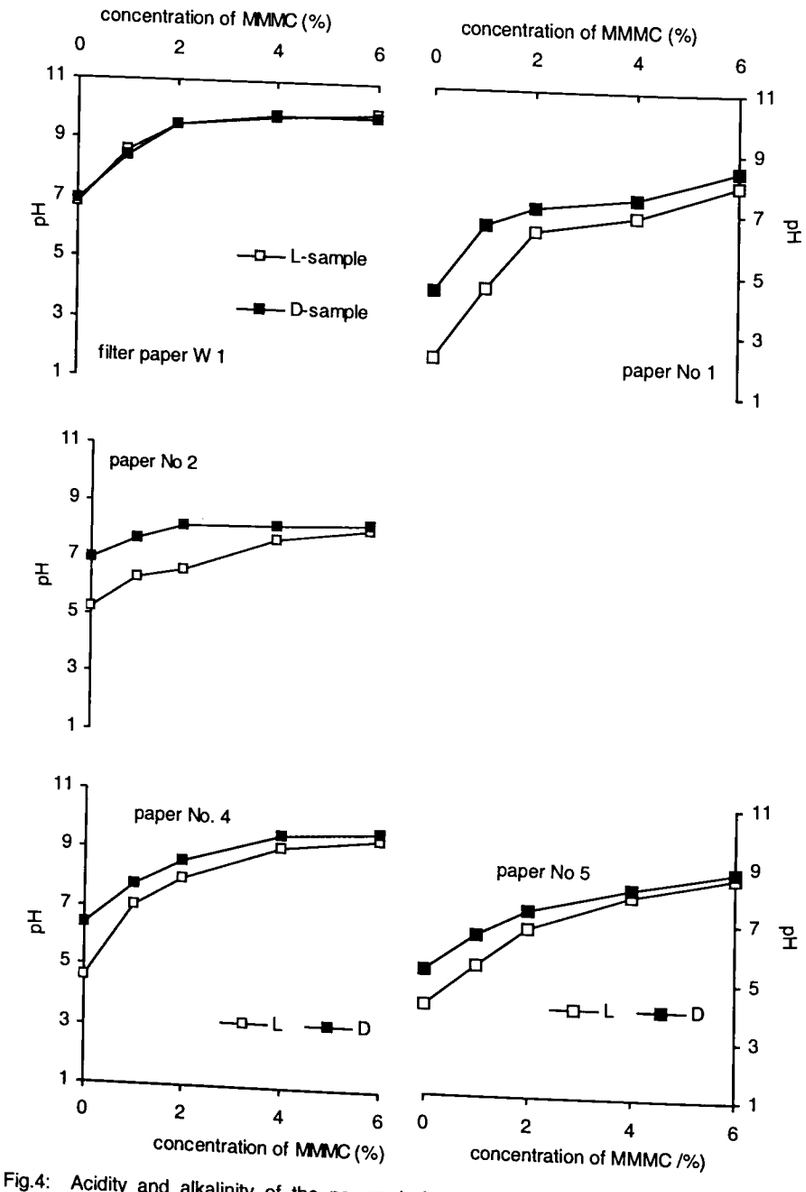

Fig.4: Acidity and alkalinity of the papers before and after deacidification with different solutions of MMMC.

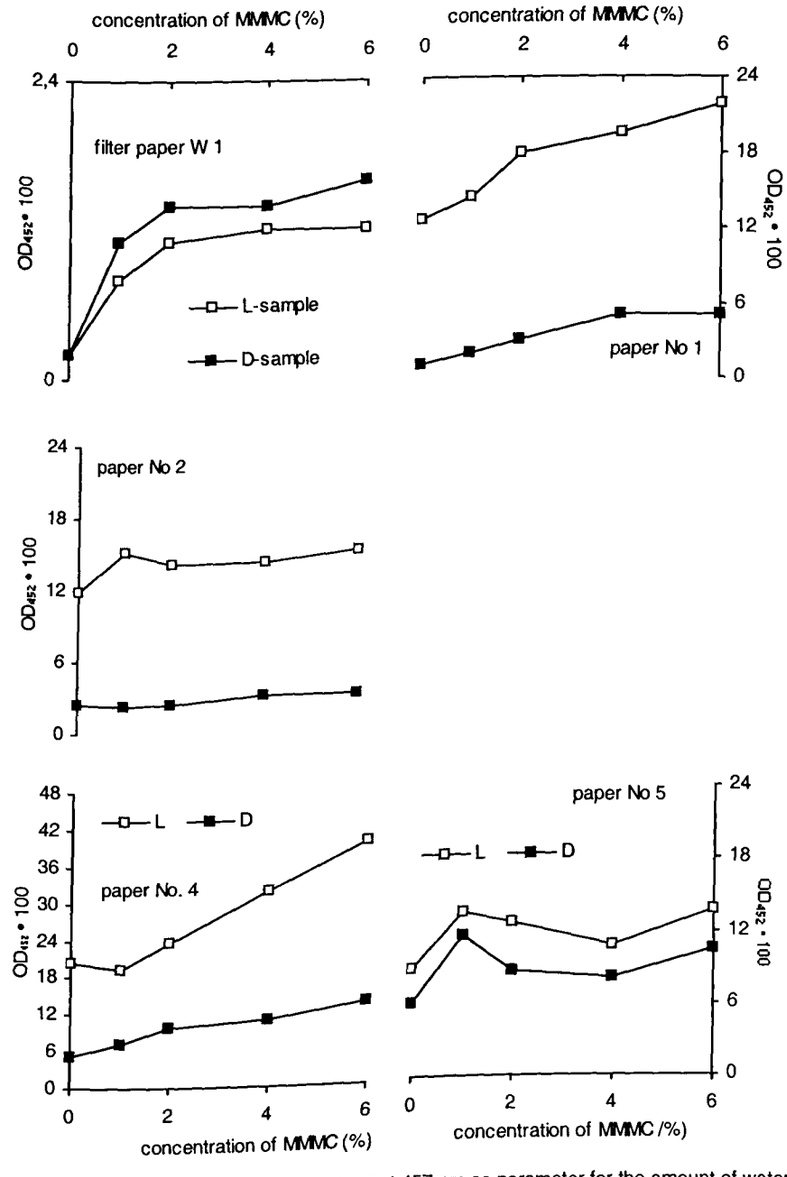

Fig. 5: Optical density of the aqueous extract at 457 nm as parameter for the amount of water soluble degradation compounds, before and after deacidification with different solutions of MMMC.

alkalinity, but this increase is not parallel. It also depends on the initial pH and the quality of paper. Deacidification assists in the formation of these agents even in the W1 paper, but in a very much lower range; cellulose seems to be resistant towards oxidation even in an alkaline environment.

Irradiation of deacidified papers and, consequently, light induced oxidation of lignin significantly speeds up the formation of degradation products. Papers 1 and 2 and, to a less extent, paper 4 show that a higher Mg content, as result of a higher MMMC concentration, decreases light induced oxidation, but only to a certain amount (Fig.8). The optimum decrease seems to be equivalent to the Mg content produced by a MMMC solution of 2.3%. Further increased Mg content does not further reduce carbonyl formation, and there is a significant amount of light induced oxidation not inhibited by Mg. The change in carbonyl content is not parallel to the change of pH.

The carbonyl content of pure cellulose (paper W1) is not significantly changed, neither by high alkaline environment nor by irradiation.

Brightness of paper

Brightness of paper (Fig. 6) reflects the degree of paper degradation caused by natural ageing, light induced oxidation, change of acidity and/or of Mg bound to lignin. It is apparent by the formation of yellow degradation products. Some of these products are tightly bound to lignin and are not extractable. Low concentrations of AR (or Mg respectively) significantly decreased the brightness of both modern newsprints[4] (papers 1 and 2). With paper 1 the greatest decrease took place as result of deacidification at a very low concentration. Higher concentrations of MMMC solution resulted in only a smaller decrease. Brightness decrease is caused by Mg bound to lignin. The presence of a low concentration of Mg is enough to cause this yellowing.

From Fig. 6 it also becomes evident that the yellowing caused by the bond of Mg to lignin significantly depends on the quality of paper. Even the pure cellulose paper W1 showed a decrease in brightness as result of deacidification. It is very small, but it suggests that there was a binding reaction of Mg to the cellulose molecule and that it increased with higher amounts of Mg.

Obviously light is reducing the brightness of paper. Deacidification most often lessens this process, with the exception of paper no. 5. An increase of the amount of AR/Mg in the paper, however, results in a further decrease of brightness. The course of yellowing of irradiated papers differs to some extent from the course of yellowing of the non-irradiated papers, definitely at the lowest concentration.

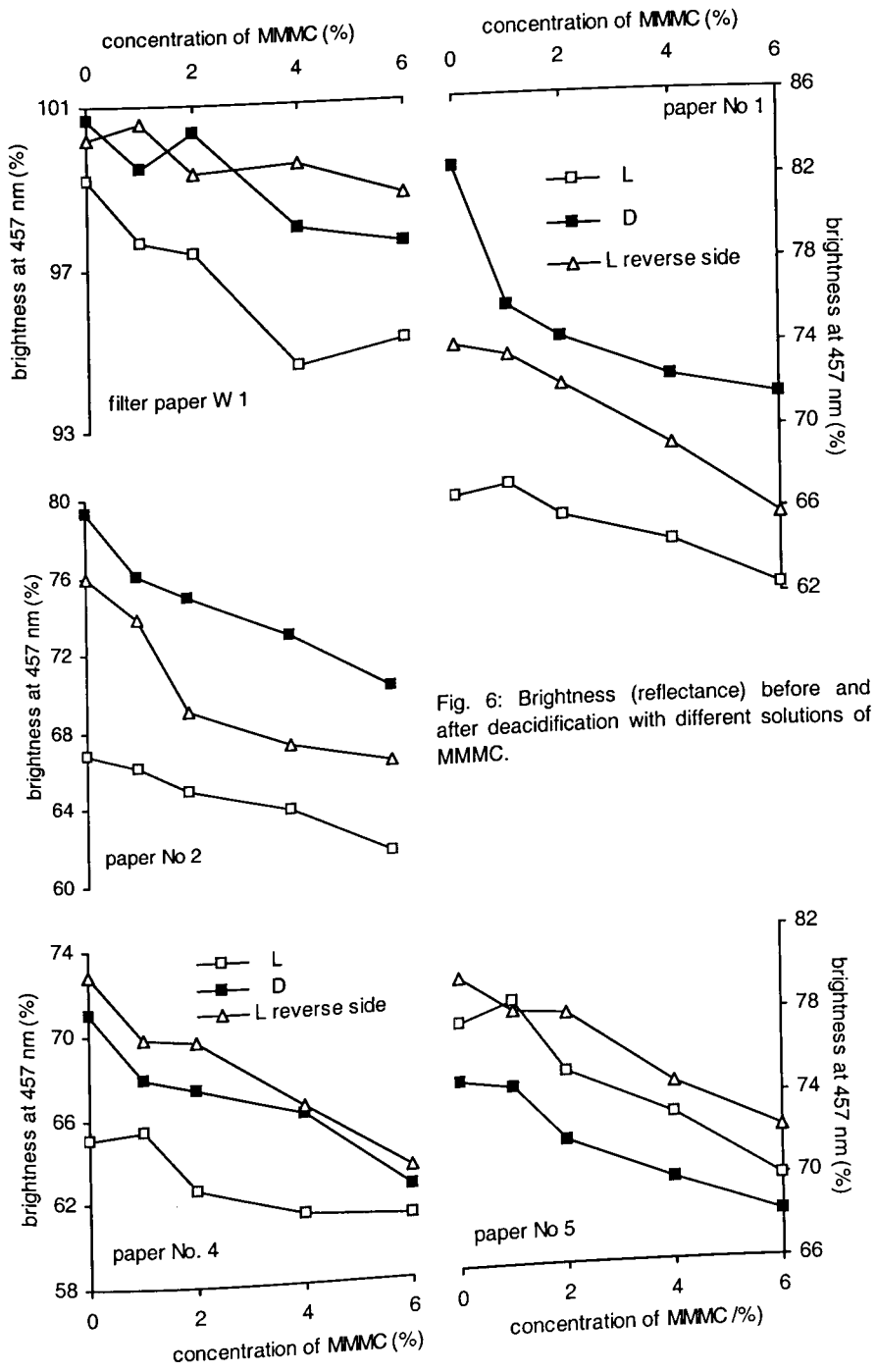

Fig. 6: Brightness (reflectance) before and after deacidification with different solutions of MMMC.

This is caused by the fact that Mg inhibits the light induced oxidation processes, at the same time as being bound to the lignin, which results in decreased brightness.

The yellowing of the non-irradiated side of modern papers copies the course of the yellowing of the irradiated side. This colour change may be caused by the diffusion of degradation products, a process that might be called "secondary yellowing". Paper no. 5 became brighter after irradiation. This bleaching effect occurred at all Mg concentrations, even though it seemed to be less pronounced at the higher concentrations. It may be assumed that, due to the degraded state of this paper, the bleaching effect of daylight (430–450 nm)[9] prevails the yellowing resulting from the Mg binding to the chemical structure of lignin, i.e. the photodegradation of lignin.

Also, the pure cellulose paper W1 lost brightness by irradiation, though to a lesser extent. A high concentration of Mg, however, had a stabilizing effect on the brightness on this paper. It occurred on the illuminated side only, while the reverse side lost brightness with a high Mg concentration in the same way as the sample stored in the dark.

Folding endurance

Folding endurance (Fig. 7) is depending on three factors: quality of paper defined as length of fibre; extent of fibre degradation and the amount of filler and sizing. The increased content of $MgCO_3$ in modern newsprint of excellent mechanical properties (paper no. 1 and 2), caused by deacidification with highly concentrated MMMC, is resulting in a reduction of folding endurance to a level of about 50% of the original value. With the historic papers (samples no. 4 and 5), the fibre proportion of which is considerably degraded, this loss is even more pronounced. Mechanical stability can be reduced to brittleness, which means that highly concentrated MMMC solutions must not be used for such papers. Of interest is the reaction of the W1 paper. Here an increased amount of AR/Mg slightly increases the folding endurance. We assume that this favourable influence is caused by the direct bond of Mg to cellulose, and this strengthening process interferes with and eliminates the reduced mechanical strength of the increased $MgCO_3$ content.

Irradiation is significantly reducing the mechanical strength of modern newsprint as well as of the pure cellulose paper W1. Deacidification with high or with low concentrations of MMMC solution did not eliminate this effect. The negative influence of light on the mechanical strength of paper is significant.

Even the pure cellulose paper W1 suffered significant light induced oxidation destruction; its folding endurance after irradiation was decreased considerably. It

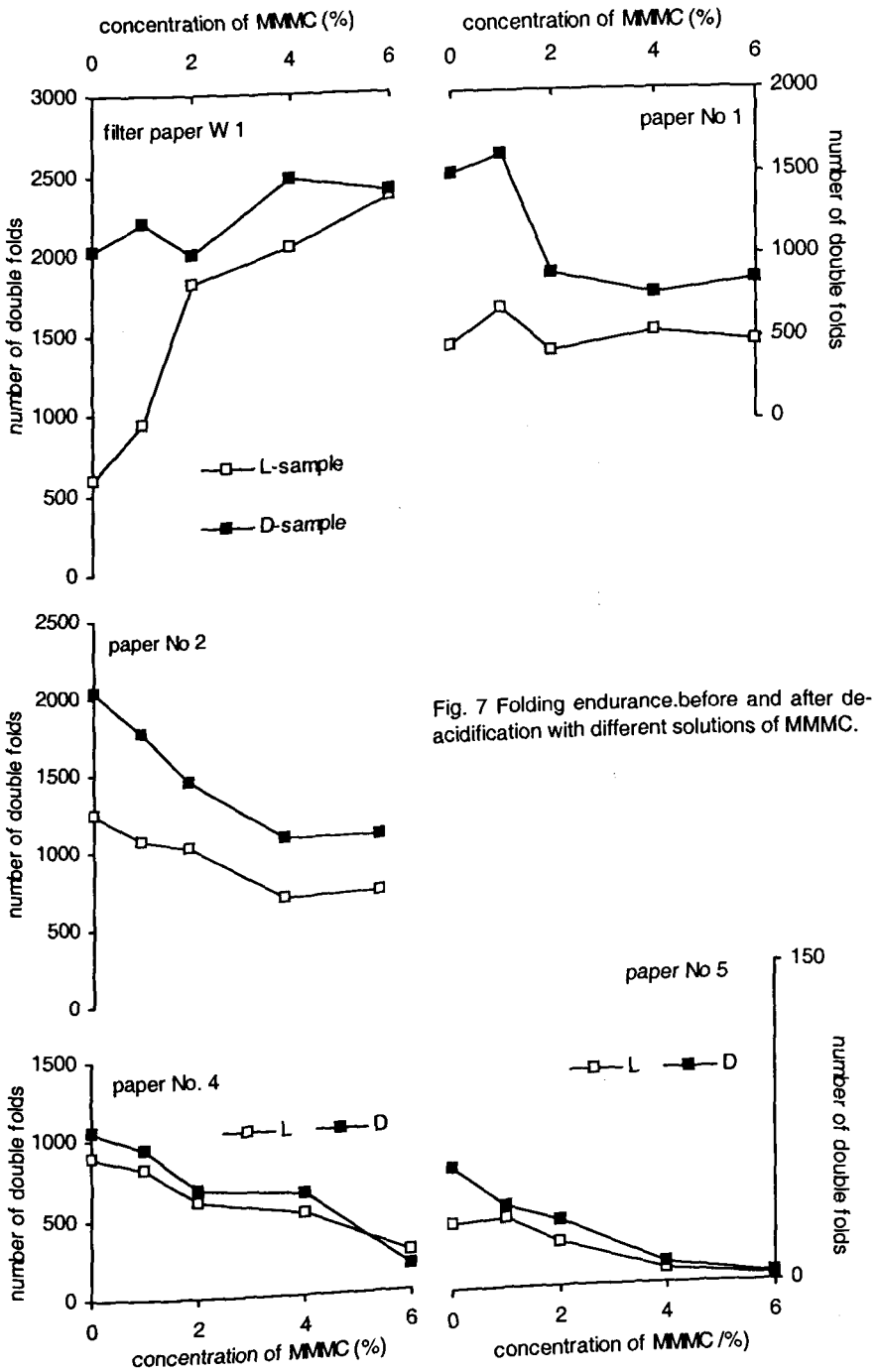

Fig. 7 Folding endurance.before and after deacidification with different solutions of MMMC.

is astonishing how significantly even a small amount of Mg (20 mmol/100 g paper) prevented the mechanical properties of this paper from light induced oxidation from worsening. The highest amount of Mg used for this work seemed to eliminate completely the influence of light on this paper.

Light induced oxidation of paper

The most obvious method to show oxidation in paper[8] is to observe the formation of carbonyls (Fig. 8). Carbonyls represent the first stage of the oxidation of cellulose and lignin, whereas the degradation products are the result of several following reactions the interpretation of which is quite complicated[21,22]. Deacidification of newsprint, either modern or historic, has little influence on carbonyl content. Even a high content of Mg, resulting from deacidification, does not influence it. The same is true for the pure cellulose paper (W1)

Light induced oxidation resulting in a huge increase of carbonyls takes place intensively in newspaper after only a short irradiation. The presence of just a very small amount of Mg, resulting from deacidification with very dilute MMMC solutions, significantly inhibits light induced oxidation, i.e. the formation of carbonyls. Even in paper No. 5, which can be supposed to have already suffered lignin degradation to a great extent, the formation of carbonyls is considerably reduced by deacidification. The formation of carbonyls by the light induced oxidation of OH-phenolic groups is significantly reduced or even stopped after a certain amount of Mg, equivalent to MMMC solution 2.3%, in the paper is reached. It seems that the presence of Mg in the paper can inhibit light induced oxidation because it works as a radical blocker[13].

The extent of light induced oxidation, which Mg is able to inhibit, is ca. 46–57% of the total amount of carbonyls formed by irradiation, equivalent to 5.1 to 7.7 mmol carbonyls/100 g paper (Table 3). In sample no. 5 the share of inhibition of the light induced oxidation caused by Mg was about 63%, i.e. 1.25 mmol carbonyls/100 g paper. The situation in the pure cellulose paper W1 is different. The lowest and the highest concentration of MMMC resulted in a relatively high reducing effect of Mg on light induced oxidation. It is therefore problematic to assume that the decrease in carbonyl formation after deacidification is connected with Mg binding to the cellulose molecule. If we admit this bond takes place, the presumption would be that carbonyl formation during irradiation is inhibited by up to 20–25%.

Based on the conversion of the amount of Mg in paper and the amount of created carbonyls we assume that for the inhibition of 1 mol of the newly forming carbonyls we need 5.1–7.60 mol of Mg in groundwood papers; 21.5 mol in paper no. 5 and about 66 mol of Mg in the W1 paper (Table 4).

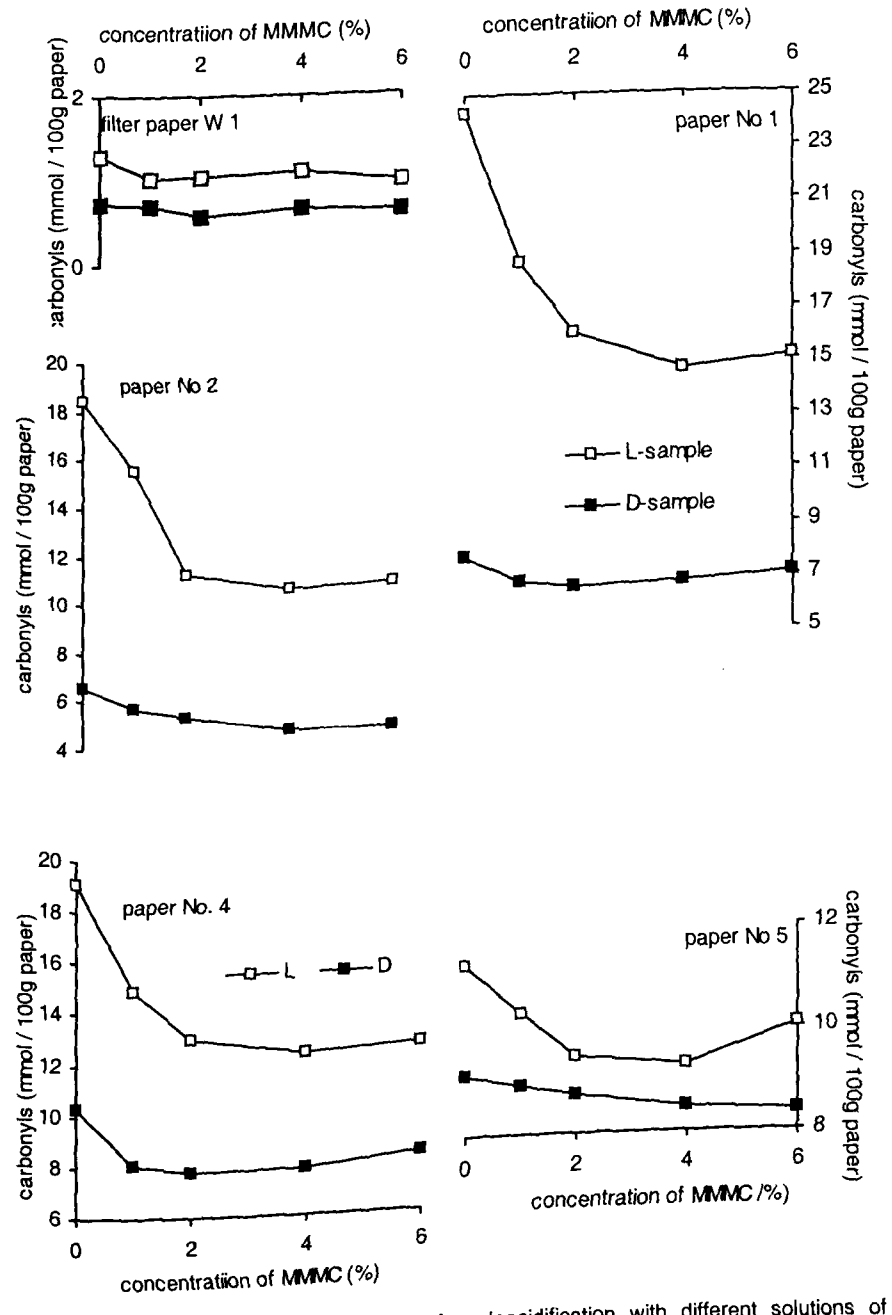

Fig. 8: Amount of carbonyls before and after deacidification with different solutions of MMMC.

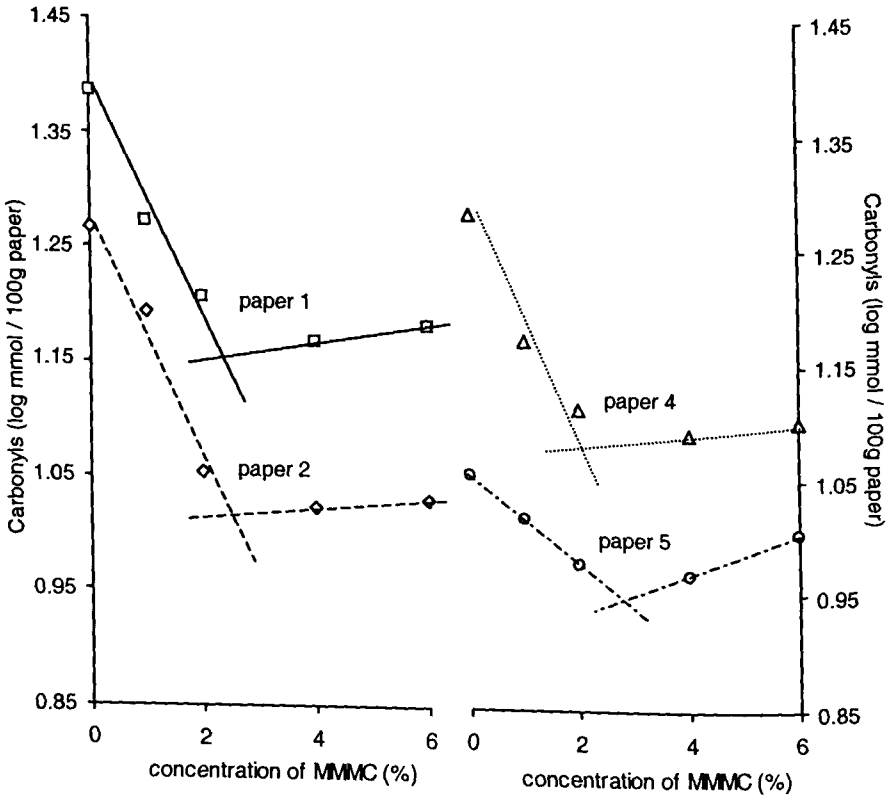

Fig. 9: Amount of carbonyls (log mmol/100g paper) in irradiated newsprint before and after deacidification with different solutions of MMMC: trendlines indicating the inhibition effect depending on the concentration of Mg in paper.

Very intense light induced oxidation of groundwood papers with a significant increase in the amount of carbonyls occurred after quite a short irradiation period (35 days). This increase is not related only to phenoxy radical pathway; phenacyl and ketyl pathways also occur in parallel and with the same intensity, even if we do not know their quantitative relation. With modern groundwood papers, in which the extent of oxidation in the process of natural ageing is negligible, we can recognize fairly well the course of light induced oxidation. To interpret the relevant numbers found with historic paper samples, in which we know neither the initial quality of paper nor the degree of degradation of lignin and cellulose, is more complicated.

Table 3: Inhibition of light induced oxidation by Mg.

		Paper No 1	2	4	5	W1****
Maximum light induced oxidation*		16.51	11.89	8.82	2.15	0.56
	%	*100*	*100*	*100*	*100*	*100*
Light induced oxidation not inhibited by Mg**		8.8	6.4	3.7	0.8	0.42
	%	*53.3*	*53.8*	*42.2*	*37.3*	*75.0*
Light induced oxidation inhibited by Mg***		7.7	5.5	5.1	1.35	0.14
	%	*46.7*	*46.2*	*57.8*	*62.7*	*25.0*

* amount of carbonyls (mmol/100 g paper) in irradiated samples minus carbonyl content in samples stored in the dark

** amount of carbonyls in papers which were deacidified with the MMMC which resulted in the highest inhibition; calculated from Figs. 8 and 9.

*** difference between maximum light induced oxidation and oxidation not inhibited by Mg

**** estimated

Table 4: Calculated amount of Mg necessary to inhibit a maximum of light induced oxidation.

	Paper No 1	2	4	5	W1
MMMC concentration necessary to inhibit a maximum of light induced oxidation*	2.4	2.6	2.4	3	1
Amount of Mg (mmol / 100 g paper) necessary to inhibit light induced oxidation**	39	42	33	29	10
Amount of Mg (mol) necessary to inhibit 1 mol carbonyls	5.1	7.6	6.5	21.5	66

* calculated from Figgs. 8 and 9

** calculated from Fig. 2

CONCLUSION

Deacidification with various MMMC concentrations results in

- considerable increase of alkaline reserve and magnesium content;
- remarkable increase of pH;
- brightness of groundwood paper is decreased and yellowing increased;
- amount of extractable degradation products is increased;
- folding endurance is decreased;

- pure cellulose paper shows a significant tendency to improved mechanical strength.

Deacidification followed by 35-day irradiation:

- low concentration deacidification results in lower pH after irradiation than after dark storage. After high concentration deacidification there is no or only little difference between the pH of irradiated and non-irradiated samples;
- some groundwood papers show a significant increase of extractable degradation products with increased deacidification concentration;
- significant decrease of brightness and increase of yellowing, together with an increase of alkaline reserve;
- the brightness of the non-irradiated side decreased as well as the irradiated side, which is related to the diffusion of degradation products through the paper;
- folding endurance after irradiation considerably decreases only in modern papers; mechanical properties in historic papers are not further reduced by irradiation;
- significant light induced oxidation related to the increase of the amount of carbonyls takes place;
- in groundwood paper deacidification with Mg compounds reduces the light induced formation of carbonyls in an amount of 46–57%, if 33–42 mmol Mg/100 g paper are provided;
- 5.1–7.6 mol of Mg are necessary to inhibit 1 mol of carbonyls to be formed in the photo-oxidation process. It is important to chose the right concentration of MMMC solution: that which provides the amount of Mg necessary for maximum inhibition of photo-oxidation in groundwood papers;
- the Mg-caused inhibition of photo-oxidation in very old groundwood paper is probably very intensive but much more Mg is necessary;
- even in pure cellulose paper a positive effect of deacidification with Mg on the light induced oxidation can be seen, but its amount and its chemical character is difficult to describe. There is only a small decrease of brightness, but a positive influence in mechanical strength.

ACKNOWLEDGEMENT

We should like to thank to Dr. Ing. Michal Ďurovič from the Central State Archives in Prague for mediating analysis of amount of Mg in papers and Ing. Peter Nemeček from the Slovak Metrological Institute in Bratislava for helping with the analysis of glass spectral transmittance.

SUMMARIES

The Influence of Mg on the Light Induced Oxidation of Newsprint

The aim of deacidification is to provide an alkaline environment in the paper as a means to guard against acid catalysed hydrolysis. A drawback is that paper in an alkaline environment is sensitive to oxidation. An important effect of deacidifying groundwood paper with methoxy methyl magnesium carbonate is that some of the Mg is bound directly to lignin, thus significantly inhibiting the light induced oxidation degradation of the paper and increasing its resistance towards irradiation. The amount of this inhibition is about 50%. In choosing the most apt concentration of MMMC solution it should be taken into account that it must be enough not only to neutralize the acid present in the paper and to provide a buffer against acid that will be formed in or picked up by the paper in the future, but enough also to limit the light induced oxidation degradation of groundwood papers to the highest possible degree.

Influence du magnésium sur l'oxydation du papier journal induite par la lumière

L'objectif poursuivi par la neutralisation consiste à créer un environnement alcalin dans le papier comme moyen de se prémunir contre une hydrolyse catalysée à l'acide. Le fait que le papier placé dans un milieu alcalin soit susceptible d'être oxydé présente un inconvénient. Un effet majeur de la désacidification du papier à pâte mécanique par le carbonate de magnésium méthoxyméthylique est qu'une partie du magnésium est liée directement à la lignine et qu'ainsi la dégradation oxydative du papier induite par la lumière est réduite et que donc la résistance du papier contre les effets néfastes de la lumière est renforcée. L'effet bénéfique obtenu à l'aide du magnésium réduit d'environ 50% la dégradation potentielle de l'irradiation. Lors du choix de la concentration de la solution de MMMC la plus apte à utiliser il faudra tenir compte du fait qu'elle doit être suffisante non seulement pour neutraliser la quantité d'acide présente dans le papier et constituer un rempart contre les acides susceptibles de se former ou d'être absorbés à l'avenir dans le papier, mais qu'elle devra également être suffisante pour réduire au maximum la dégradation oxydative induite par la lumière du papier à pâte mécanique.

Der Einfluß von Magnesium auf die lichtinduzierte Oxidation von Holzschliffpapier

Der Zweck einer Neutralisierung ist die Schaffung einer alkalischen Umgebung im Papier als Mittel gegen die säurekatalysierte Hydrolyse, und ein Nachteil ist, daß im alkalischen Milieu Papier zur Oxidation neigt. Es ist ein wichtiger Effekt der Neutralisierung von Holzschliffpapier mit Methylmethoxymagnesiumcarbonat, daß ein Teil des Magnesiums direkt an das Lignin gebunden und daß dadurch der lichtinduzierte oxidative Abbau vermindert und Resistenz des Papiers gegen Schädigung durch Licht erhöht wird. Die mit Magnesium zu erreichende Verbesserung erreicht die Hälfte der potentiellen Schädigung durch Licht. Bei der Wahl der bestgeeigneten Konzentration der eingesetzten MMMC-Lösung ist zu bedenken, daß nicht nur im Papier vorhandene Säuren neutralisiert und ein Puffer gegen künftig im Papier entstehende oder vom Papier absorbierte gebildet werden, sondern daß auch der lichtinduzierte oxidative Abbau im höchstmöglichen Grad reduziert werden soll.

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Distribution of Chemical Elements of Iron-Gall Ink Writing Studied by the PIXE Method

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INTRODUCTION

Problems relating to the damage of support materials (paper, parchment, papyrus) by iron-gall inks and other metal pigments have been known for a long time[1]. The complex chemical processes between the ink and the support depend on several factors, ranging from the materials' composition to environmental influences. However, a complete understanding of the phenomena is not available yet and is a matter of serious investigation[2, 10, 11, 12, 13].

It would be very useful to find a non-destructive analytical method, which would be able to detect and trace chemical changes both during and after conservation treatment. It would also be useful if the same method could be used after some time on the same sample to trace the longer term effects of iron-gall inks or other metallic pigments on the manuscripts. For high quality conservation it is important to have a good understanding of the materials under treatment, particularly the likely compositional changes of the ink and the support so that the conservator has an idea of how the chosen conservation procedure will affect the materials.

In the following, an analytical method is suggested which can fulfil the above demands at least in some respects. It is called the Proton Induced X-ray Emission (PIXE)[3, 4] and is based on the use of protons from a particle accelerator, which irradiates a sample and records characteristic X-ray radiation produced. The PIXE method[3] is a well-established analytical tool for the detection of the elemental composition of various samples, especially in fields such as environmental science, geology and biomedicine. Recently, it proved its versatility when it was used on archaeological objects[9].

There are several advantages of using the PIXE method to study manuscripts. For example, the distribution of the elements in the inks can be studied with

greater precision than looking at the width of the writing itself. The PIXE method can offer a quantitative multi-elemental determination of the concentration profiles across the writing[5–8] for the elements of the periodic system, from Na upward. The other very important advantage is that the method can be classified as a non-destructive one as the damage on the analyzed document, if any, can be completely avoided if the proton beam intensity is low enough. Therefore, by applying the PIXE method the elemental composition changes can be investigated as a function of the conservation procedures. This is a prerequisite for a better understanding of the chemistry taking place during the treatment, which can contribute to the conservation of paper documents being still more scientifically approved.

In the following the method and the results from the analysis of a 17th century rag paper used for iron-gall manuscripts are given. The elemental profiles of ink as well as paper composition were deduced. The chosen manuscripts were analyzed before and after treatment (water washing and calcium hydroxide deacidification) and significant changes in the elemental concentrations were detected.

It is clear that PIXE is only one of the quantitative methods, which can offer at least part of the information needed. It seems very useful for the analysis of the documents written in inks and pigments containing metal ions. As PIXE can give elemental concentrations but not the chemical specification it should be combined with other approaches to illuminate the complex chemical processes in more detail[2,10]. The final understanding of iron-gall ink damage requires therefore further measurements, analysis and study to improve the statistical relevance of the results.

EXPERIMENTAL AND ANALYTICAL PROCEDURES

Samples and points of measurement

As a first attempt to apply the proposed approach we selected two pages, numbered 22 and 23, of the 17th century document *Notarile Antecosimiano No.2193* from Archivio di Stato (Firenze) for analysis. The manuscript was written in iron-gall ink on rag paper and some irreversible damage produced by the ink could be clearly observed. The layout of the page 22 is shown in Fig.1.

On the two selected pages a few letters were chosen for scans with the proton beam; the inset in Fig.1. shows a detail of the chosen area. Besides scanning, several individual points belonging to ink and paper were measured to confirm the composition deduced from the scans. Altogether more than 200 measurements were done with the aim of tracing the material composition, the ink elemental profiles and to appreciate changes in the composition due to the conservation treatment.

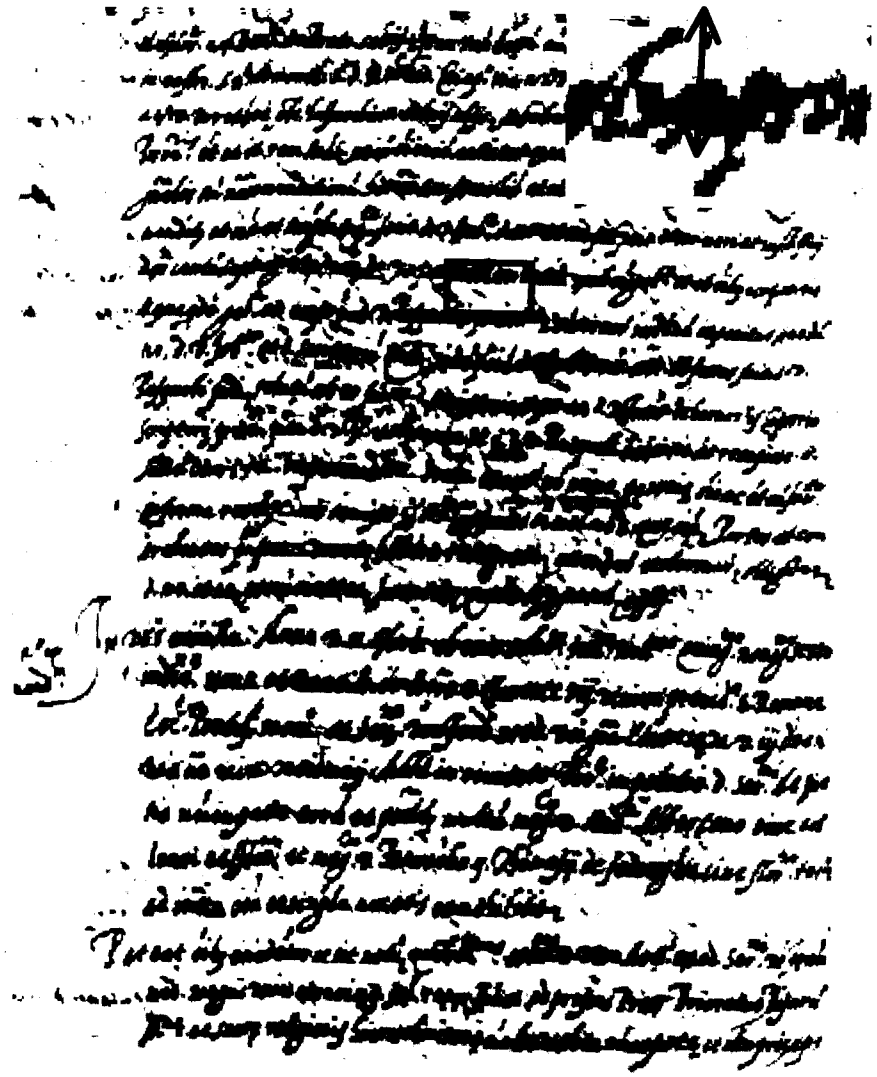

Fig.1. Photograph of page 22 with an inset enlarging the region of the scanned letter.

Conservation treatment

The selected pages were measured using PIXE prior to the conservation to discover the original composition of the iron-gall ink and paper. Then the pages were returned to the conservation laboratory of Archivio di Stato for treatment.

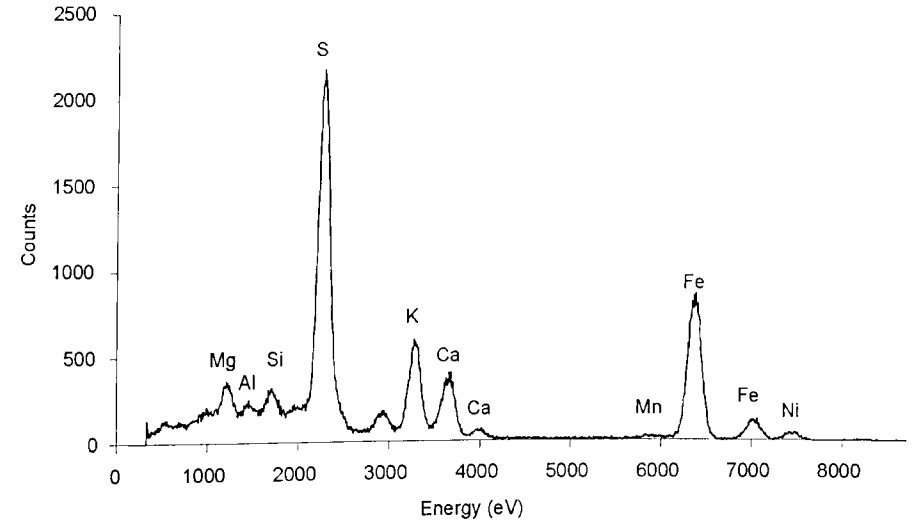

Fig.2.: PIXE spectrum of the iron-gall ink from page 22 before treatment as measured by one of the two X-ray detectors.

Two standard conservation procedures used in the Archivio were selected. For page 22 water washing was applied, i.e. the document was put into a tap water bath for about 30 min at room temperature and then dried. Page 23 was treated with a deacidification procedure, i.e. the document was first rinsed in a tap water bath and then soaked in a calcium hydroxide bath for 20 min at room temperature and dried.

Experimental set-up

The element profiles across the writing were studied using an external beam PIXE set-up at the Florence 3 MV Van de Graaff accelerator. This experimental arrangement is specially designed for the study of manuscripts and is described in more detail elsewhere[5–8].

The manuscript was fixed on the manipulation table, which moved the document laterally in front of the proton beam for irradiation. The exact position of the beam spot can be identified and reproduced with an accuracy of more than 0.1 mm. For irradiation the protons with an energy of 2.8 MeV from the Van de Graaff accelerator were used. The beam current was about 300 pA and each point was measured for around 150 s. The size of the beam spot was 0.3 mm

FWHM (Full Width Half Maximum). The beam profile was determined by scanning over a 0.015 mm thick tungsten wire through the detection of its characteristic L X-rays. The characteristic X-rays produced from the analyzed spot on the manuscript was measured by two Si(Li) detectors, simultaneously. The X-ray spectrum corresponding to the ink deposited on page 22 as measured by one of the two detectors is shown in Fig. 2.

The measuring procedure was such that the information about the sample position was correlated with the simultaneous acquisition of the X-ray spectra and the proton dose. This meant that the measurements were done fully automatically, which was crucial for scanning across the tiny letters on the manuscripts. In our case the scan steps were 0.3 mm. The measured X-ray yields corresponding to the elements present in the sample were transformed into the elemental concentrations of the sample components (ink, paper). For determining the concentrations the thin target approximation which neglects the matrix effects was applied[3-4]. In this way it was possible to calculate within a few percentage uncertainty the composition of the materials tested.

Sample damage was checked visually and the effects produced by the proton beam on the paper were practically negligible.

Results and Discussion

The elemental concentrations obtained by the external PIXE method can be used for analysis of the manuscript composition as well as for tracing the compositional changes due to the different conservation treatments. The elements detected by the PIXE method are those heavier than Na. All light elements (H, C, N, and O), which are important constituents of paper and are present in iron-gall ink also, were not measured. As the whole set of the determined elements can be considered as a representative "finger print" of the ink and paper used, the omission of the lighter elements was not considered a drawback and does not influence the data shown here.

Among the detected elements it was possible to select those which belonged solely to the ink, those which were present in the ink and the paper and those which were found in the paper only. The determined elemental concentrations (expressed in $\mu g/cm^2$) for page 22 of both ink and paper before and after the water washing procedure, are given in Table 1. Similar effects for page 23 of the deacidification procedure are presented in Table 2. The elements Mg, Al, S, K, Cr, Mn, Fe, Ni, Zn could be clearly identified as the ink components. For proving that assumption the scans across some selected letters were done for the both

Table 1. Page 22 ink and paper elemental concentrations ($\mu g/cm^2$) before and after the conservation treatment (water washing). In the parentheses the range of values is given.

	Ink		Paper	
	Before treatment	After treatment	Before treatment	After treatment
Na	0.65 (0.1 - 1.24)	0.52 (0.1 - 1.24)	Below detection level	
Mg	3.20 (2.2 - 4.22)	1.15 (0.83 - 1.47)	0.72 (0.56 - 0.96)	0.29 (0.1 - 0.60)
Al	0.93 (0.65 - 1.30)	0.56 (0.29 - 0.87)	0.49 (0.32 - 0.58)	0.32 (0.1 - 0.72
Si	2.74 (1.65 - 3.92)	3.16 (2.74 - 3.65)	2.55 (2.37 - 2.74)	2.74 (2.37 - 3.40)
P	0.75 (0.13 - 1.35)	0.45 (0.12 - 0.87)	0.93 (0.52 - 1.33)	0.38 (0.1 - 0.81)
S	45.3 (31.6 - 56.2)	3.16 (1.15 - 5.62)	1.07 (0.70 - 1.54)	0.72 (0.60 - 0.83)
Cl	< 0.24	0.29 (0.12 - 0.49)	4.22 (2.06 - 6.49)	0.29 (0.1 - 0.60)
K	13.3 (9.30 - 17.8)	5.62 (2.94 - 8.06)	Below detection level	0.17 (0.1 - 0.34)
Ca	10.0 (7.50 - 13.3)	19.1 (15.4 - 23.7)	12.4 (8.66 - 15.4)	13.5 (11.5 - 17.8)
Ti	Below detection level			
Cr	0.21 (0.15 - 0.27)	0.15 (0.12 - 0.19)	Below detection level	
Mn	1.65 (1.15 - 2.21)	1.15 (1.00 - 1.33)	0.52 (0.49 - 0.60)	0.29 (0.21 - 0.37)
Fe	111 (108 - 133)	93.1 (75.0 - 116)	1.91 (1.33 - 2.37)	2.05 (1.78 - 2.37)
Ni	10.7 (7.50 - 13.3)	5.23 (3.92 - 6.49)	Below detection level	0.12 (0.1 - 0.15)
Cu	< 0.15	0.16 (0.15 - 0.18)	Below detection level	
Z	0.24 (0.18 - 0.29)	0.39 (0.29 - 0.49)	Below detection level	0.15 (0.1 - 0.21)

pages, 22 and 23, and the concentration profiles of the elements listed were traced. The results for one of the selected letters on page 22 are presented in Fig. 3 before treatment. The scan is indicated by the arrow ↕ in the inset in Fig. 1. The measured profiles evidently confirm the selection of the "ink elements", as their profiles excellently agree with the shape of the letter. Since S, K and Fe were found where there was a high concentration of ink, and Ca was the most relevant detected element in the paper, these elements were used to study further the effects of the conservation procedures.

The measured concentrations ($\mu g/cm^2$) for the four selected elements (S, K, Ca, Fe) at the ink spots on the pages 22, 23 are given in Figs.4 and 5. The distributions of the data shown illustrate the changes due to the conservation treatments. For all the measured elements (Na – Zn) the situation at ink and paper is additionally illustrated in Figs.6 and 7. Here, the ink values were extracted from the scans across the letter and the paper values from the random measurements on the spots far from the ink. The effects of the treatment can be concluded from

Table 2. Page 23 ink and paper elemental concentrations (μg/cm²) before and after the conservation treatment (deacidification). In the parentheses the range of values is given.

	Ink		Paper	
	Before treatment	After treatment	Before treatment	After treatment
Na	1.07 (0.1 - 2.74)	1.15 (0.1 - 2.74)	0.17 (0.1 - 0.34)	0.36 (0.1 - 0.81)
Mg	2.55 (1.54 - 3.65)	0.70 (0.25 - 1.15)	0.89 (0.52 - 1.24)	0.37 (0.1 - 0.76)
Al	0.93 (0.14 - 1.65)	0.83 (0.27 - 1.43)	0.52 (0.29 - 0.79)	0.42 (0.1 - 0.87)
Si	1.24 (0.1 - 2.74)	1.70 (0.70 - 2.74)	2.82 (1.91 - 3.65)	1.91 (0.70 - 3.16)
P	1.07 (0.42 - 1.78)	1.54 (1.15 - 2.05)	0.42 (0.19 - 0.65)	0.29 (0.1 - 0.60)
S	75.0 (65.0 - 93.1)	26.6 (19.1 - 34.0)	4.73 (2.05 - 7.50)	1.15 (0.71 - 1.65)
Cl	Below detection level	0.29 (0.1 - 0.70)	1.68 (0.42 - 2.94)	0.30 (0.1 - 0.56)
K	21.1 (19.1 - 23.7)	20.5 (14.3 - 27.4)	0.93 (0.60 - 1.37)	0.27 (0.1 - 0.55)
Ca	10.9 (7.72 - 14.3)	35.0 (31.6 - 37.6)	10.7 (7.94 - 13.3)	7.50 (3.65 - 11.5)
Ti	Below detection level	0.14 (0.1 - 0.32)	Below detection level	
Cr	0.56 (0.42 - 0.70)	0.42 (0.32 - 0.60)	Below detection level	
Mn	2.21 (1.78 - 2.74)	1.56 (1.31 - 1.88)	0.45 (0.42 - 0.50)	0.22 (0.1 - 0.37)
Fe	294 (255 - 321)	259 (205 - 307)	4.28 (2.66 - 6.21)	3.65 (1.65 - 5.62)
Ni	22.7 (20.5 - 25.9)	8.66 (6.49 - 10.7)	0.29 (0.15 - 0.45)	0.20 (0.1 - 0.29)
Cu	9.31 (6.98 - 12.4)	9.72 (8.06 - 11.5)	Below detection level	
Zn	5.23 (3.76 - 6.31)	4.16 (2.94 - 5.46)	Below detection level	

these distributions. The amount of sulfur decreased, this was more pronounced after the water washing in comparison to the deacidification with calcium hydroxide. The reduction in the concentrations could be observed for K (only at water washing) and some other elements (Mg, Al, Cr, Mn, and Ni) also. The amount of Fe diminished by about 20%. This could be attributed to the presence of water soluble Fe(II) compounds. The rather high reduction of S at the same time, which is close to a factor of 15 for page 22 (water washing), and around 3 for page 23 (deacidification), could be explained by the migration of S as sulfuric acid, as this is the only other water soluble sulfur-containing compound present in the ink besides iron (II) sulfate [10].

It is interesting to note that at the ink locations there was a marked increase in the concentration of Ca during the treatment for page 22 (water treatment) also. This can probably be explained by the formation of organic and/or inorganic insoluble paper and ink compounds with Ca being present in water during the treatment.

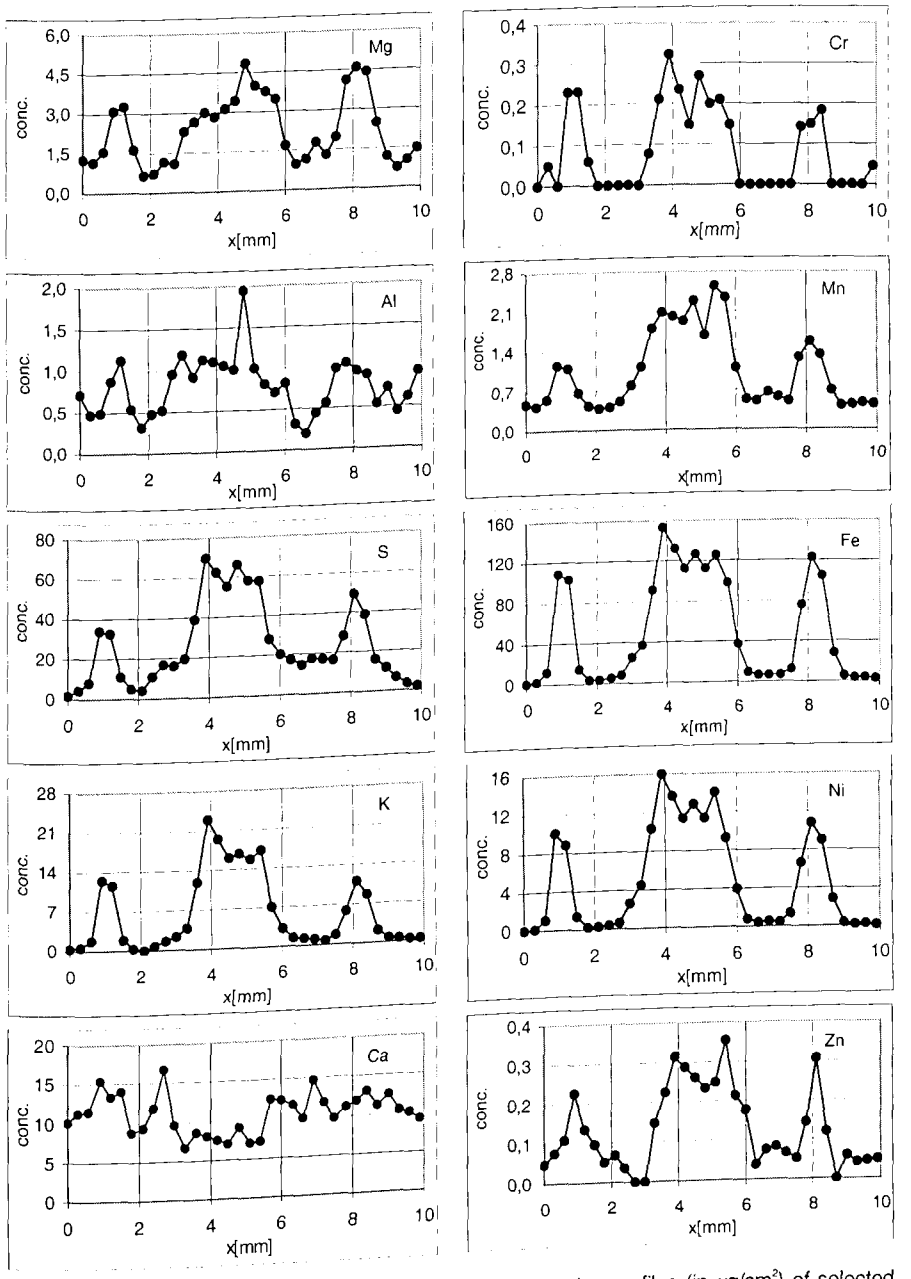

Fig. 3: Page 22 before treatment. The elemental concentration profiles (in μg/cm²) of selected elements that correspond to the scan across the letter as shown in the inset of Fig1.

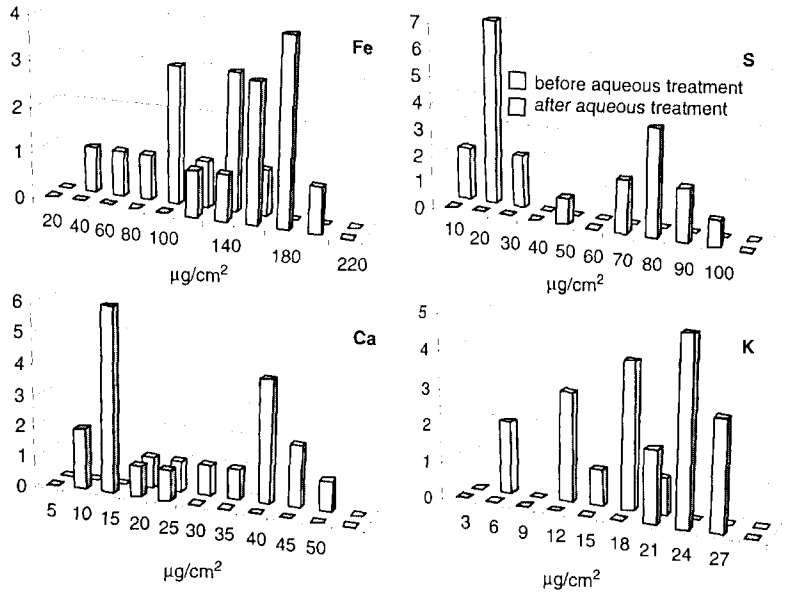

Fig. 4: Page 22. Concentration distributions ($\mu g/cm^2$) of elements Fe, S, Ca and K at the ink locations before and after the treatment (water washing). The ordinate gives the number of cases corresponding to the particular concentration.

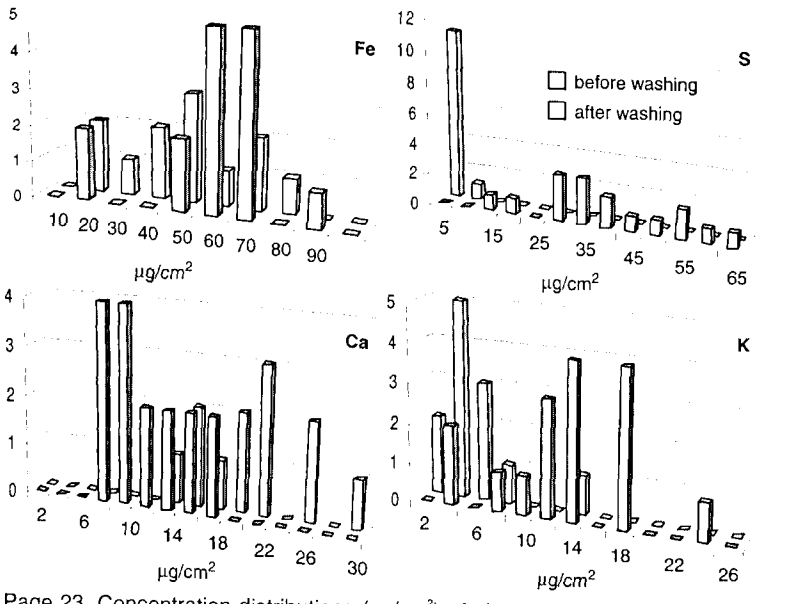

Fig. 5: Page 23. Concentration distributions ($\mu g/cm^2$) of elements Fe, S, Ca and K at the ink locations before and after the treatment (deacidification). The ordinate is gives the number of cases corresponding to the particular concentration.

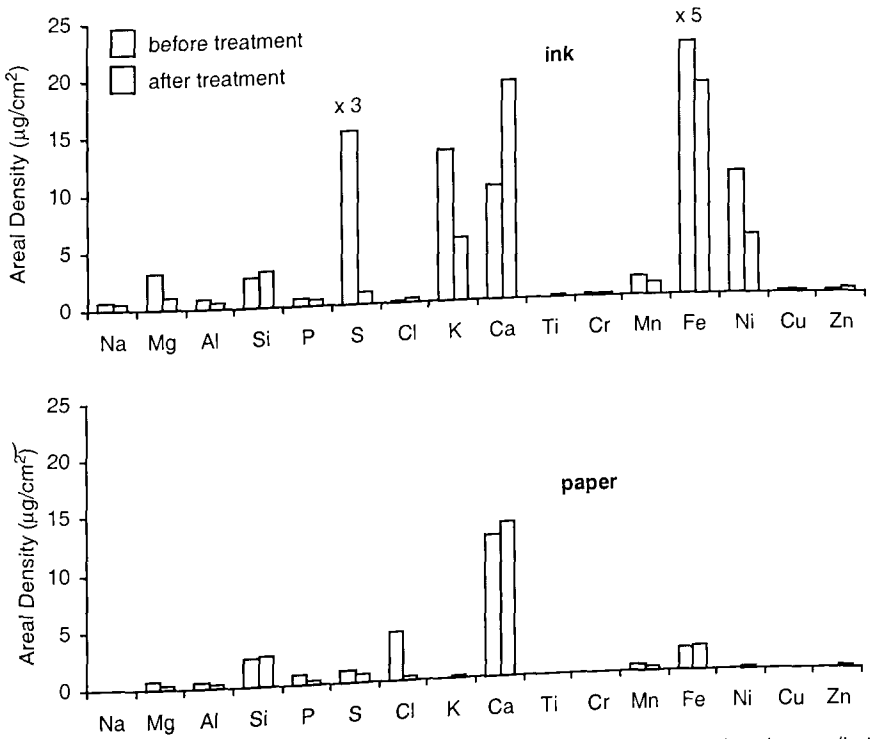

Fig. 6: Concentration values ($\mu g/cm^2$) for all the measured elements at ink (top) and paper (bottom) locations of page 22 before and after the treatment (water washing). The multiplication factors in the ink histogram (3 for S, 5 for Fe) are valid for both values, before and after treatment.

From the elemental concentration profiles (Fig. 3) some additional information about edge effects between the ink and the paper can be deduced. It would seem that the chemical compounds containing S, and some other elements (Mg, Al, Mn, Cu) demonstrated broader concentration profiles while for many "ink elements" (Na, K, Cr, Fe, Ni, Zn) the profiles seemed narrower. A possible explanation for the observed phenomena could be that there was a different chromatography migration for each particular compound[10].

For further analysis of the manuscripts with the proposed approach it could be concluded that the method should be applied with great care and a sufficient number of measurments. It is recommended that the measuring points on the blank paper should be well separated from the ink (at least by a few mm). For the determination of the ink composition individual points on the ink are not enough. Reliable information can be obtained only by scans across the writing.

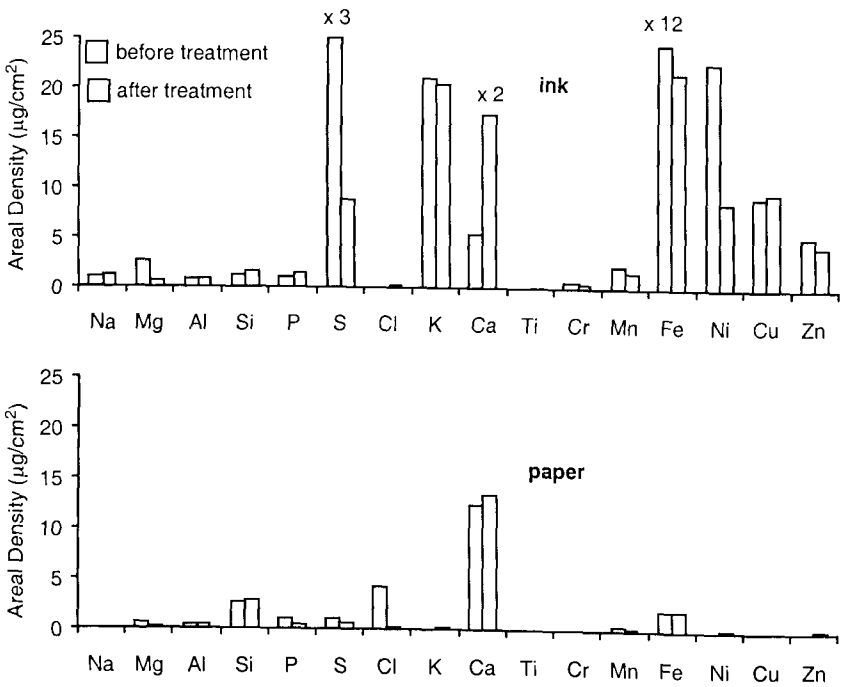

Fig. 7: Concentration values ($\mu g/cm^2$) for all the measured elements at ink (top) and paper locations of page 23 before and after the treatment (deacidification). The multiplication factors in the ink histogram (3 for S, 12 for Fe, 2 for Ca) are valid for both values, before and after treatment.

Conclusions

The initiative phase of the analysis given shows the applicability of the PIXE method for ink and paper elemental composition studies on rag paper manuscripts. When applied to the investigation of aqueous treatments on the 17th century manuscript it was proved that the method can be used to trace the composition of the iron-gall manuscripts before and after conservation, to follow the compositional changes caused by the treatment. It has been shown quantitatively how water treatment affects the iron-gall writing as well as how deacidification using calcium hydroxide influences the ink's and paper's elemental composition. As a proton beam offers a good enough lateral resolution (< 0.3 mm) the migration of the ink elements into the paper was traced after treatment. One of the main advantages of this kind of approach is that it works in a non-destructive manner, which means that the manuscripts remained practically undamaged in the study. The only drawback was that the analysis gave elemental concentrations and not the

chemical composition. However, the method was multi-elemental and all relevant elements constituting the iron-gall ink could be deduced simultaneously. Furthermore, at least partial chemical specification can be obtained from the elemental concentration ratios. The next phase of the study would be to apply the method to other deacidification treatments and those based on the application of complex formers (phytates, e.g.)[2].

It has been shown that the method described can be applied on original documents in a non-destructive way. However, it is quite obvious that for a better understanding of the damage provoked by inks, as well as analyzing conservation treatment effects, the PIXE method should be combined with other methods. Namely, for a definite understanding of the chemical processes taking place between ink and paper when triggered by the environment (humidity, temperature, pollution) the changes in the chemical state of the elements involved should be studied also.

One of the interesting fields where the method could also be usefully applied is for the investigation of the provenance of the documents. Namely, the trace element composition of the inks and papers can be considered as the "finger print" of the document, which could be related to the technology applied at the time as well as to the author(s) identification.

Acknowledgment

The authors acknowledge the collaboration within the EU Action COST G1, which contributed to the continuing interest of the application of IBA methods into the field of manuscripts conservation.

Summaries

Distribution of Chemical Elements of Iron-Gall Ink Writing Studied by the PIXE Method.

The chemical element profiles of iron-gall ink writing before and after water treatment and deacidification were determined. A 17th century manuscript of rag paper was used in the study. The chemical elemental analysis was performed non-destructively by the Proton Induced X-ray Emission (PIXE) method. The concentration profiles of 15 elements ranging from Na to Pb were measured with the precision of 0.3 mm. Quantitative composition of ink and paper was determined and the elemental concentration changes due to the aqueous treatments were traced by PIXE. It is considered that the method can be developed and could help conservators in a decision making process.

Analyse de la répartition des éléments chimiques de l'encre gallique au moyen de la méthode PIXE

L'objet de l'analyse consistait à déterminer le profil des éléments chimiques de l'encre gallique sur un document écrit avant et après un traitement aqueux et une désacidification. A cet effet une étude a été réalisée sur un manuscrit en papier chiffon datant du 17ème siècle. La méthode utilisée pour cette analyse, consistant dans l'émission de rayons X induite par des protons (Proton Induced X-ray Emission) est une méthode qui ne détruit pas les éléments chimiques. Les profils de concentration de 15 éléments allant de Na à Pb ont été mesurés avec une précision de 0,3 mm. De cette façon il a été possible de déterminer la composition quantitative d'encre et de papier ainsi que de suivre les changements de concentration subis par les éléments au cours des traitements aqueux enregistrés par la méthode PIXE. Il semble que cette méthode mériterait d'être développée et qu'elle pourrait devenir un instrument de travail efficace pour les conservateurs.

Untersuchung der Verteilung der Elemente von Eisengallustintenschrift mit Hilfe der PIXE Methode.

Es wurde ein Profil der Elemente in einem im 17. Jh. mit Eisengallustinte beschriebenen Blatt Hadernpapier erstellt. Hierzu wurde eine nicht-materialzerstörende Methode eingesetzt, nämlich die Proton-induzierte Röntgenstrahlenemmission PIXE (Proton Induced X-ray Emission). Die Verteilungsprofile der Konzentration von 15 Elementen zwischen Na und Pb wurde mit einer Genauigkeit von 0,3 mm gemessen. Auf diese Weise wurde die quantitative Zusammensetzung von Tinte und Papier erfaßt sowie die Veränderungen, welche die gemessenen Elemente infolge einer wäßtigen Behandlung erfuhren. Die Methode kann zu Werkstattroutine entwickelt und so zu einer Entscheidungshilfe für den Konservator werden.

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Damage Caused by Destructive Insects to Cellulose Previously Subjected to Gamma-Ray Irradiation and Artificial Ageing

by G. MAGAUDDA, M. ADAMO, & F. ROCCHETTI

INTRODUCTION

Numerous experimental studies have proved the effectiveness of ionizing irradiation to control pest infestation and to disinfect books and archival documents, which have been damaged by both insects and microscopic fungi. In a recent study conducted on the *Periplaneta americana* (American cockroach)[1] – a widespread omnivorous insect, known to cause significant damage in libraries and archives – we demonstrated that a very modest quantity of radiation (in the dosage range of 200–300 Gy) was sufficient to kill both adults and larvae of these voracious pests very quickly.

At the same time, it is known that while radiation can kill living organisms, it can also have negative effects on cellulose, a macromolecule that forms the structure of paper, accelerating its depolymerization more rapidly than during natural ageing[2–3].

With this experimental study – as with another study published recently on the behaviour of microscopic fungi responsible for the biodeterioration of paper [4] – we wanted to investigate whether, and up to what point, the chemical and physical alterations induced in cellulose by irradiation and/or ageing could negatively predispose this material, once treated, to the attack of destructive insects, increasing their harmfulness.

MATERIALS AND METHODS

The cellulosic material chosen was Whatman paper (manufactured by Carlo Erba), produced with pure, chlorine- and impurity-free cellulose fiber, which has a composition that is very suitable as an experimental model for our purposes even though, due to its characteristics, it cannot be considered printing paper.

Irradiation technologies

The irradiation of the paper was carried out at the "Calliope" plant of the Ente per le Nuove Tecnologie l'Energia e l'Ambiente (ENEA) in its Research Center at the Casaccia. The Calliope plant is a pool-type irradiation facility equipped with a CO-60 source of a cylindrical geometry licensed for a maximum nominal activity of 3.7×10^{15} Bq (100,000 Ci).

To determine the levels of the pre-set dosages to be used in the experimental program, Fricke dosimetry was used, following ASTM Standard D 1671-72.

A dose rate of 13 kGy/h, doses of 3 and 10 kGy (quantities of radiation from 10 to 50 times higher than that necessary for eradicating insects from books) was used in our experiment. The Gray (Gy) corresponds to an absorption of ionizing energy equal to 1 Joule per kg of material treated. These doses were compared to non-irradiated control material. In order to exacerbate further the effect of the irradiation on the depolymerization of the cellulose, and to make the consequences of this phenomenon more evident, doses of 100 and 200 kGy (radiation doses from 300 to 1,000 times higher than necessary) were also administered.

Accelerated ageing

In order to verify the effect of radiation over time, accelerated ageing was carried out. The irradiated samples and the corresponding controls were kept in a climatic oven at 65% R.H. and a temperature of 80°C for 12 and 24 days (ISO 5630/3).

Analysis procedure

In order to evaluate the attack of destructive insects (*P. americana*) or, in other words, to evaluate the appeal to them and thus the vulnerability of the cellulose, the sheets of Whatman paper that had been subjected to the two treatments described above were used to cover the bottom of boxes in which the insects were bred, under the best environmental conditions for their development in a controlled environment. In each box 28 specimens, equally divided between adult males and females and larvae chosen from three different larval stages, were bred; 5 repetitions were prepared for each experimental point. During the experiment, care was taken to ensure keeping the number and stages of insects in the different boxes rigorously constant, removing newborn individuals and replacing any, although infrequent, dead specimens.

The insects were fed a quantity of food (food pellets used in research institutes for feeding small rodent mammals and a few apple slices) that was just sufficient for their nutritional needs. In similar breeding conditions, very frequently the in-

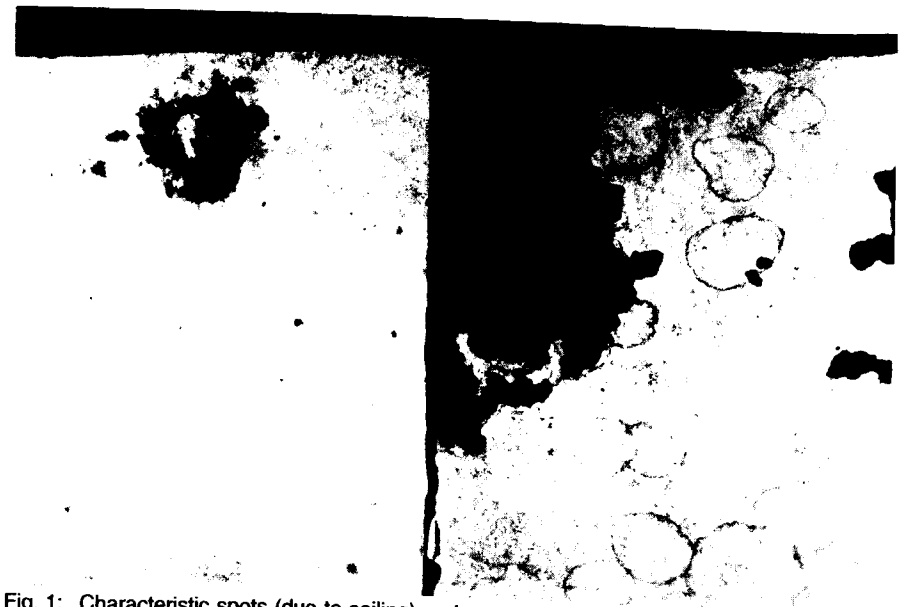

Fig. 1: Characteristic spots (due to soiling) and erosion caused by cockroaches. On the left, an untreated Whatman sheet and, on the right, the same kind irradiated with a very high dosage of gamma rays (200 kGy).

sects would resort to paper as a supplementary source of nourishment. We expected that an insect capable of eating cellulose would have been potentially more destructive to a material that had already deteriorated, compared to one that was still intact. The extent of the damage was calculated very simply by weighing the sheets of Whatman paper over a 21–28 day period.

The Whatman sheets, after weighing, were put back into the breeding boxes so that the cockroach population could continue their destructive action.

The results of the deterioration of the paper were expressed as the percentage ratio of the weight of the sample examined, calculated day by day, to that of the corresponding untreated control sheet.

Results

The damage caused by destructive insects to paper, which makes up books and archival documents, is mainly of a mechanical-physical nature. It can vary in degree leading to the loss of vital information on individual pages or even the complete destruction of whole books.

In the case of cockroaches, this type of damage is accompanied by the soiling of the paper in the form of characteristic spots, due to the habit of these pests of

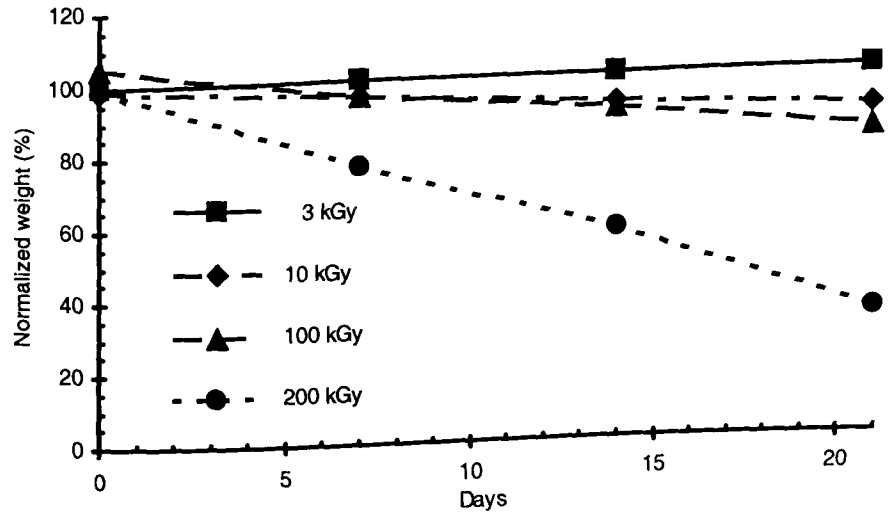

Fig. 2: Weight trend over time, on the basis of the erosion caused by cockroaches, of the Whatman paper samples subjected to graduated doses of gamma-ray radiation.

regurgitating their food and leaving their physiological excrations on the page surface. Fig. 1 shows both types of damage caused by the *P. americana* and the extent of the erosion depending on the irradiation to which the paper has been subtent previously. The extremely high quantity of radiation absorbed by the cellulose – in this specific case 200 kGy – resulted in a higher degree of erosion caused by the insects. However, during the short experimentation time and the period immediately following, the sample on the left, which was not irradiated, was also eroded in just a few weeks.

Fig. 2 shows the trend over time (3 weeks) of the weight of the cellulose samples, depending on the different doses of gamma-ray irradiation received, after being subjected to erosion by *P. americana*. There was clearly a close cause-effect relationship between the extent of the erosion and the radiation doses absorbed by the cellulose beforehand. The values which, for the first measurement, exceed 100% are to be considered in relation to the increase in the weight which (for some values regardless of the destruction caused by the insect) is due to the greater absorption of moisture in the breeding environment of the cockroaches compared to that of the environment in which the initial weighing of cellulose was carried out.

Fig. 3 shows the trend over time (4 weeks) of the weight of the cellulose sheets subjected beforehand to artificial ageing for 12 and 24 days. There was virtually no difference in the erosion of the samples aged for double the times; both keep

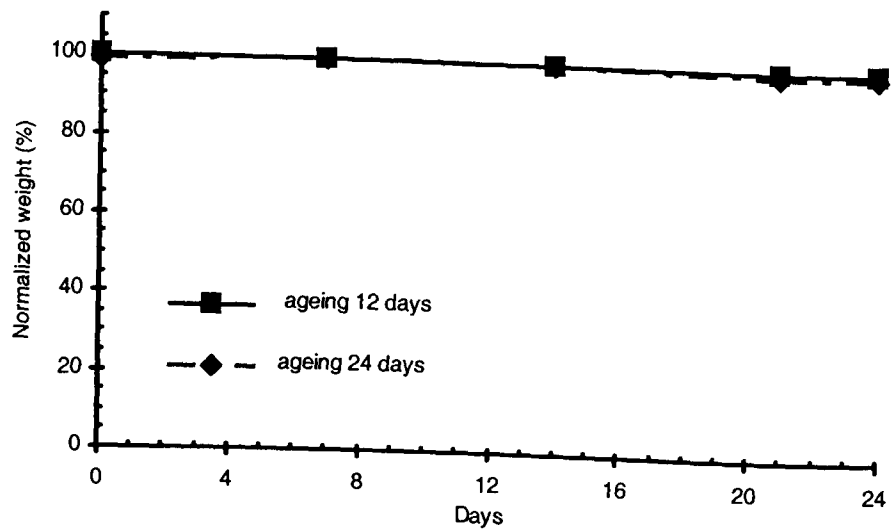

Fig. 3: Weight trend over time, on the basis of the erosion caused by cockroaches, of the Whatman paper samples subjected to artificial ageing for 12 and for 24 days.

their weight over the test time (24 days) comparable with that one of the untreated control.

Figs. 4 and 5 refer to the extent of the erosion caused on the sheets of cellulose that had been irradiated at different doses and then subjected to artificial ageing for 12 and 24 days, respectively. There were no significant differences that may be attributed to the different lengths of the ageing treatment. The effect of the ionizing radiation in relation to the absorbed doses is highly prevailing the effect of artificial ageing: cf. Figs. 2, 4 and 5.

Conclusions

Irradiated Whatman paper (filter paper) subjected to the action of destructive insects shows in our experimental conditions more erosion than the non irradiated control paper. This phenomenon could be related to the depolymerization of the macromolecules of the cellulose, which as has been shown previously[2, 5, 6], is proportional to the gamma dosage absorbed by the material. On the other hand, the ageing treatment seemed to have no influence.

For those who are interested in using radiation as a method for disinfecting/disinfesting paper material, it is necessary to make a distinction between the radiation dosages necessary for the relevant treatment of the material – which in

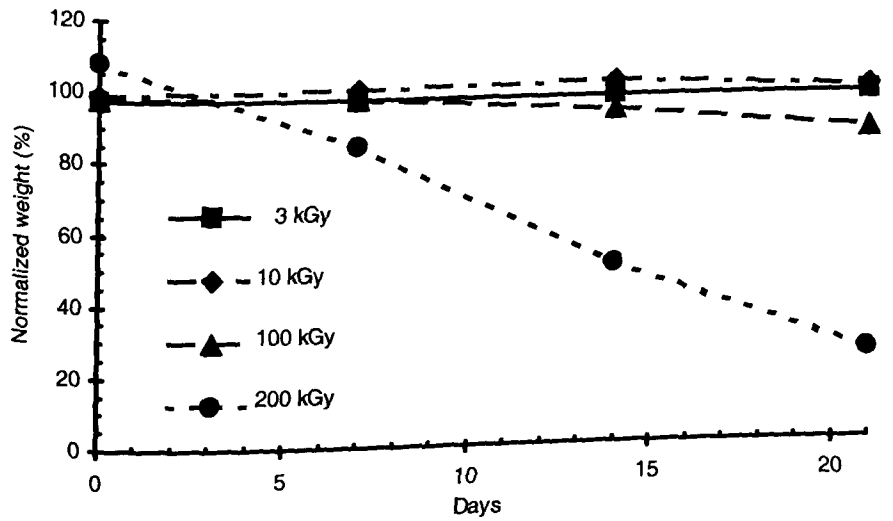

Fig. 4: Weight trend over time, on the basis of the erosion caused by cockroaches, of the Whatman paper samples subjected to combined irradiation + ageing treatment (12 days).

experiments did not cause appreciable negative effects – and the much higher dosage used intentionally by us only for speculative purposes.

Experimenting with extremely high radiation dosages enabled us to demonstrate that when the phenomena we want to measure are present, our analytical instruments are able to detect them. Already, two days after the start of the experiment, the sheets of Whatman paper subjected to extremely high radiation dosages appeared to be attacked by the cockroaches to a greater extent than the control sheets (Fig. 1). In other words, the accuracy of these analytic instruments allows us to assert the harmlessness of the treatment if the radiation dosages are around 3 kGy, which is what we would recommend. Moreover, it should be taken into account that the differences in the degree of erosion are measurable only if they are observed during the days immediately after the treatment since, as time goes on, even the non-irradiated control samples and those irradiated with low doses as well as the samples submitted to ageing only, were also irremediably attacked and destroyed by the insects.

As has been said several times in the past that destructive living organisms become truly harmful for collections of organic based materials such as books, when the environmental conditions exceed known control parameters. Though cockroaches are described in literature as responsible for the biodeterioration of paper, it goes without saying that these insects should be not in libraries! Negative environmental conditions are always the main reason for the development of

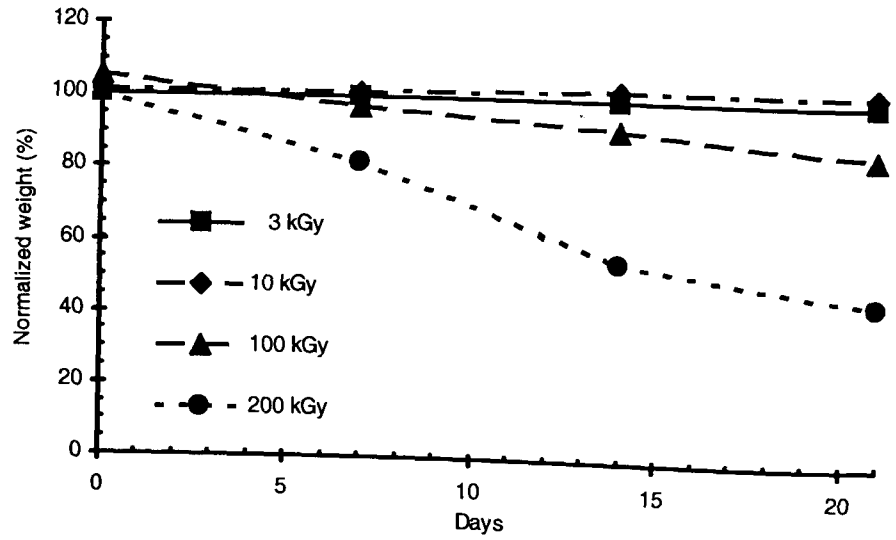

Fig. 5: Weight trend over time, on the basis of the erosion caused by cockroaches, of the Whatman paper samples subjected to combined irradiation + ageing treatment (24 days).

a pest problem. Only after having paid rigorous attention to the correct environmental conditions for keeping books and paper documents, may disinfection/disinfestation measures be considered, knowing that the expected benefit of any chemical or physical treatment on that material must be weighed against the risk of a negative side-effect, which even if minimal or even unmeasurable, is always present.

In the case of gamma-ray irradiation used to kill destructive insects, the treatment proved to be very effective even at the maximum dosages of 300 Gy[1]. The depolymerization induced by the irradiation of the cellulose did not cause any negative effects at dosages lower than 10 kGy. This is pertinent mainly to the susceptibility of the material to the attack of insects that may come into contact with it after the treatment, even after long periods of time.

SUMMARIES

Damage Caused by Destructive Insects to Cellulose Previously Subjected to Gamma-Ray Irradiation and Artificial Ageing

The aim of the present paper is to develop a new system that is able to kill insects and microscopic fungi responsible for the destruction of books and documents, using gamma radiation. The authors particularly wanted to verify if the increase of depolimerization of cellulose, that is accelerated by gamma radiation and is related to the absorbed dose, could make treated material more susceptible to attack by chewing insects. For the trials a cockroach (*Periplaneta americana*) was selected as the insect and Whatman paper selected as a source of pure cellulose. The phenomenon is particularly evident with doses higher than 10 kGy but this dosage is much higher than that necessary for a practical application in libraries and archives. Artificial ageing does not cause cellulose to become more susceptible to insects attack.

Dommages causés par les insectes taraudeurs à la cellulose préalablement irradiée aux rayons gamma et ayant subi un traitement de vieillissement accéléré

Cette étude expérimentale a pour objectif de mettre au point un nouveau système capable de détruire les insectes et les champignons microscopiques qui détériorent les livres et les documents d'archives au cours de leur conservation en utilisant l'irradiation de rayons gamma. Les chercheurs tenaient surtout à vérifier si l'augmentation de la dépolymérisation de la cellulose, qui est accélérée par l'irradiation des rayons gamma – et ceci proportionellement à la dose absorbée – était susceptible d'accroître la vulnérabilité du matériel traité à l'agression des insectes taraudeurs. Pour réaliser l'expérience on a utilisé comme insecte une blatte (Periplaneta americana) et du papier filtre Whatman en cellulose pure. L'hypothèse formulée sur le phénomène de dégradation ne se vérifie qu'à des doses supérieures à 10 kGy mais un tel dosage est nettement supérieur à celui nécessaire pour une application pratique dans les bibliothèques et les archives. Le vieillissement artificiel n'est pas un facteur qui aurait pour effet d'augmenter la vulnérabilité de la cellulose à l'agression des insectes taraudeurs.

Insektenschaden als Folge einer Gammabestrahlung und einer beschleunigten Alterung

Zweck der Untersuchung, über die hier berichtet wird, ist die Entwicklung eines neuen Systems (Gamma-Bestrahlung) zum Abtöten von buchschädigenden Insekten und sporenbildenden Mikroorganismen (Schimmel). Ein besonderes Anliegen der Autoren war es festzustellen, ob der Rückgang des Polymerisationsgrades der Cellulose, der von der Gamma-Bestrahlung, abhängig von deren Dosierung, bewirkt wird, das behandelte Material für Fraßinsekten attraktiver macht. Der Untersuchung unterworfen wurde eine Schabenart (*Periplaneta americana*) and Whatman Filtrierpapier, bestehend aus reiner Cellulose. Eine Schädigung in dem umrissenen Sinn tritt ein bei Dosierungen über 10 kGy, was jedoch weitaus mehr ist als für Schädlingsbekämpfung in Bibliothek und Archiv erforderlich. Beschleunigte Alterung macht Cellulose nicht anfälliger für Insektenfraß.

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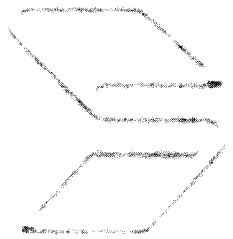

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