Comparison of Aqueous and Non-Aqueous Treatments of Cellulose to Reduce Copper-Catalyzed Oxidation Processes

Ute Henniges,[1] *Gerhard Banik,*[2] *Antje Potthast**[1]

Summary. The present paper examines oxidative degradation of cellulose catalyzed by presence of $Cu^{1+}$and Cu^{2+} ions in the context of historic paper conservation treatments. Aqueous treatments of degraded papers further spread transition metal ions, such as copper, across the fibre matrix, and therefore augment the detrimental effect of these ions. In the paper industry, the inhibiting effects of magnesium ions on metal-catalyzed degradation of cellulose contaminated with metal impurities have been observed. Also, magnesium compounds dissolved in alcoholic or aqueous solutions are generally used in paper conservation as deacidification agents. Paper samples with artificially produced copper corrosion served as mock-ups for examination and comparison of different treatments which focused on the inhibiting effect of magnesium and antioxidants. Analytical examination of molecular weight distribution, carbonyl content, carboxyl content, and surface pH was performed. Results show an inhibiting effect of magnesium on copper-catalyzed cellulose degradation, although less pronounced than expected.

Keywords: ageing; carbonyl groups; carboxyl groups; cellulose degradation; copper ions; fluorescence labeling; gel permeation chromatography; molecular weight distribution; paper conservation

Introduction

Deterioration of historical papers is caused by several processes, such as acid hydrolysis or autoxidation. Even though rag papers are usually of very good quality and resist accelerated acid hydrolysis, they may suffer from oxidative degradation, due to the presence of metal ions contained in inks or pigments. Both processes, acid hydrolysis and oxidation, can be studied by a novel analytical approach, fluorescence labeling of carbonyl and carboxyl groups in combination with gel permeation chromatography and multi-angle laser light scattering detection (GPC-MALLS). This technique allows not only determining the extent of hydrolysis, but also measuring the concentration of oxidized functionalities within very small sample amounts.

To investigate the so-called copper corrosion caused by copper ions released from historic copper-containing pigments, thermally aged rag papers with lines of copper pigments have been investigated. The copper-containing lines were used to simulate green or blue copper pigments in historic papers. Such valuable historical objects are threatened by massive deterioration.[1,2] In Figure 1, this degradation process is exemplarily shown on a historical wallpaper, which exhibits severe copper corrosion. Parts of the copper acetate pigment and the surrounding paper are heavily browned (Figure 1). Micro chemical analyses revealed $Cu^{1+}$and Cu^{2+} ions in

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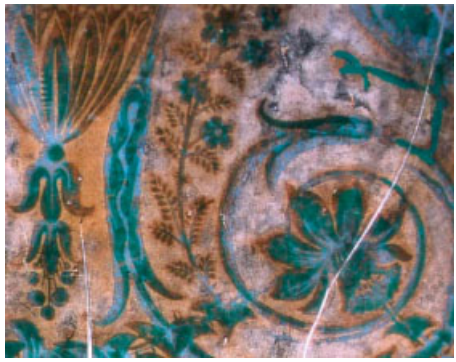

Figure 1.
Details of a wallpaper showing signs of copper corrosion. Browning of the paper starts next to pigment.

the browned areas of paper, and thus confirmed the supposition that copper ions have migrated from the copper acetate pigment into paper, catalyzing degradation reactions[3].

Aqueous and non-aqueous solutions of magnesium compounds are generally used in paper conservation as deacidification agents.[4,5] Since literature reports a decrease of catalytic activity of metal ions in presence of magnesium compounds,[6,7] our investigations focused on such applications and effects. To evaluate the further distribution of copper ions in the paper matrix, a non-aqueous solution was chosen and compared to an aqueous one. Furthermore, the influence of antioxidant addition was investigated, using a mixture of methyl *p*-hydroxybenzoate and propyl *p*-hydroxybenzoate to learn about their capacity to reduce oxidative processes in paper.[8]

The present study focuses on the comparison between aqueous and non-aqueous protocols of applying magnesium compounds to a damaged paper sample with simulated copper corrosion.[9] For this purpose, the course of surface pH, and changes in carbonyl and carboxyl groups as well as molecular weight distributions were studied.

Materials and Methods

Chemicals were obtained from commercial sources and were of the highest purity available. Magnesium alcoholate solution and antioxidants were obtained from Conservación de Sustratos Celulósicos S.A., Terrassa, Spain. To test a high concentration of antioxidants, 1.5:1 (w/w) methyl *p*-hydroxybenzoate and propyl *p*-hydroxybenzoate were dissolved in 75 ml 2-propanole + 100 ml treatment solution, the lower concentrated solution contained 1:1 (w/w) methyl *p*-hydroxybenzoate and propyl *p*-hydroxybenzoate in 134ml treatment solution.

The CCOA labeling was performed as described earlier.[10,11,12] FDAM labeling was performed as described by Bohrn.[13]

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) and Agilent FLD G1321A (FDAM); 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 AI 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), $\lambda_{ex} = 252$ nm, $\lambda_{em} = 323$ nm (FDAM); injection volume, 100 μl; run time, 45 min. DMAc/LiCl (0.9% w/v), filtered through a 0.02 μm filter, was used as the eluant.

Test 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 non-sized paper. According to historical sources, the pigment was bound in skin glue media. Copper corrosion was simulated with accelerated ageing at 55 °C and

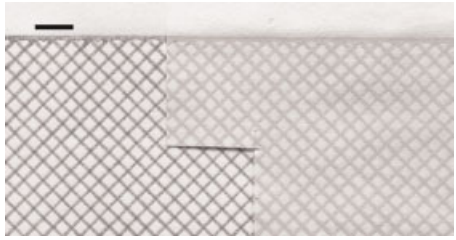

Figure 2.
Test samples before and after accelerated ageing. Black line at the top left indicates 1 cm.
Left: Paper as received from the manufacturer.
Right: Paper sample after accelerated ageing with simulated copper degradation.

fluctuating humidity from 35–80 % relative humidity (RH) every 6 hours.

All other substances are applied on damage-aged paper samples using an air-brush with compressed air or with spray cans. After treatment, the paper samples and untreated references were subjected to artificial ageing for several days at 80 °C and 65% RH [14].

Results and Discussion

A change in pigment color was observed after accelerated ageing. The penetration properties of water changed, and the pigment sank more deeply into the paper matrix (Figure 2). This indicates that the simulation of copper corrosion was successful, so that further treatments will be performed as on pre-damaged paper. Further analysis dealing with characterization of simulated copper corrosion on paper, e.g. differences in copper ion distribution and possible correlation with pronounced oxidation, are published elsewhere[15].

To avoid difficulties when analyzing aged and less permeable paper zones close to pigment lines, the pH surface measurements according to TAPPI were performed on paper areas besides the pigment lines only. Unfortunately, magnesium alcoholate treatments tend to leave magnesium salt deposits on the paper surface, which might result in too high pH values.

Untreated paper was not subjected to changes in pH. It stayed in the neutral region around pH 7 during the whole ageing period. All other treatments realized a pH between 10 and 10.5, which was stable throughout the ageing period (see Figure 3).

As generally the concentration of carbonyl and carboxyl groups in cellulosic

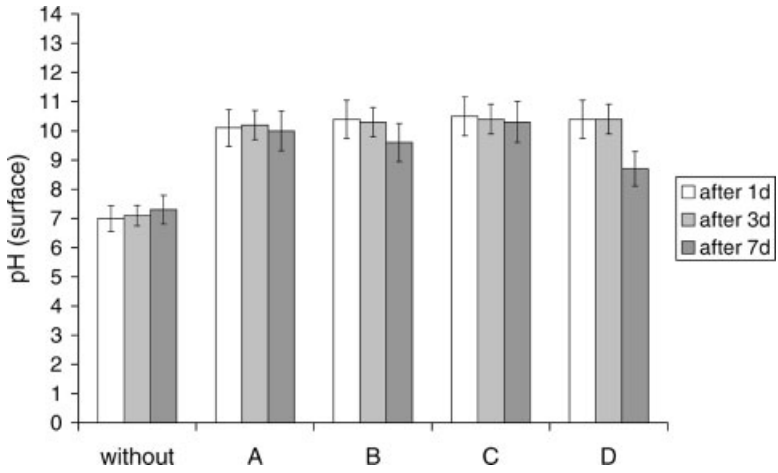

Figure 3.
Surface pH after different treatments measured on samples without copper pigments. A: aqueous magnesium hydrogen carbonate, B: non aqueous magnesium alcoholate, C: non aqueous magnesium alcoholate + high concentrated antioxidant, D: non aqueous magnesium alcoholate + low concentrated antioxidant, without: unsized, untreated, unaged paper without copper pigment, after 1, 3 and 7 d: treated according to letters after 1, 3 and 7 days of accelerated ageing at 80 °C and 65% RH.

materials is very low, highly sensitive analytical methods are required to detect such minute amounts of oxidized groups. In this study, the CCOA and FDAM methods were applied, consisting in a group-selective fluorescence labeling of carbonyls and carboxyls, respectively. The fluorescence of the label after excitation with UV light is detected and quantified in combination with size exclusion chromatography after dissolution of the cellulose in *N*,*N*-dimethylacetamide/lithium chloride. Thus, the total amount of oxidized groups, the molecular weight distribution, and the distribution of oxidized groups along cellulose chains (carbonyl and carboxyl profiles) are determined at the same time. For measurement a piece of about 1cm^2 was taken, containing a mixture of printed on areas and blank spaces, data obtained are therefore average values.

As expected a general increase in the carbonyl group content was observed with progressing aging time (see Figure 4). After only 1 day of accelerated ageing, the carbonyl content of all treatment types doubled in comparison to reference material. After 7 days though, it was evident that least increase occurred according to treatment D, while treatments A and C yielded the highest amount of carbonyl groups. It was even higher than without any treatment at all, indicating a negative influence of the treatment on the sample material.

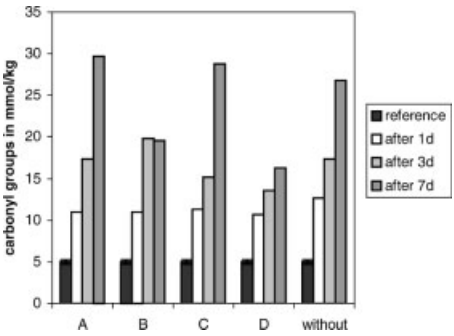

Figure 4.
Comparison of the total amount of carbonyl groups after different ageing periods. A: aqueous magnesium hydrogen carbonate, B: non-aqueous magnesium alcoholate, C: non-aqueous magnesium alcoholate + high concentrated antioxidant, D: non-aqueous magnesium alcoholate + low concentrated antioxidant, reference: non-sized, untreated, unaged paper without copper pigment, after 1, 3 and 7 d: non-sized paper with copper pigment, treated according to A-D, after 1, 3, and 7 days of accelerated ageing at 80 °C and 65% RH.

With regard to the molecular weight distributions, all samples showed a quite narrow distribution (PDI = Mw/Mn around 2), which was in most cases equally distributed. This leads to the conclusion that degradation of cellulose molecules occurred statistically, i.e., without a preference of certain molecular regions. Aqueous treatment (A) caused a stronger shift of molecular weight distribution to lower molecular weight fractions. While treatment D (low concentrated antioxidant) provided better results as compared to reference samples without treatment, the opposite is true for treatment C (high concentrated antioxidant). Furthermore, sample C exhibited a slight shoulder in its distribution at the high-molecular region indicating a different degradation path, most probably caused by the high amount of antioxidant (see Figure 5). The molecular weight distribution of paper without copper pigment (measured at the edge of the material) remained unchanged compared to the curves obtained prior to ageing. Oxidation of these areas is less pronounced, too. Paper without copper pigment is therefore considered to be significantly more stable.

The GPC analysis provided values for Mw as shown in table 1. Of special interest was aqueous treatment A, which caused a pronounced decrease of Mw. Generally, all treated samples suffered from a significant loss in molecular weight, yet treatment D at the end had the least damaging effect.

Estimation of the amount of reducing end groups in the samples will induce a certain error due to the fact that Mn determination is less exact than Mw determination, and some of the reducing end groups are probably already oxidized to carboxyl groups. Nevertheless, an

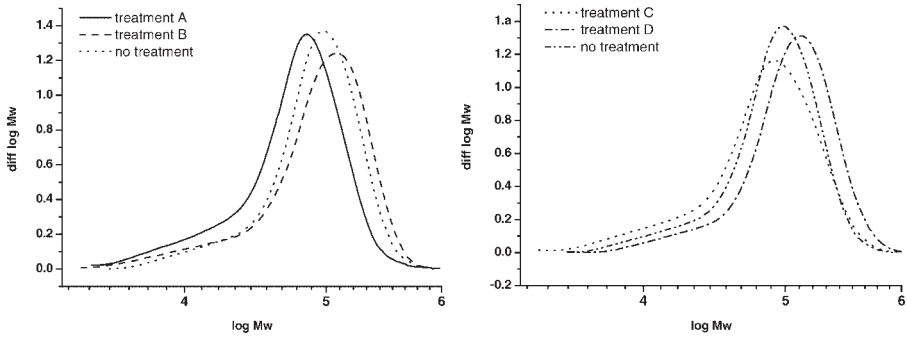

Figure 5.
Molecular weight distribution of paper with copper pigment, submitted to different treatments with magnesium compounds after 7 days of accelerated ageing at 80 °C and 65% RH. Left: Comparison between aqueous (A), non aqueous (B) and no treatment. Right: Comparison between high (C) and low (D) concentration of antioxidant with no treatment.

increase in reducing end groups indicates degradation processes caused by hydrolytic chain scission and β-elimination. In order to get information about the amount of carbonyl groups that has been introduced by oxidation processes, the calculated number of reducing end groups was subtracted from the total number of carbonyl groups measured by CCOA analysis, which gave a good estimation of those carbonyl groups along the cellulose chain that where formed by oxidation of C2, C3, and C6. As chain scission and oxidation reactions will occur at the same time, the parallel determination of total amount of carbonyl groups and molecular weight distribution is a very important tool to address underlying mechanisms. Figure 6 compares the amount of reducing end groups and additional oxidized groups along the cellulose chain. It was clear that all treatments containing magnesium compounds suppressed oxidative influences as compared to untreated sample material, which confirmed the notion that magnesium salts inhibit oxidative degradation of cellulosics. Another remarkable observation was the outcome of treatment B, which introduced magnesium ions in a non-aqueous way. Here, oxidative processes were even less pronounced. Even though also treatments C and D were based on a non-aqueous application of magnesium ions, the presence of antioxidants seemed to influence the generation of oxidized groups negatively, whereas especially treatment D significantly reduced newly formed reducing end groups (formed hydrolytically or after β-elimination) and therefore resulted in a good overall performance.

When trying to distinguish between oxidative and hydrolytic processes it must

Table 1.
Summary of data, CCOA method. 7 days of accelerated ageing at 80 °C and 65% rH, reference material before accelerated ageing.

Treatment	C=O μmol/g	Mw kg/mol	Mn kg/mol	REG[1] from Mn	Δ C=O[2]
aqueous $Mg(HCO_3)_2$	**29.7**	80.8	37.6	26.6	**3.1**
Non aqueous magnesium alcoholate	**19.5**	124.1	52.4	19.1	**0.4**
Non aqueous magensium alcoholate + hight concentrated antioxidant	**28.8**	104.3	43.5	23.0	**5.8**
Non aqueous magnesium alcoholate + low concentrated antioxidant	**16.3**	150.3	77.7	12.9	**3.4**
Without treatment	**26.8**	110.2	57.5	17.4	**9.3**

[1] reducing end groups (REG), calculated from Mn
[2] difference between measured carbonyl groups and calculated REG, index for oxidative influences

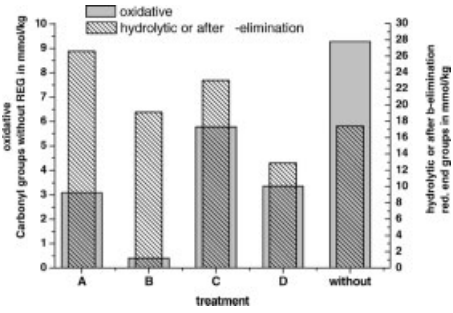

Figure 6.
Comparison between oxidative and hydrolytic damage of sample papers after different treatments after seven days of accelerated ageing at 80 °C and 65% RH. A: aqueous magnesium hydrogen carbonate, B: non-aqueous magnesium alcoholate, C: non-aqueous magnesium alcoholate + high concentrated antioxidant, D: non-aqueous magnesium alcoholate + low concentrated antioxidant, without: non-sized, untreated, unaged paper without copper pigment.

be considered that heavily damaged sample papers react very sensitive towards the alkalinity of non-aqueous treatment solutions. These might cause immediate β-elimination, which produces one new reducing end group per chain scission, as does hydrolytic chain scission. Thus, keto groups reflect the influence of oxidation, while the amount of reducing end groups reports both hydrolytic reactions and β-elimination.

With regard to the antioxidant chosen, two aspects need to be considered in more detail. First, alkyl *p*-hydroxybenzoates will be hydrolyzed into salt of hydroxybenzoic acid and alcohol immediately after contact with the highly alkaline treatment solution of magnesium alcoholates. The resulting acid might act as a buffer substance, thus reducing to a certain extent the impact of alkaline treatment substances, which in turn might lead to a better protection towards β-elimination and a higher amount of keto groups along the cellulose chain. Second, *p*-hydroxybenzoic acid will capture magnesium ions. Their protective action might therefore be reduced, which would cause more oxidation along the cellulose chain. This complex situation prevents conclusive interpretation of the results in the case of antioxidant treatments C and D as shown in Figure 6.

Determination of carboxyl groups gave further insight into possible reaction mechanisms. Carboxyl groups are mostly formed after β-elimination and by oxidation of aldehyde groups, but not during purely hydrolytic processes. Whereas samples without treatment and after treatment B did not suffer further formation of carboxyl groups, these groups increased significantly after treatment A (see Figure 7)

Changes in the molecular weight distribution are shown as log Mw/diff log Mw plots in figure 8. The overall molecular weight distribution shows a slight change after 7 days of aging independent on the

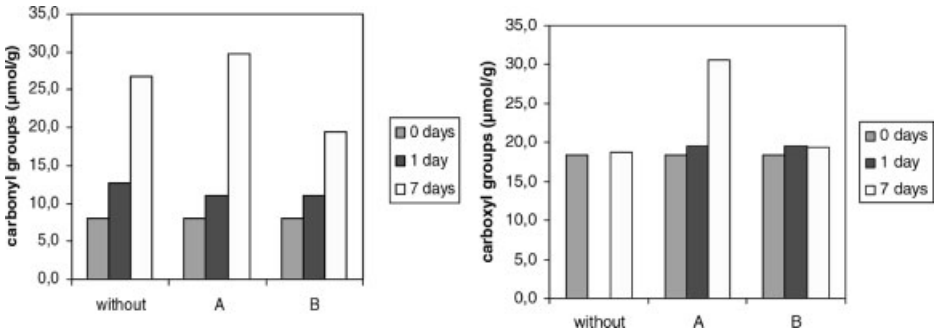

Figure 7.
Comparison between the development of carbonyl and carboxyl groups after one day and seven days of accelerated ageing. A: aqueous magnesium hydrogen carbonate, B: non-aqueous magnesium alcoholate, without: non-sized, untreated, unaged paper without copper pigment, after 1 and 7 d: non-sized paper with copper pigment, treated according to letters after 1 and 7 days of accelerated ageing at 80 °C and 65% RH.

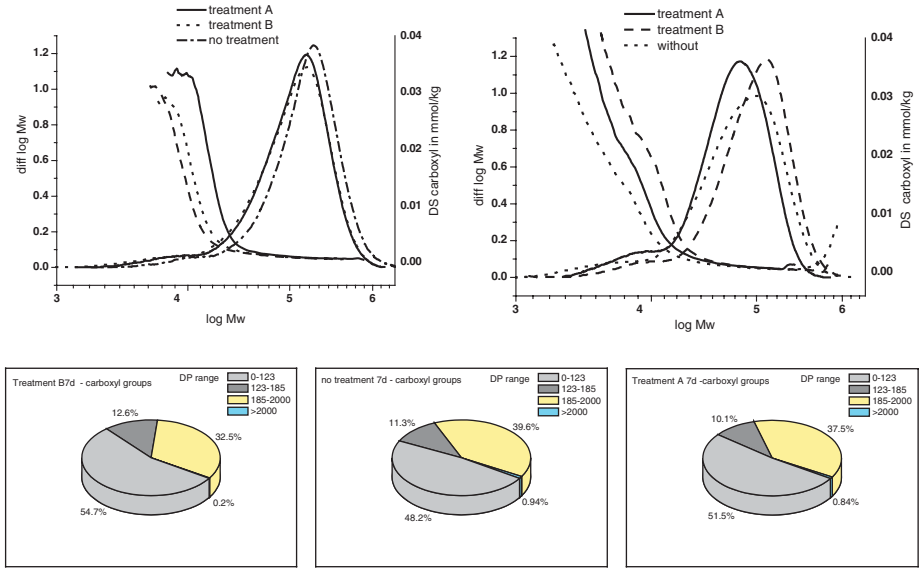

Figure 8.
Development of molecular weight distribution and carboxyl-degree of substitution in the course of accelerated ageing. Top left: without ageing (no treatment) and after one day of ageing (treatment A and B). Top right: after seven days of accelerated ageing. Changes in carboxyl groups profiles are shown in the lower part. A: aqueous magnesium hydrogen carbonate, B: non aqueous magnesium alcoholate, without: non-sized, untreated, unaged paper without copper pigment, after 1 and 7 d: unsized paper with copper pigment, treated according to letters after 1 and 7 days of accelerated ageing at 80 °C and 65% RH.

respective treatment. Significant changes can be observed at the carboxyl group profiles. In all cases oxidation to carboxyl groups occurs mainly in the low molecular weight region up to a DP of 150–200.

An inhibiting action of magnesium alcoholate towards copper degradation was clearly visible, but less pronounced than expected. Sensitive analysis methods, such as the determination of molecular weight distribution, revealed nevertheless that in contrast to the untreated reference paper, a reduction of molecular weight occurred even after application of non-aqueous magnesium alcoholates combined with antioxidant, but more moderate than after any other treatment. Thus, degradation processes were not blocked, but their rate slowed down. Samples treated with aqueous $Mg(HCO_3)_2$ solution by immersion gave the ''worst'' analytical data, even though visual results were very good. These observations contribute to the notion that the use of aqueous immersions causes an uncontrolled distribution of transition metal ions in paper, thus accelerating its further deterioration. The negative results might also be explained by a change of the water content in the paper due to the aqueous treatment which influences and changes the kinetics of degradation.

Antioxidants in low concentrations revealed good results in inhibiting oxidation reactions in the course of accelerated ageing. They were tested in combination with non-aqueous magnesium alcoholate. Antioxidants are oxidized instead of cellulose, but will be consumed during (natural) ageing leaving behind reaction products in the paper matrix. These newly formed, antioxidant-derived products consist in the best case of inert compounds deposited in the paper. However, it cannot be ruled out that yellowing or browning of those products might occur under ageing conditions, even if antioxidant is applied in low concentration. Thus, the long-term effects of antioxidants needs to be studied in more

detail, before their application can be recommended for restoration treatments. It is remarkable though, that a high concentration of antioxidants will cause rather negative results than improvements. One explanation might be the existence of a threshold concentration. Passing this concentration might result in pro-oxidative effects, which are known for many (phenolic) antioxidants. On the other hand, a larger amount of antioxidants might trap magnesium ions, thus impeding their protective efficiency.

A main drawback of applying aqueous just as well as non-aqueous magnesium compounds is the high alkalinity imposed on the paper. The pH of both treatment solutions gained values up to pH 10 or 10.5. Whether such solutions can be employed on historic papers or not is determined by the oxidative pre-damage, due to alkaline degradation of oxycellulose under alkaline conditions. With copper ions present, which are active at high alkalinity, cellulose is even more sensitive to degradation.[16] Thus, the use of alkaline substances on oxidized cellulose must be seen rather critical.[17] Furthermore, an alteration of pigments may occur, since some pigments are sensitive to pH changes. On the other hand, application of alkaline compounds on almost neutral paper without sizing and fillers will strongly increase the pH, while it will raise less on an acidic paper or on paper filled with pigment and size.[18]

Nevertheless, samples treated with non-aqueous magnesium compounds showed a better resistance against aging than untreated ones, even though the advantages of protection against oxidation by magnesium compounds only slightly outweighed the drawbacks caused by high pH. When high humidity occurs, the moist conditions within the paper will allow the applied magnesium compounds to generate a strongly alkaline environment. The main advantage of non-aqueous treatments is therefore the avoidance of water application in a reaction system strongly influenced by the presence of water.

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