 DOI: 10.1002/masy.200651218

Copper Corrosion: Comparison between Naturally Aged Papers and Artificially Aged Model Papers

Ute Henniges,[1] *Ulrike Bürger,*[2] *Gerhard Banik,*[3] *Thomas Rosenau,*[1] *Antje Potthast**[1]

Summary: Copper corrosion on paper works of art is commonly explained by copper ion-catalysed cellulose oxidation, usually reflected by discoloration of pigment and surrounding paper as well as by loss of mechanical strength. In this study, model paper and historic paper samples, both containing copper pigments, were compared using fluorescence labelling of carbonyl groups and subsequent GPC analysis. The historic paper samples did not show any typical sign of copper pigment induced discoloration, but high brittleness. In artificially copper-corroded paper samples the distribution of carbonyl groups in combination with the molecular weight distribution of cellulose clearly indicated the occurrence of oxidative processes. In contrast, only insignificant oxidative damage was detected in the case of the paper fragments from an original work of art, a codex from the 15th century. Here, mostly degradation by hydrolytic action was revealed. There was no introduction of carbonyl groups into the bulk section of the molecular weight distribution, and the gain in new carbonyl groups corresponded to the number of reducing end groups newly generated by hydrolysis.

Keywords: carbonyl groups; cellulose degradation; copper corrosion; fluorescence labelling; historic papers; model papers; molecular weight distribution

Introduction

Paper material, mainly made up of the natural polymer cellulose, is subject to complex aging processes. Acidic hydrolysis is considered to be the predominant degradation pathway for celluloses in paper, but oxidative processes may also play an important role. Frequently used writing and painting media, such as iron gall ink and copper pigments, often cause oxidative damage to historical works of art. Migration of transition metal ions from pigments or inks into the surrounding or underlying paper material has been recognized since long as serious threat to the preservation of our cultural heritage in the form of historical paper and parchment objects.[1,2] Under certain conditions, such as changing humidity, transition metal ions are released from painting or printing pigments, provoking catalytic and thus accelerated oxidation of celluloses.[3]

In historical preparations for painting purposes, copper acetate-based pigments are a mixture of neutral and basic copper acetates, which are partly water soluble from the beginning. During natural aging and by accelerated degradation of the binding agent, mostly glue or gum arabic, more and more ions are mobilized and released into the surrounding paper matrix. During this process, cellulose is chemically altered, and in the worst cases deteriorated or even fully destroyed.[4] Visually, this process can often

[1] University of Natural Resources and Applied Life Sciences, Department of Chemistry, Institute of Organic Chemistry, Muthgasse 18, A–1190 Vienna, Austria Member of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu
E-mail: antje.potthast@boku.ac.at
[2] Stadt- und Universitätsbibliothek Bern, Papierrestaurierung, Münstergasse 63, CH-3011 Bern, Switzerland
[3] Staatliche Akademie der Bildenden Künste Stuttgart, Höhenstraße 16, D-70736 Fellbach, Germany
Fax: (+43) 1 36006 6059

be perceived by browning of pigment and surrounding paper, increased brittleness as well as by pronounced loss of mechanical strength properties.

In order to study in detail the degradation pathways in papers covered with copper pigments and in order to test new conservatory treatments as well as storage options for historical papers, mostly model papers have been used. Precious originals cannot be employed in studies with unknown results and cannot provide sufficient amounts of sample material for large numbers of screening tests. The question arises to what degree artificially aged model papers reflect the situation in historical paper material. Does artificial aging under the stress of thermal, irradiation and moisture treatment induce the same effects as prolonged storage (sometimes over centuries) of the material under less drastic conditions? First of all, the choice of paper making fibers, pigments, binders and preparation techniques is crucial for obtaining authentic model material. A similarity of these factors with regard to historic samples is the prerequisite to conclude from artificial sample material to original, historic papers. Yet, some doubts remain whether artificially aged modern sample material will follow a similar degradation pathway as historic papers of comparable constitution. While for (iron gall) ink corrosion a large number of naturally aged material has been investigated in numerous tests - also destructive ones -, the number of studies about historic papers and manuscripts exhibiting degradation induced by copper pigments – so-called ''copper corrosion'' is rather limited.

The aim of the present study was to characterize the deterioration state of an original, naturally aged paper with copper corrosion and to compare the results with artificially aged sample paper material. For this purpose, we compared three historic paper samples with different degrees of copper corrosion to model papers with artificially induced copper corrosion using fluorescence labelling of oxidized groups in cellulose and subsequent GPC analysis.

Material and Methods

Labelling:

Carbazole-9-**C**arbonyl-**O**xy-**A**mine(CCOA) labelling of carbonyl groups was performed as described earlier.[5–7] The labelling procedure was scaled down to 4-5 mg of paper material.

General Analytics:

Gel permeation chromatography (GPC) measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; autosampler, HP 1100 column oven, Gynkotek STH 585, fluorescence detector TSP FL2000 (CCOA); multiple-angle laser light scattering (MALLS) detector, Wyatt Dawn DSP with argon ion laser ($\lambda_0 = 488$ nm); refractive index (RI) detector, Shodex RI-71; Data evaluation was performed with standard Chromeleon, Astra and GRAMS/32 software.

GPC Method:

The following parameters were used in the GPC measurements: flow, 1.00 mL min^{-1}; columns, four PL gel mixedA ALS, 20 μm, 7.5×300 mm; fluorescence detection, $\lambda_{ex} = 290$ nm, $\lambda_{em} = 340$ nm (CCOA); injection volume, 100 μL; run time, 45 min. *N*,*N*-dimethylacetamide/ lithium chloride (0.9% w/v), filtered through a 0.02 μm filter, was used as the eluant.

Model Papers:

Test papers were prepared of modern handmade paper composed of linen and flax fibers without additional sizing or fillers. Copper acetate (90% basic and 10% neutral copper acetate) was printed on unsized paper according to historical protocols. The pigment was bound in skin glue media. Copper corrosion was simulated with accelerated aging at 55 °C and fluctuating humidity from 35–80% relative humidity (RH) every 6 hours to enforce water migration within the paper matrix. Furthermore, paper samples were subjected to artificial aging for seven days at 80 °C and 65% RH.

Carbonyl group distribution according to the CCOA protocol as well as changes in the molecular weight distribution were measured to reflect oxidative changes. The sample paper with simulated copper corrosion was cut into pieces, which were investigated separately. Details on the cutting scheme were described previously.[3] In addition, paper from the margin of the aged material was chosen as reference without copper corrosion effects.

Historic Material:

Loose fragments from the prayer book of Ursula Begerin, Codex 801 of the Burger Library Bern, (Burgerbibliothek Bern), Switzerland, have been analysed. Codex 801 dates back to 1390–1494.[8] It contains handwritten prayers and paintings from the *Reuerinnen* convent Strasbourg, presented on 195 pages (140 × 90–95 mm) with a leather-bound wooden cover. The rag paper appeared rather thick to the grip, but was apparently weakened at spots covered with green pigment. In contrast to typical copper corrosion phenomena, which show a brownish discoloration of the pigment and paper, the codex paper appeared flawless white, also at the cross-sections of broken-off fragments. All fragments are from pages dated before 1494. (Figure 1).

Results

The shortening of cellulose chains by cleavage of the glycosidic bond linking adjacent anhydroglucose (AHG) units and the oxidation of the cellulosic hydroxyls are the two major results of aging processes. Cellulose chain splitting is mainly attributed to hydrolytic mechanisms triggered by acidic compounds (or just water) present in the material or generated as aging proceeds.

Changes in the chain length distribution and a more or less pronounced introduction of oxidized functionalities are reflected by the macroscopic results of aging: discoloration and loss of mechanical strength. Low-molecular weight degradation products may accumulate in or on the paper or

Figure 1.
Examples of copper corrosion from codex 801, f.160r and f. 169r, Burger Library Bern, (Burgerbibliothek Bern), Switzerland.

may evaporate, depending on storage and handling conditions.

The analytical protocol referred to as CCOA method yields a number of important parameters to estimate the deterioration state of cellulose. Fluorescence labelling of oxidized functionalities, such as keto- and aldehyde groups, in combination with gel permeation chromatography for determination of the molecular weight distribution allows for an in-depth examination of hydrolytic and oxidative processes.

Historical paper material (obtained from Burger Library Bern (Burgerbibliothek Bern))

The fragments investigated originated from different pages of codex 801. One fragment contained a green copper pigment (f. 169), another fragment an additional red pigment (f. 60), and one piece was without pigment coverage (f. 137). The red pigment was identified as minimum (red lead pigment) and cinnabar[9] (reddish mercuric sulfide), which are insoluble substances being highly unlikely to be involved in any hydrolytic process or in cellulose degradation. The originally used green copper pigment could not be identified as the copper corrosion was too advanced.

Table 1 summarizes the data obtained by the CCOA method applied to the three historical paper samples. The fragment without any pigment reflects the mere aging of the paper during the last 500 years. The DP of this pigment-free sample was comparable to other paper samples of this age. The paper was still in an acceptable condition with regard to degradation of the material and overall strength properties.

Model Papers

Fragments from artificially aged papers were taken as in the case of the historic samples, i.e. pieces with pigment coverage or far from the pigment. In addition, sample material from close vicinity to a pigment line was retrieved.

It was demonstrated by LA-ICP-MS [3] that copper ions diffused into neighbouring paper areas upon accelerated aging and that the degradation in those areas was even more pronounced as directly underneath the pigment. A more detailed description of the analysis of cellulosic material beneath, in close vicinity, and remote from copper pigment lines and of copper ion migration is given in [3].

Table 2 summarizes the data for the model papers obtained according to the CCOA-method.

Discussion

The distribution of the molecular weight for both model papers and historic papers showed the typical shape for rag papers (Figure 2) with a PDI of about 2. For the pigment-free historic sample the weight average molecular weight was 168500 g/mol, which corresponds to a DP_w of 1040. This value represents the action of natural aging without the additional effects of pigment coverage. The fragment containing both green and red pigments represented an intermediate condition. The red pigment

Table 1.
Summary of Carbazole-9-carbonyl-oxy-amine data, historical paper samples.

Sample	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_z$	$\overline{DP}_w$	PDI[1]	REG[2]	CO in μmol/g
	kg/mol	kg/mol	kg/mol			theor.	
Cod. 801 green pigment	66.71	14.58	288.6	411	4.573	69.06	68.7
Cod. 801 green and red pigment	113.1	28.08	374.1	697	4.027	35.61	45.22
Cod. 801 no pigment	168.5	78.59	318.5	1039	2.144	12.73	18.22

[1] PDI: Polydispersity index: $\overline{M}_w/\overline{M}_n$.
[2] REG: Reducing end groups calculated from Mn (please note: this value assumes that reducing ends are not further oxidized and that determination of Mn is accurate).

Table 2.
Summary of carbazole-9-carbonyl-oxy-amine data, model paper samples.

Sample	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_z$	PDI[1]	REG[2]	CO in μmol/g
	kg/mol	kg/mol	kg/mol	Mw/Mn	theor.	
No contact with pigment	251.4	100.8	501	2.49	9.9	9.5
Direct contact with pigment	105	46.85	107.5	2.24	21.3	31.3
Adjacent to pigment line	114.4	60.51	215.4	1.89	16.5	37.8

[1]PDI: Polydispersity index: $\overline{M}_w/\overline{M}_n$.
[2]REG: Reducing end groups calculated from Mn (please note: this value assumes that reducing ends are not further oxidized and that determination of Mn is accurate).

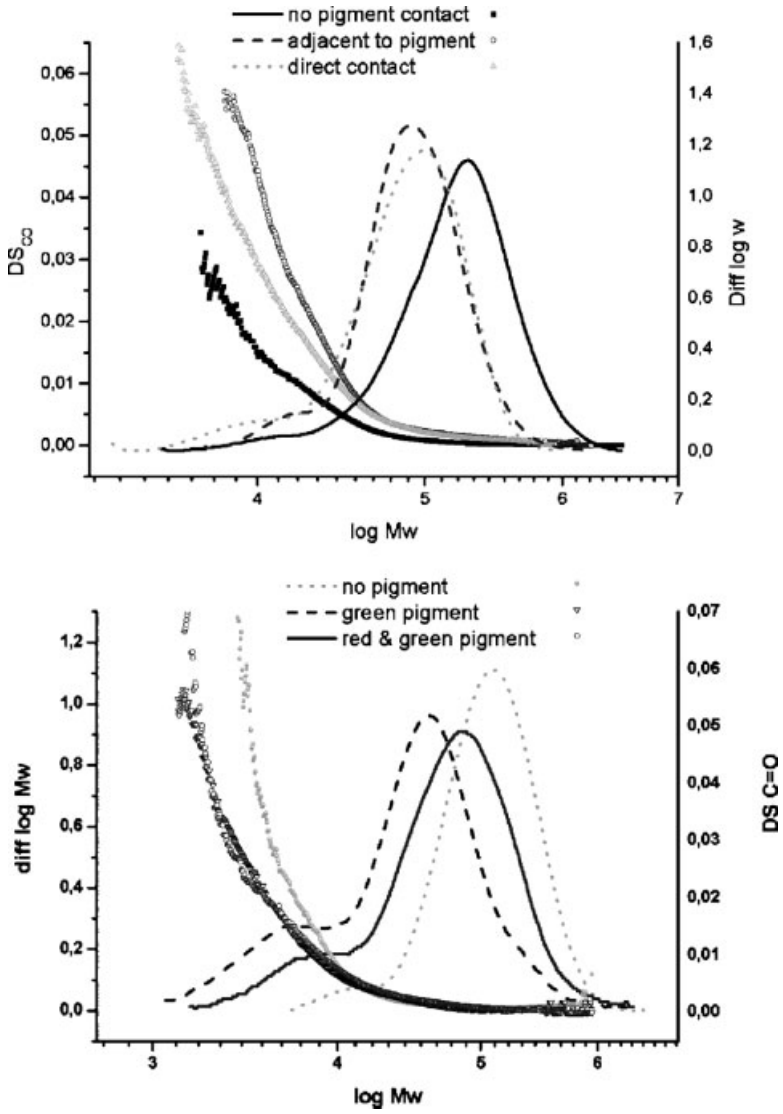

Figure 2.
Molecular weight distribution and degree of substitution ($DS_{C=O}$) plots for carbonyl groups. Top: model paper, bottom: historical samples.

had no negative effect on the cellulose as expected, which is readily explained by the lacking solubility of this inorganic pigment. The degradation of the cellulose was evident, but did not reach the extent of the parts covered solely with green pigment. In the fragment with green pigment only, the molecular weight distribution was broadened, the PDI doubled. A drastic decrease of the molecular weight of the cellulose was observed. While for the fragment with green and the red pigment the Mw dropped by 33%, paper parts covered entirely with green pigment lost even 60% in cellulose DP.

In the case of model papers, areas in contact with copper ions were significantly degraded. However, the PDI did not change to higher values as in the case of the historic samples. The accumulation of low-DP material - to be seen as a distinct shoulder below 10000 g/mol – was more pronounced for the historic sample, but also the artificial aging in the case of the model papers increased the amount of material in this MW region.

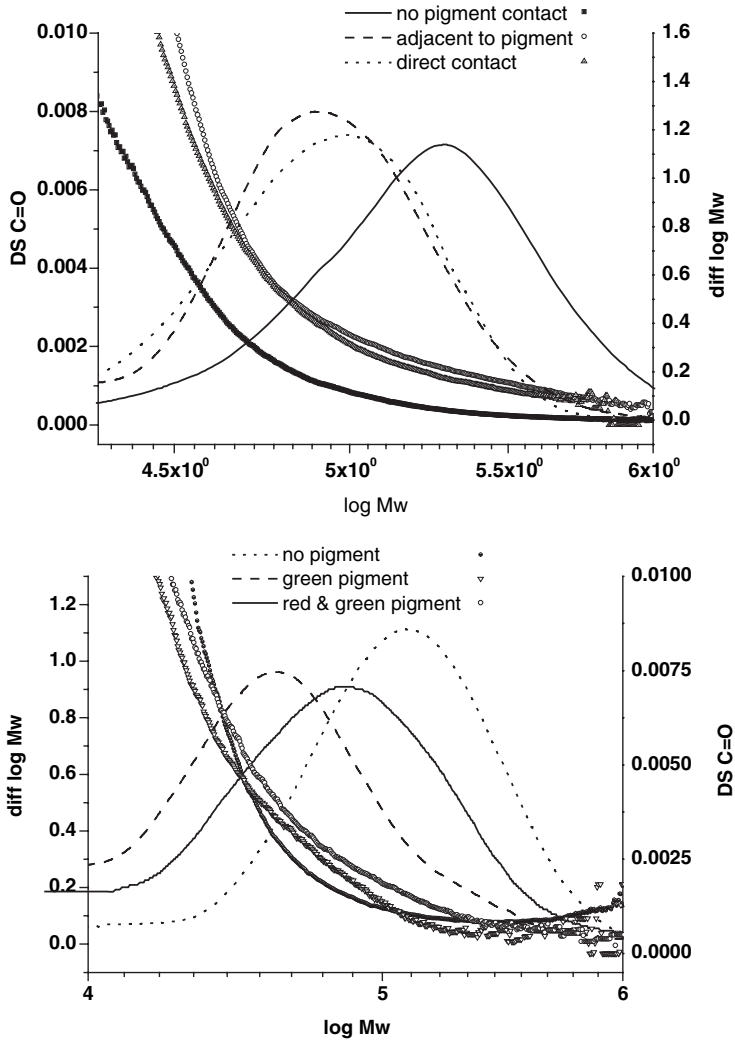

Figure 3.
Enlargement of the molecular weight distribution and degree of substitution ($DS_{C=O}$) plots for carbonyl groups. Top: model paper, bottom: historical samples.

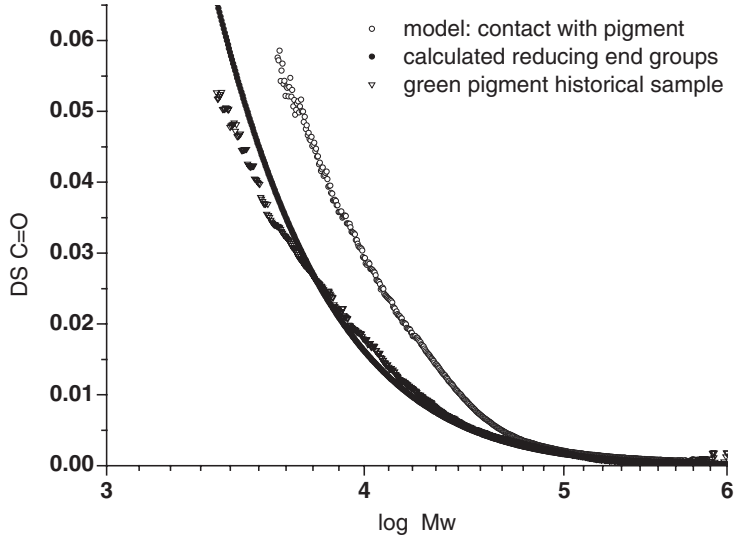

Figure 4.
Comparison carbonyl-DS curves: calculated plots for a material containing only reducing ends without additional carbonyls, measured carbonyl profiles for the historical paper fragment with green pigment coverage and the artificially copper-corroded sample paper.

A peculiar feature of the copper corrosion in the historic samples was the lack of any discoloration: neither the cellulose nor the green pigments depict any yellowing or showed the presence of chromophores. Also the cross section of the paper was still white. The lack of discoloration was sharply contrasted by the deteriorated mechanical properties, with small pieces falling completely loose.

In case of the historical material the calculated reducing end groups ranged quite close to the measured carbonyl data. This proved that the cellulose degradation was largely due to hydrolytic influence and only insignificantly due to oxidative impact. The white paper appearance, also in the cross-section, sustains this fact, since oxidative modifications of cellulose usually translate into severe discoloration. However, the pH of the paper has been measured to be around 6.1 to 6.5.

In order to have a closer look at the distribution of oxidized groups across

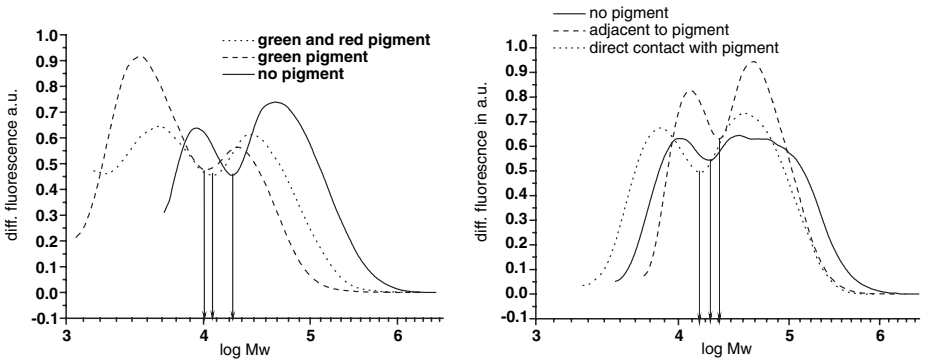

Figure 5.
Fluorescence signal (carbonyl groups) in relation to the molecular weight. left: historical paper fragments, right: artificially aged samples.

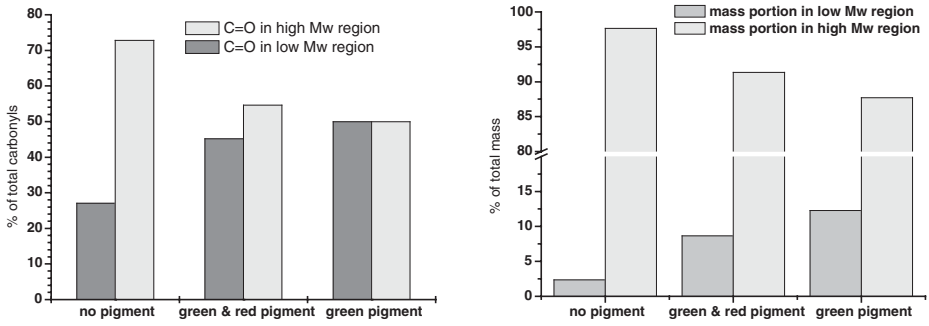

Figure 6.
Distribution of carbonyls and mass portion within the high/bulk-Mw and the low-Mw region for the historic samples. Borderlines were set as indicated by the arrows in Figure 5.

the molecular weight distribution, the carbonyl-DS plots have to be considered. Figures 2 and 3 give the molecular weight distribution curves along with the carbonyl group profiles. Figure 3 represents an enlargement of the high-Mw region of the plots in Figure 2, given for better illustration of the discussed effects. For the historic samples the carbonyl profiles of all three samples were similar within the error limits. Neither in the bulk nor in the high Mw part significant oxidation effects were found (cf. Figure 3, bottom).

In contrast, model copper corrosion caused pronounced oxidation of the cellulose. High-Mw regions and low-Mw material were affected likewise. The carbonyl profile curves were not identical anymore, but showed a clear vertical shift, typical of oxidative carbonyl group introduction. This offset of the DS plot (Figure 3, top) clearly proved the oxidation of the bulk material where copper ions were present. The intimate contact with the pigment was not necessary to induce oxidative processes. In accordance with previous studies, overall cellulose oxidation was even higher in areas adjacent to the pigment coverage than in regions directly below the pigment. This result once more emphasizes the role of copper ion migration in copper corrosion.

Purely hydrolytic degradation of the cellulose generates novel reducing end groups without additional carbonyls being introduced along the cellulose backbone. Exclusive generation of novel reducing ends thus reflects a pure hydrolytic mechanism. The DS of such materials – containing only naturally occurring reducing ends but no oxidatively generated carbonyls – can be expressed mathematically. Figure 4 shows a comparison between a calculated curve

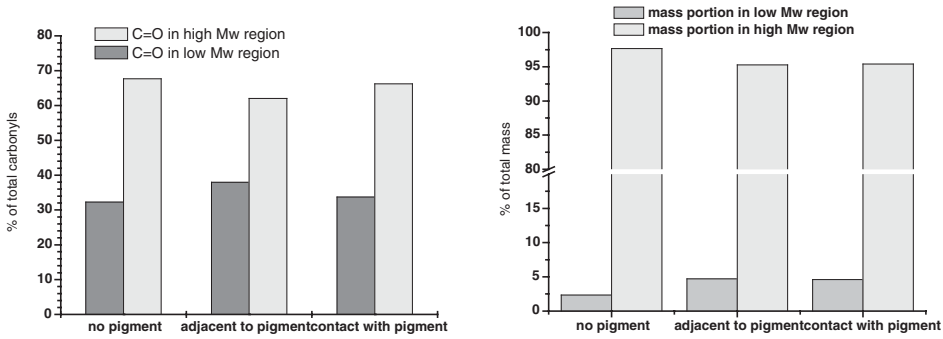

Figure 7.
Distribution of carbonyls and mass portion within the high/bulk Mw and the low-Mw region for the model paper sample. Borderlines were set as indicated by the arrows in Figure 5.

representing just reducing ends with the measured carbonyl-DS plots. While the DS curve from the historical paper fragment with green copper pigment mainly followed the computed DS plot, the curve of the artificially copper-corroded paper sample was significantly shifted to higher carbonyl values. This is again indicative of hydrolytic degradation largely dominating in the historical sample and – in contrast to that – the unambiguous occurrence of additional oxidative degradation in the artificially aged material. The different curve shape in the case of the samples with accelerated aging was due to a superposition of two effects: the generation of new reducing end groups by degradation mechanisms, and the oxidative introduction of carbonyls along the cellulose chains of a DP between 60 and 10.

The DS plots are based on both the carbonyl-proportional fluorescence signal and the mass-proportional signal of the refractive index detector. While fluorescence is highly sensitive, the refractive index is less responsive to the outer limits of the distribution due to the low concentration of the material. For a better visualization of the observed effects, the fluorescence responses relative to the molecular weight are given in Figure 5. The fluorescence signal, reflecting directly the amount of carbonyl groups, showed a distinct bimodal distribution in all cases (with the exception of the model starting material), i.e. low- and high-molecular weight fractions were clearly separated (cf. Figure 5). In order to correct for the over all Mw shift due to the degradation of the material, the borderline between low- and high-Mw part was set individually for each sample (cf. Figure 5, down arrows). For the two Mw regions, the portion of carbonyls contained (%) and the mass portion was calculated (Figure 6). The historic sample showed an obvious trend towards accumulation of carbonyl-containing fractions in the low Mw part with increasing cellulose degradation. In the green-pigment fragment about 50% of the carbonyls were present in the region below DP 60 (cf. Figure 6). This was once more indicative of hydrolytic degradation processes. As expected for such a type of degradation, the course of the low-Mw and high-Mw mass portions were counter-directed, decreasing portions of high-Mw material and increasing portions on the low-Mw side.

The situation is different if oxidation plays a more dominant role. Figure 7 shows the same plots for the artificially aged paper. The ratio of carbonyl groups in the high- and low-Mw part of the MWD was rather constant, as oxidation was occurring in both Mw regions. The course of the mass ratio was much less dramatic than for the historical paper sample.

Conclusion

The copper corrosion in the paper fragments taken from the prayer book of Ursula Begerin, Codex 801, of the Burger Library (Burgerbibliothek Bern), Switzerland, was demonstrated to be caused mainly by hydrolysis. Oxidative degradation, if occurring at all, played a minor role only. The missing discoloration of the paper supports this finding. The hydrolytic degradation is catalysed by the green copper pigment present. The red pigment did not influence cellulose deterioration, the paper part covered with both green and red pigment was significantly less affected as compared to parts with complete coverage by green copper pigment. The strong presence of a hydrolytic degradation mechanism with much less pronounced oxidation at the same time is a rather unexpected finding when usual copper corrosion of paper is considered.

Cellulose oxidation with concomitant distinct discoloration effects are considered to be typical manifestations of copper corrosion. This was also be demonstrated by artificial aging of copper pigments on rag paper, which was also used in the present study for comparison. The case of the merely hydrolytic degradation of the codex frag-

ment studied must thus be considered a rather rare exception, probably caused by special storage conditions or special pigment types used. Further analysis of real-world samples have to be performed to finally allow for a more comprehensive understanding of copper corrosion in paper.

Acknowledgement: We would like to thank Dr. Sonja Schiehser for practical assistance. We are grateful for the financial support by PAL GmbH, Leipzig, Germany.

[1] C. Shahani, F. Hengemihle, in: "*Preservation of Historic Textile and Paper Materials*" S. H. Zeronian, H. Needles, Eds., Advances in Chemistry Series 212, American Chemical Society, Washington, D.C., **1986**, 387–409.

[2] J. C. Williams, C. S. Fowler, M. S. Lyon, T. I. Merrill, in: "*Preservation of Paper and Textiles of Historic and Artistic Value*" J. C. Williams (ed.), Advances in Chemistry Series 164, ACS, Washington D.C., **1977**, 37–61.

[3] U. Henniges, T. Prohaska, G. Banik, A. Potthast, *Cellulose* **2005**, *13*, 421.

[4] M. Lewin, H. F. Mark, *Macromol. Symp.* **1997**, *118*, 715.

[5] J. Röhrling, A. Potthast, T. Rosenau, T. Lange, G. Ebner, H. Sixta, P. Kosma, *Biomacromolecules* **2002**, *3*, 959.

[6] J. Röhrling, A. Potthast, T. Rosenau, T. Lange, A. Borgards, H. Sixta, P. Kosma, *Biomacromolecules* **2002**, *3*, 969.

[7] A. Potthast, J. Röhrling, T. Rosenau, A. Borgards, H. Sixta, P. Kosma, *Biomacromolecules* **2003**, *4*, 743.

[8] R. Cermann, 43.1.30, Bern Burgerbibliothek, Cod. 801, in: Katalog der deutsch-sprachigen illustrierten Handschriften des Mittelalters, Bd.5,1/2, München 2002, 103 ff.

[9] J. Wouters, Laboratory for Materials and Techniques, Royal Institute for the Study and the Conservation of Belgium's Artistic Heritage, Brussels, 2004, personal communication.

