A STUDY OF THE EFFECTS OF IRON AND COPPER ON THE DEGRADATION OF PAPER AND EVALUATION OF DIFFERENT CONSERVATION TREATMENTS

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Introduction

In the practice of the book- and paperconservator ink- and coppercorrosion present difficult problems. Though much research has been done with respect to the mechanism of these, respectively by iron and copper catalysed degradation processes (1-3), many questions have still remained. In this connection it is also not yet clear which conservation treatments are most suitable. Nevertheless a number of methods are used which are primarily based on the supposition that by these treatments the respective metals are shielded from the paper fibres. In this way a stabilising, metalcomplexing effect would be obtained by treatment with low-viscosity sizes and magnesium-containing deacidification products (4,5). In addition, the use of EDTA is also recommended as complexing agent. The actual effects of these treatments however are hardly investigated.
In the present study we examined if the conservation treatments mentioned are in fact capable to retard the damaging effects of metal ions artificially applied to paper. For this purpose a number of test papers were in first instance enriched with different concentrations of iron - and copper salts, and the effects of these metals measured by the determination of the folding endurance and tear resistance of the paper after accelerated aging. Then a limited number of experiments was done to compare these data with the paperstrength values remaining after accelerated aging when enriched papers were treated first with EDTA, magnesiumbicarbonate, methoxymagnesiummethylcarbonate (MMMC), hydroxypropylcellulose (Klucel G) and ammoniumcaseinate.
On basis of this pilot study more extended and detailed experiments were conducted in order to examine the effects of these compounds in practice. In these experiments paper was used which was enriched with a mixture of ferrosulphate and tannin (gallic acid), with the intention to simulate the irongall ink induced inkcorrosion problem.

Materials and methods

Test paper
The following papers were used: Hollands normaal 1 (Schut), 120 g/m^2, ash-content 1.5-2%; VGF document (Van Gelder Fijnpapier), 90 g/m^2, ash-content 1.5-2%; 17th century rag paper (blank leafs of a register), 100 g/m^2; and 18th century rag paper (blank leafs of a book dummy), 100 g/m^2.

Enrichment procedure
The paper was immersed per leaf (A4 dimensions) for 2 minutes in 1 l solution and subsequently air dried. In order to accomplish a fast and uniform impregnation, the leafs were pretreated with ethanol. The following solutions (in demineralised water) were used for the enrichment: 7.4 - 29.6 mM ferrichloride, 7.4 - 29.6 mM copper(I)chloride, 7.4 - 29.6 mM copper(II)chloride and a mixture of 6 g/l ferrosulphate.7aq and 6 g/l tannin.

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Conservation treatments

The enriched papers were treated with the following solutions: demineralised water (30 min immersion), 2% EDTA (30 min immersion followed by 30 min immersion in water), saturated magnesiumbicarbonate (30 min immersion), methoxymagnesiummethylcarbonate (MMMC) in freon/methanol (Wei T'o spray, nr 11), 2% hydroxypropylcellulose (Klucel G; applied by brushing) and a mixture of 10% ammoniumcaseinate (DMV Campina) and 10% urea (applied by brushing). As references also the non-enriched papers were treated with these solutions. After treatment the samples were air dried.

Accelerated aging

The paper was artificially aged for 2, 4, 6 and 8 days at 90 °C and a relative humidity changing every 3 hours between 80 and 35%.

Paperstrength measurements

After an acclimatisation period of minimal 96 hours, strips were cut for the determination of the folding endurance using a Schopper tester (Frank) or a M.I.T. (0.5 kg tension) tester (Tinius Olsen) and the tear resistance using an Elmendorf tester (Lorentzen & Wettre). For both tests 10 measurements were performed and the mean value and standard deviation (SD) calculated.

Other tests

For the determination of the iron residue in the paper an atomic absorption spectrometer (Perkin-Elmer) was used. Paper extracts were obtained by acid destruction according to NEN 6465.

Cold extraction pH values of paper were determined according to NEN 2151.

Results and discussion

Figure 1 shows a representative example of the results of a pilot study in which Hollands normaal 1 and 18th century rag paper were enriched with different amounts of iron and copper, and subsequently artificially aged and examined by the determination of the folding endurance and the tear resistance. For iron (III) and copper(I) there clearly appears to be a concentration dependent acceleration of the degradation of paper. The apparent higher catalytic activity of iron compared to copper has been demonstrated earlier (6). Copper(II) shows a strong effect at the lowest concentration used, after which a plateau of saturation seems to be reached. A possible explanation for this could be the formation of unstable copper(II)-cellulose complexes (7).

It was verified that the effects observed are caused by the metal ions and not by the chlorides, which are also present in the enrichment solutions, by reference paper samples which were treated with calcium- and potassiumchloride solutions with the same chloride concentrations as the ferri- and copperchloride solutions used. Both calcium and potassiumchloride appeared to have no measurable effect.

Also the possibility that the results with iron are due to the strong acidity of the ferrichloride solution (pH 2.1) could be excluded, as treatment of the paper with diluted HCl and citrate buffer of the same pH was ineffectual.

Using the same test papers, enriched with 22.8 mM ferrichloride solution, some preliminary experiments were done to examine the effect of the different treatments. By comparing the paperstrength characteristics of these, enriched and treated, papers with references, non-enriched but treated in the same way, indications were found that demineralised water, magnesiumbicarbonate, MMMC, ammoniumcaseinate and, in a smaller measure, Klucel G had a positive effect, i.e. a slowing-down of the iron-caused degradation. EDTA appeared to have a negative effect on the reference papers, and no effect at all on the enriched samples.

Because of the uncertainty with regard to the effect of the treatments on the iron-content of the paper, and in order to simulate the inkcorrosion problem more realistically, the following set of experiments was extended with iron- and cold extraction pH measurements, and performed on VGF document paper and 17th century rag paper enriched with a mixture of ferrosulphate and tannin.

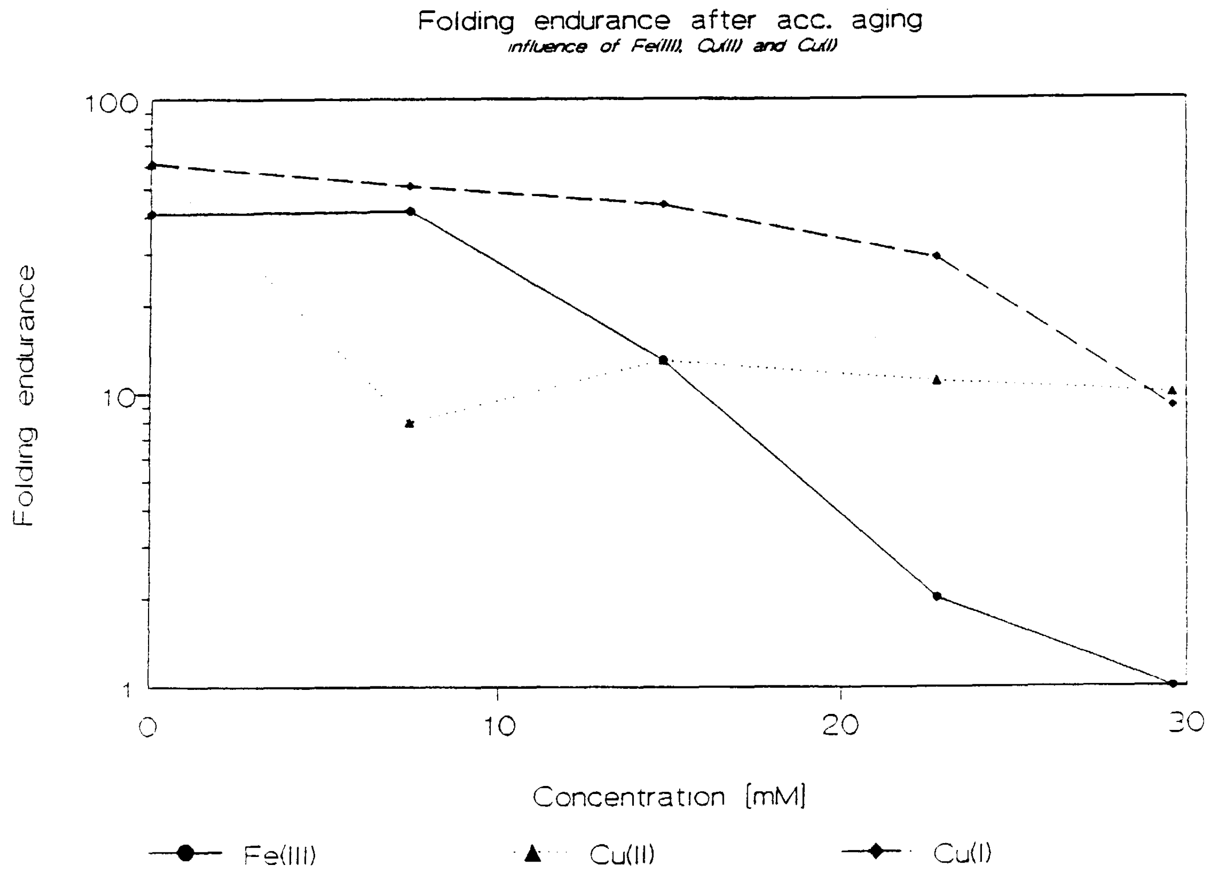

Figure 1. Folding endurance (Schopper) values of Hollands normaal 1 paper, enriched with 7.4, 14.8, 22.8 and 29.6 mM ferrichloride, copper(I)chloride and copper(II)chloride, and subsequently artificially aged for 4 days. Mean values are indicated (SD ≤ 20%).

In addition, the accelerated aging was conducted for different periods, i.e. 2, 4, 6 and 8 days. The results of the VGF document paper and the 17th century rag paper appeared to be comparable and in the main in agreement with the preliminary findings in our pilot study. In order to assess the effects of the different treatments as correct as possible, the results of the folding endurance and tear resistance measurements of both the treated and untreated enriched paper and the treated and untreated non-enriched reference paper are presented for each treatment individually (Figures 2 and 3).
Especially with respect to the tear resistance, treatment with demineralised water indicates a positive effect, i.e. shows an evident retardation of the paperdegradation caused by the enrichment. With respect to the folding endurance, the influence is far less clear.
Both with regard to the folding endurance and tear resistance, EDTA treatment does not appear to have a positive effect on the enriched paper. This is a notable result as the determination of residual iron after treatment shows a marked loss of iron from the enriched paper by EDTA, in fact it appears the only treatment which resulted in removal of iron in significant amounts (Table 1). A negative effect of EDTA is apparent for the non-enriched reference paper, especially concerning the tear resistance.
Though magnesiumbicarbonate seems to have a favourable effect on the enriched paper, comparison with treatment with demineralised water clearly indicates that this effect may be completely attributed to the fact that we are dealing with an aqueous treatment. Although a positive effect of bicarbonate treatment has also been demonstrated by Shahani (8), his findings indicate, as opposed to our results, an adverse effect of demineralised water.

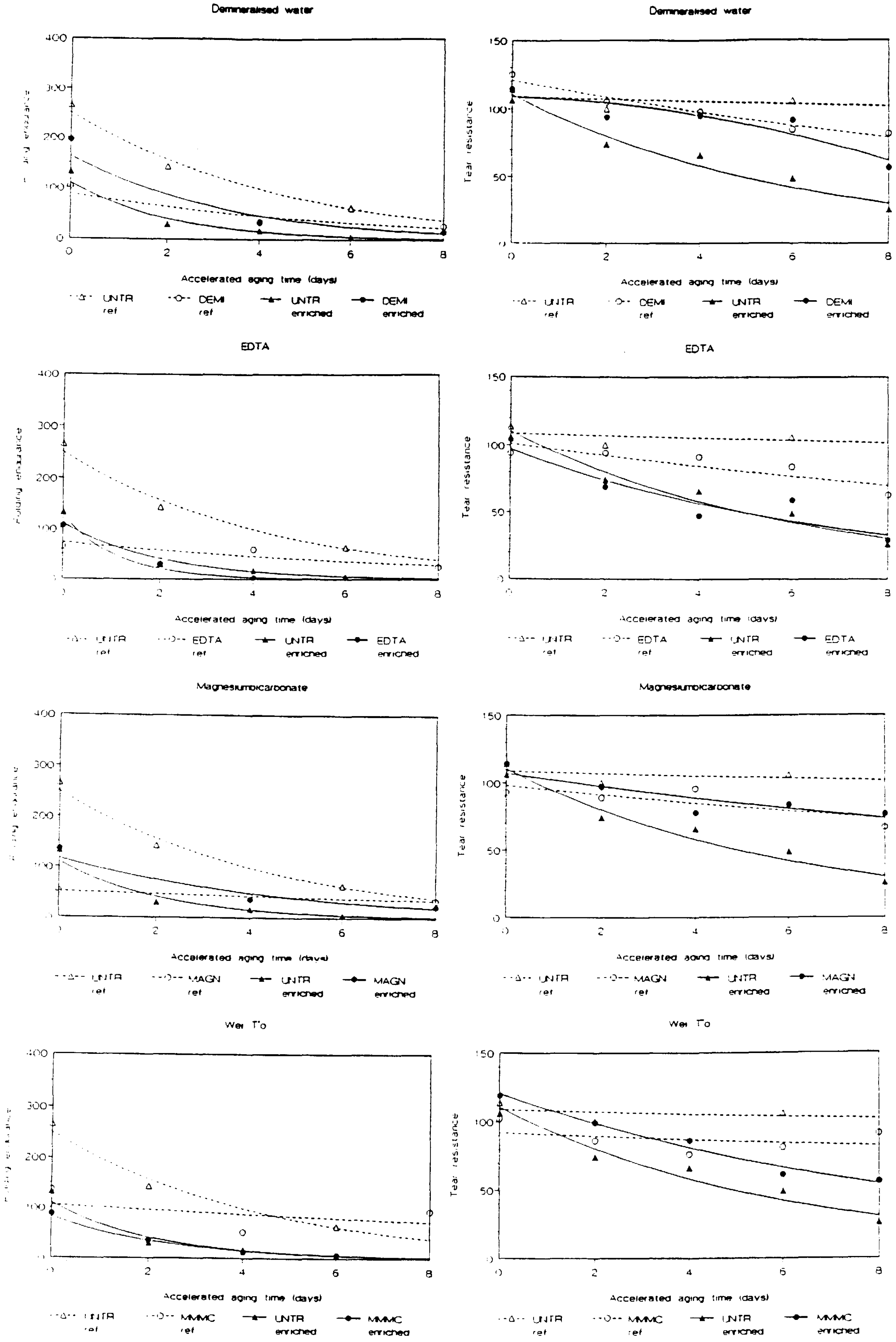

Figure 2. Folding endurance (M.I.T.) and tear resistance values of 17th century rag paper, enriched with ferrosulphate/tannin and non-enriched (ref), treated and untreated (UNTR), and subsequently artificially aged for 2,4,6 and 8 days. Mean values are indicated.

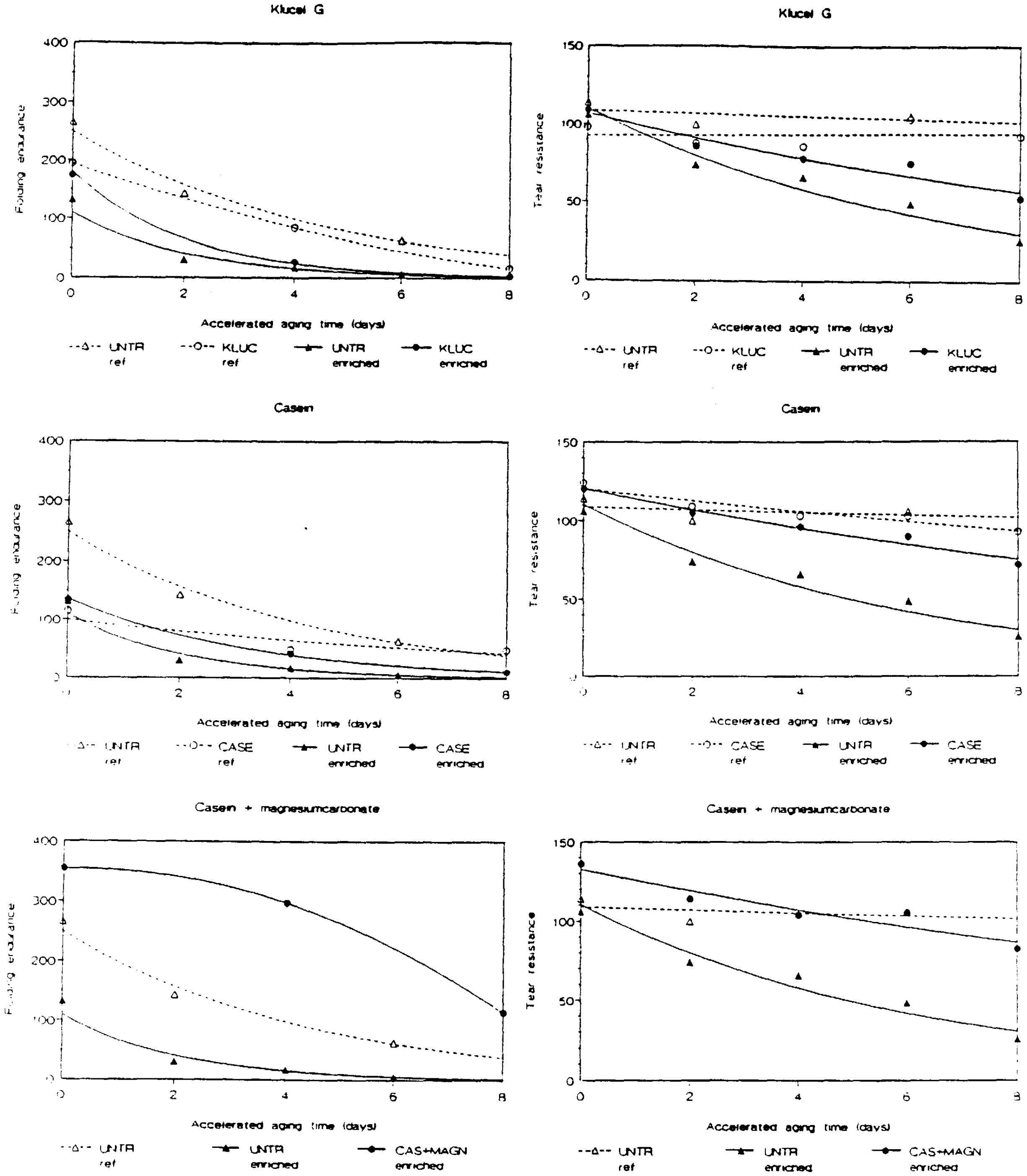

Figure 3. Folding endurance (M.I.T.) and tear resistance values of 17th century rag paper, enriched with ferrosulphate/tannin and non-enriched (ref), treated and untreated (UNTR), and subsequently artificially aged for 2,4,6 and 8 days. Mean values are indicated.

treatment	Fe(mg/g paper)	cold extr. pH
UNTR	2.78	7.9
DEMI	2.97	7.8
EDTA	0.94	6.5
MAGN	2.47	7.9
MMMC	3.01	10.1
CASE	3.17	7.5

Table 1. Iron (Fe) and pH values of ferrosulphate/tannin enriched VGF document paper, untreated (UNTR) and after the different treatments.

Treatment with MMMC (Wei T'o) does not show a measurable effect with respect to the folding endurance, whereas a positive influence on the tear resistance is evident. Though in comparison with treatment with demineralised water, this effect is rather limited. Compared to the 17th century rag paper as presented in Figures 2 and 3, the MMMC treatment of VGF document paper resulted in a more negative effect. Possibly, the extremely high pH (10.1) of the VGF paper (Table 1), as compared to the pH of the 17th century material (7.0) after treatment, may play a role in this respect.
A moderate positive influence of Klucel G treatment is only indicated in case of the tear resistance.
Ammoniumcaseinate appears to exhibit a strong positive effect on the tear resistance of the enriched paper. This finding may be related with the large binding capacity for acids and metal ions which has been established for casein (9). In this connection an additional experiment was performed, using a mixture of the ammoniumcaseinate solution and magnesiumcarbonate (0.2%). A 30 min immersion of the enriched paper in this solution resulted in a remarkably large positive effect: the tear resistance attained values comparable to the non-enriched paper, while the folding endurance even reached values higher than the non-enriched references (Figure 3).

Though the investigations done so far have generated useful information, we are aware of the fact that it is not yet allowed to draw definitive conclusions. Our next work will be concentrated on the evaluation of the conservation treatments on test paper in which the coppercorrosion problem is simulated. Then we will continue in order to achieve the ultimate goal of our research project, i.e. the development of methods by which the actual ink- and coppercorrosion and the frequently occurring combination of these problems, can be treated reliably and selectively.

Summary

Several conservation treatments proposed for ink- and coppercorrosion were examined with different test papers which were artificially enriched with iron- and copper compounds. The effects of the introduced metals and subsequent treatments were analysed by the determination of the folding endurance and the tear resistance after accelerated aging. Preparative experiments clearly demonstrated a concentration dependent acceleration of paper degradation for iron(III) and copper(I). A stabilisation after a strong initial effect was found for copper(II). With respect to the treatment procedures, the findings indicate an evident positive effect for ammoniumcaseinate. Smaller positive effects were found for Klucel G and magnesiumbicarbonate. The influence of treatment with magnesiumbicarbonate may be attributed to the solvent, i.e. demineralised water. In comparison with demineralised water, treatment with MMMC also indicated a very limited positive influence. Treatment with EDTA did not appear to be successful at all, and rather showed a negative effect on the paper.

Acknowledgments

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