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Editorial

The major topics for the 1996 to 1999 Triennial Program of the Working Group Graphic Documents as decided on the occasion of the Triennial Meeting in 1996 in Edinburgh were:

- Research on iron-gall ink and pigment decay
- New developments and materials in paper and parchment conservation
- Ageing / analysis of decomposition phenomena
- Biodeterioration / desinfestation

Within the framework of this program the co-ordinators of the working group received in total 33 contributions of which, for space reasons, only 10 contributions and 6 poster abstracts could be accepted to be published within the preprints of 12th Triennial Meeting in Lyon.

Thanks to the traditional close co-operation of the Working Group Graphic Documents with the RESTAURATOR, which has been established by Francoise Flieder years ago, it was possible to print in addition, nine very interesting contributions to the working group session in Lyon in one special issue of this journal which is dedicated to the activities of the Working Group Graphic Documents of the ICOM Committee for Conservation. This made it possible to present a much broader range of the working group activities on the occasion of the Triennial Meeting in Lyon and to demonstrate to what extent results could be carried out within the suggested program of the working group.

In total five contributions deal with recent research on iron-gall ink and pigment decay, eight contributions present new developments and materials in paper and parchment conservation. The planned topic "Ageing / analysis of decomposition phenomena" is represented by four contributions and two members present results of recent research in desinfestation and biodeterioration. Considering the contributions and the posters presented in addition, one can look back to a very successful triennial period witnessing the improvement of knowledge in the fields concerned.

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The working group held one interim meeting at the Institute for the Preservation of Library and Archival Material in Ludwigsburg near Stuttgart from 20th to 22nd April 1998 which was organised as a joint meeting together with the Working Group Photographic Documents. This meeting attracted 122 participants. The interim meeting was a good opportunity to judge the status of the research within the suggested working program. In addition, this meeting became and outstanding event because one day of the sessions was dedicated to the memory of Klaus B. Hendriks where eleven of his colleagues and co-workers presented an overview of his scientific contribution to the conservation of photographic materials and paper objects.

The other event that has been organised by the co-ordinator of the working group in co-operation with the Institute for the Preservation of Library and Archival Material in Ludwigsburg has been already held from 14th to 15th April 1997. The meeting was dedicated exclusively to recent developments in the research of paper decay caused by iron-gall ink. On that occasion a number of working group members gave presentations of their research followed by fruitful discussions. It should be stated here that this event contributed to a high extent to the further developments in the field to be presented in Lyon.

As co-ordinator of the working group whose term is ending at the end of this triennial period I would like to thank firstly the two assistant-coordinators Jan Wouters and Dianne van der Reyden for their support. Further I would like to thank the members of the working group and all authors for their willingness to contribute to the working group activities.

On behalf of all working group members I express my gratitude to Helmut Bansa, the editor-in-chief of the RESTAURATOR, for his continuous support and the extensive editorial work involved in the preparation of this issue. I am convinced that the contributions that could be additionally accepted and printed due to this co-operation will enrich the field and the forthcoming meeting in Lyon. It is to be hoped that the co-operation between the Working Group Graphic Documents and the RESTAURATOR will continue during the forthcoming triennial period.

Gerhard Banik
Co-ordinator of Working Group Graphic Documents

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The Effect of Cooking Agents on Japanese Paper*

by TANYA T. UYEDA, KYOKO SAITO, MASAMITSU INABA & AKINORI OKAWA

INTRODUCTION

The effect of the application of an acidic sizing agent onto Japanese paper (*Washi*) has been investigated by Inaba and Sugista[1, 2]. When the pH of *Washi* dropped below 5, the deterioration rates of the strength properties and discoloration increased radically with the decrease of pH. On the other hand, the pH decrease of *Washi* after application of the sizing agent depended on the buffering ability of the *Washi*. The durability of *Washi* also varied according to its buffering capacity. Samejima et. al.[3] investigated different types of wood ash used in papermaking, and their effect on paper properties. Saeki and Miyawaki[4] tested the strength and pH of a variety of commercially available Japanese papers, but no experiments have been made to date on papers made of the same fiber under the same conditions. In this report we compared the durability of *kozo* papers cooked in different agents, such as wood ash, soda ash (sodium carbonate), lime (calcium hydroxide), and caustic soda (sodium hydroxide) in order to determine what makes a more durable *kozo* paper.

EXPERIMENT

Fiber, cooking and paper making

Kozo white bark, produced in Kochi prefecture, was cooked under normal conditions using cooking agents representative of those used in modern Japanese papermaking: wood ash , soda ash, lime and caustic soda. The cooking conditions are given in Table 1. Part of the sample cooked with caustic soda was bleached using sodium hypochlorite (15%). A portion of the fibre cooked in lime was

* This article can be seen as continuation, i.e. Part III of Ref. 1 and 2.

Table 1: Cooking conditions

	bark (kg)	amount of chemical (g)	water (l)	pH
wood ash	2		25	11.4
soda ash (Na2CO3)	2	350	30	
lime (Ca(OH)2)	2	300	30	
caustic soda (NaOH)	3	450	29	

washed in a cloth bag, a traditional method for whitening and removal of fine particles. A portion of each type was also left in the cooking vessel overnight. Hand papermaking was carried out by the usual *nagashizuki* method, i.e. sheet forming by moving the mould back and forth and sometimes side to side after having charged it with fibre, and repeating this procedure several times, using *tororo-aoi* ("Hibiscus manihot") as a dispersant. Wet sheets were dried on steam-heated stainless steel. The sample sheets had an average basis weight range of 24.5–30.1 g/m^2.

Ageing and measurement

The samples were aged at 80°C 65% RH for up to 12 weeks. Tensile strength, tear strength, folding endurance and brightness were measured according Japanese Industry Standard (JIS) and TAPPI test method. For chemical analysis *kozo* white bark was powdered and extracted with ether, 80% aqueous ethanol, hot water, successively. *Washi* samples were powdered but were not extracted. Ten to twelve mg of samples were hydrolyzed by sulphuric acid. The amounts of alditol acetates of neutral sugars were measured using gas chromatograph[5]. Amount of acidic sugars were determined colourimetrically[6]. Lignin contents were determine using acetyl bromide method[7]. Ash contents were measured by JIS P8204.

RESULT AND DISCUSSION

Texture

All the papers made in this experiment demonstrated an overall soft texture. The lime cooked papers were finer than the others, and washing treatment of the pulp in the cloth bag softened this type further. The wood ash cooked papers had a crispier feel than the others.

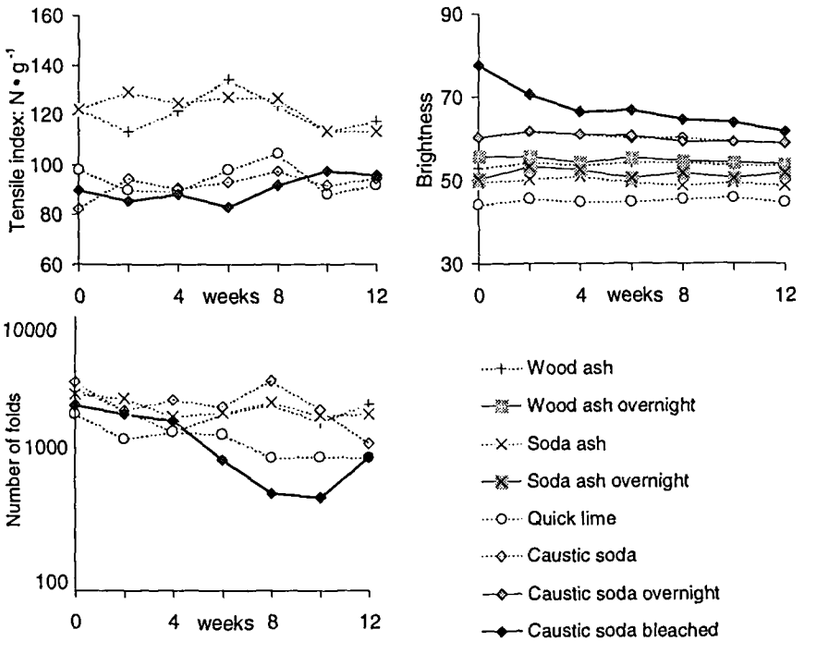

Fig.1: Relationship between cooking agent and physical properties.

Strength properties

Tensile indices of the samples are shown in Fig. 1a. The papers cooked with wood ash and soda ash have higher tensile strength than those cooked with lime and caustic soda. This difference showed that milder alkali caused less damage to the fibre than the stronger alkali. Furthermore, papers left overnight in cooking lye after the cooking process resulted in a lower tensile index than those washed immediately, indicating that cooking progressed further in the former case. Twelve weeks of accelerated aging did not lower the tensile index of the papers. It is presumed that the high pH values (pH 7–9) of the samples account for this.

The folding endurance of the papers is shown in Fig. 1c. In this figure, we could not group the papers based on their alkali strength. The rate of deterioration of folding endurance was calculated using the formula $S=S_0\exp(-Kt)$ where S is the folding endurance of the sample, K is the deterioration rate constant, and t is the treatment time (Fig. 2). This graph clearly shows the effect of cooking agents on the permanence of *Washi*. Again, those papers cooked with wood ash and soda ash have higher durability than those cooked with lime and caustic

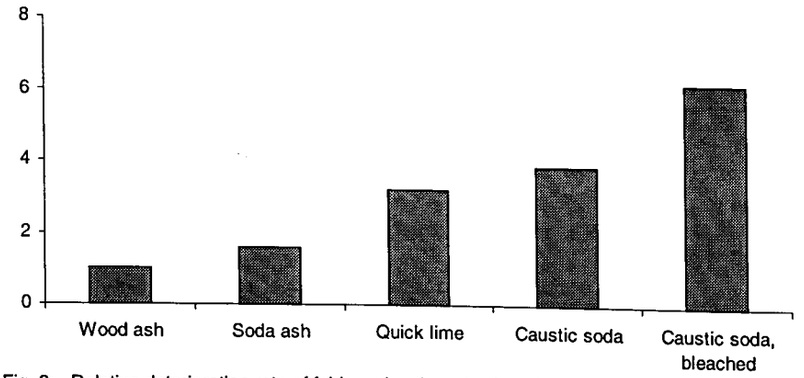

Fig. 2: Relative deterioration rate of fold number (wood ash = 1).

soda. Bleaching of the caustic soda cooked fiber destabilized the paper. The mild alkali resulted in a more durable paper, while the strong chemicals including bleaching lowered the durability of the *Washi.*

We also attempted to draw a comparison between the strength properties based on the drying method, such as natural drying on wood board under sun versus artificial drying on steam heated stainless steel. However, the strength of naturally dried papers deviated too greatly to draw any conclusions. This deviation was due probably to the uneven natural drying conditions caused by different weather during the sample making period.

Colour change

The lime cooked paper had the lowest brightness (Fig. 1b). Brightness increased in the order of soda ash, wood ash, caustic soda and its bleached sample. Stronger agents produced a brighter paper. After twelve weeks of aging treatment, the brightness of the unbleached papers decreased minimally, while that of the bleached sample decreased by 21%, reverting to a level similar to that of the unbleached ones.

Chemical properties and composition

The pH of papers was 7 to 9 and decreased little during twelve weeks ageing treatment. The overall pH was presumed to be high enough that acid hydrolysis of the cellulose did not take place.

Table 2: Chemical composition (%) of paper prepared from differently cooked *kozo* fiber.

	untreated fiber	Wood ash		Soda ash		Caustic soda			Quick lime	
		iac*	ovn**	iac*	ovn**	iac*	ovn**	bleahed	iac*	washed
Ash	1.3	1.6	1.3	1.5	1.8	0.8	0.5	0.5	1.0	0.4
Rhamnose	3.3	0.9	0.7	0.8	0.7	0.0	0.0	0.0	0.0	0.0
Arabinose	2.8	0.5	0.4	0.5	0.6	0.0	0.0	0.0	0.0	0.0
Xylose	4.6	3.3	3.0	2.8	3.1	2.8	3.0	2.8	3.0	3.1
Mannose	2.0	0.8	0.7	0.7	0.9	0.0	0.0	0.0	0.0	0.0
Glucose	68.0	73.1	75.8	74.4	70.0	82.7	91.0	98.5	93.3	93.4
Galactose	3.0	1.3	1.7	2.3	1.7	0.0	0.0	0.0	0.0	0.0
All neutral sugars	83.9	79.9	82.3	81.5	77.0	85.6	94.0	101.4	96.4	96.5
Galacturonic acid	5.5	1.6	1.8	1.9	1.6	0.7	0.8	0.9	1.2	0.9
Glucuronic acid	6.1	2.5	1.8	2.0	2.6	0.2	0.0	0.0	0.0	0.1
All acidic sugars	11.6	4.1	3.6	4.0	4.2	0.9	0.8	0.9	1.2	1.0
Lignin	2.3	1.5	1.3	1.8	1.7	1.5	1.5	1.0	2.0	1.6

* immediately after cooking

** left in cooking solution overnight

Chemical composition of the papers is shown in Table 2. Ash content of the caustic soda cooked paper was 0.8%, while those of others were more than 1%. Caustic soda rinses out more than the other cooking agents due to its higher solubility in water. In contrast, wood ash and soda ash remain as a reserve, and inhibit acid-caused deterioration. In the case of the lime cooked papers, ash content was decreased to 0.4% from 1.0% by washing in a cloth bag. This result indicates that a fair amount of lime is precipitated outside the fibre.

Amounts of rhamnose, arabinose, mannose and galactose in neutral carbohydrates were lower than detection limits by cooking with either caustic soda or lime. The amount of acidic carbohydrates were also reduced by about one third by these agents. The reduction in the amounts of these carbohydrates indicates the effect of the cooking chemicals on hemicellulose content. The change of chemical composition formed a good correlation with the changes in physical strength.

CONCLUSION

The deterioration rate of folding endurance and original strength of tensile index demonstrates that using milder alkali, such as wood ash and soda ash, resulted in a more durable paper than stronger alkali, such as caustic soda and lime. The bleached paper was most unstable in strength and colour. These stability differences were effected by the degree of damage during cooking and bleaching.

Higher damage by the stronger alkali was also demonstrated by chemical composition analysis.

ACKNOWLEDGEMENT

We want to express our thanks to the staff of the Kochi Prefectural Paper Technology Center for their help in the making of the paper samples, and to the Paper Science Laboratory of the University of Tokyo for use of their paper testing equipment. Part of this experiment was funded by a grant from the Fukutake Science and Culture Foundation.

SUMMARIES

The Effect of Cooking Agents on Japanese Paper

The strength and durability of *kozo* papers made from fibre cooked in different chemicals, such as wood ash, soda ash (sodium carbonate), lime (calcium hydroxide), and caustic soda (sodium hydroxide) were compared in order to determine what makes a more durable *kozo* paper. The deterioration rate of folding endurance and original strength of tensile index showed that milder alkali, such as wood ash and soda ash, have a more favourable effect on the durability of papers rather than stronger alkali, such as caustic soda and lime. Bleached paper was most unstable in strength and colour. These stability differences were attributed to the degree of damage to the fiber during cooking and bleaching. Higher damage by stronger chemicals was also demonstrated by chemical composition analysis. The above results proved the commonly held belief that mild alkali is better than stronger chemicals in papermaking.

L'effet des différentes solutions de traitement sur le papier Japon

On a analysé et comparé la durabilité des fibres de papier *kozo* selon les différents procédés chimiques auxquels elles ont été soumises, tels que la cendre de bois, le carbonate de soude, la chaux (l'hydroxyde de calcium), et la soude caustique (l'hydroxyde de sodium) afin d'être en mesure de déterminer ce qui renforçait la durabilité du papier *kozo*. Les taux de détérioration de la résistance au pliage et à la traction ont mis en évidence que des traitements alcalins plus doux comme la cendre de bois et le carbonate de sodium avaient un effet plus bénéfique sur la durabilité du papier que des produits alcalins plus forts tels que la soude caustique et la chaux. Ces différences dans la stabilité du papier sont le résultat du degré de dégradation des fibres subie au cours des procédures de lavage alcalin et du blanchiment. L'analyse chimique a démontré qu'une dégradation plus grave des fibres avait lieu lorsque la concentration chimique des produits utilisés était plus forte. Ces constatations confirment l'opinion générale selon laquelle le fait de réduire les fibres de papier en pâte avec des moyens alcalins doux est dans la fabrication du papier préférable à l'utilisation de produits plus forts.

Der Einfluß der Kochlauge auf Japanpapier

Es wurde die Dauerhaftigkeit von Papier aus *Kozo*-Fasern untersucht, die in verschiedenen Kochlaugen aufbereitet waren: Holzasche, Soda, gebrannter Kalk, Bleichsoda, mit dem Ziel, die bestgeeignete Aufschlußmethode hinsichtlich der Dauerhaftigkeit zu finden. Der Rückgang von Falzzahl und Bruchkraft zeigte, daß milde Alkalien wie Holzasche und Soda die Dauerhaftigkeit günstig beeinflussen. Gebleichtes Papier wies die geringste Stabilität in Festigkeit und Farbe auf. Dies ist zu sehen als Folge unterschiedlicher Faserschädigung während des Koch- und des Bleichprozesses. Stärkere Faserschädigung durch stärkere Chemikalien wurde auch in der chemischen Analyse deutlich. Diese Feststellungen bestätigen die allgemeine Meinung, daß der Faseraufschluß durch milde Alkalien für die Papierherstellung besser ist als der durch starke.

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Determination of the Content of Alkalis and Acids in Paper*

by JOACHIM LIERS

INTRODUCTION

It has long been widely acknowledged that paper which is produced in an industrial way is endangered by acid decomposition[1]. Therefore, deacidification of paper is a very important component of book and paper conservation. At the moment many individual deacidification methods exist[2], or deacidification is integrated in a complex paper conservation method like paper splitting[3].

From the chemical point of view, the effectiveness of deacidification is valued by the pH-value of the paper, the content of alkaline buffer in the paper and the evenness of deacidification. The alkaline buffer protects the treated paper against the further formation of acids and environmental poisons like SO_2 and NO_x. Therefore the value of the alkaline buffer is very important for the further ageing durability of the deacidified paper.

DETERMINATION OF THE CONTENT OF ALKALIS AND ACIDS IN PAPER

The Zellchemische Merkblatt IV/58/80[4] gives instructions for the determination of alkaline buffer in paper by simple acidic titration of alkalis after the paper has been extracted in water. The problem of this method is that it is not possible to quantify alkaline earth compounds (e.g. Ca- and Mg-compounds) in this way because of their poor water-solubility. Therefore, very often the paper is extracted with a defined quantity of acid and the alkaline buffer is determined by back-titration[5].

Sometimes the alkaline buffer of paper is analyzed by quantifying a preferred element of the deacidification compound (e.g. Ca or Mg) using a spectroscopical method, like electron beam micro probe[6]. The advantage of spectroscopical measurements is that for tests only very small quantities of paper samples are

* A German version of this report has been published in Das Papier 53 (1999): 154-161.

needed. Therefore, spectroscopical methods could allow a non-destructive determination of alkaline buffer in paper. The problem with these kinds of measurements is, a part of the alkaline earth elements is bound to acids in the paper, forming neutral salts. Therefore it is problematic to calculate the content of alkaline buffer by using the concentration of the alkaline earth elements only.

For determination of the content of acids in paper a comparable problem that for the analysis of alkalis in paper exists. The sources of acids in paper are, besides aluminium sulfate and sulfuric acid, carboxylate groups and acidic residues from the chemical pulping and bleaching processes. Therefore it is not possible to determine these different water-soluble and strong acids in paper after a simple extraction in water by direct titration with a base as suggested by Zellchemische Merkblatt IV/58/80[4].

Katz et. al.[7] described two methods for the determination of strong (sulfonate) and weak (carboxylate) acidic groups in sulfite pulps. One method involves the initial conversion of the groups to their magnesium salts. A differentiation of the two types of groups is then made based upon the liberation of magnesium from the carboxylate groups by acetic acid followed by the elution of magnesium from the sulfonate groups by hydrochloric acid. In the other method, the groups are converted to hydrogen form and are then titrated conductometrically with sodium hydroxide in the presence of sodium chloride.

Because these methods are costly, in the present study a method has been devised, which determines the alkalis and acids in the paper using a simple acid-base back-titration.

EXPERIMENTAL

The content of acids and alkalis should be determined by acid-base back-titration. In a titration the equivalent points are often not located on the theoretically calculated pH-value, because the location of the equivalent point can be verified by the composition of the test sample and the condition of the experiments. Therefore the titration curve for titration of a pure strong acid and base should be discussed first of all.

When a strong acid (e.g. H_2SO_4) is titrated by a strong base (e.g. NaOH) it is possible to observe two equivalent points – at a pH-value of 5.0 (Fig. 1a: EP1) and at a pH-value of 7.6 (Fig. 1a: EP 2). First of all, this result is surprising because, from the theoretical point of view, with titration of a strong acid only one equivalent point, at a pH-value of around 7, is expected. But the two steps in the titration curve are the result of two titration curves – the titration of a strong and a weak acid. Whereas the first equivalent point corresponds to the neutralization

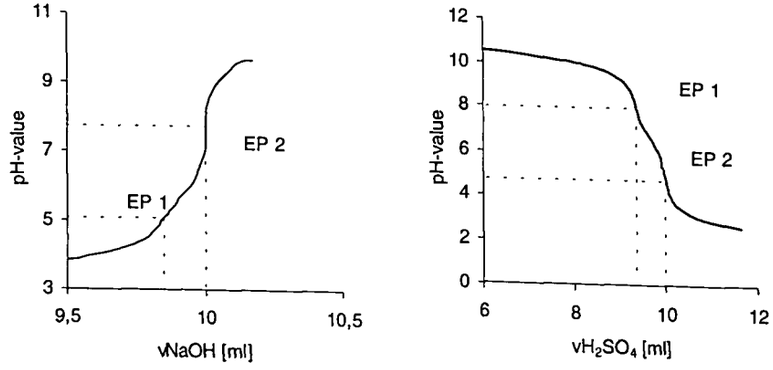

Fig. 1: Detail of the titration curve for titration; a (left): 10ml 0.05m H_2SO_4 by 0.1 m NaOH; b (right) 10 ml 0.1m NaOH by 0.05 m H_2SO_4.

of the strong acid (in this case H_2SO_4) the second equivalent point refers to the fact that additionally a weak acid exists[8]. In this case the weak acid is carbon dioxide, which is dissolved in the sodium hydroxide solution and produces carbonate and hydrogen carbonate. If the titration contains a paper sample, the second equivalent point can represent weak acids of the paper as well.

Therefore, to determine only the strong acids, the curve should be evaluated on EP1. To determine the weak acids in the paper, the carbon dioxide must be boiled-away or determined by blank test beforehand and the titration must be continued up to EP2. In the following experiments the CO_2 was determined by blank tests in advance.

When a strong base (e.g. NaOH) is titrated by a strong acid (e.g. H_2SO_4), two equivalent points – at a pH-value of 8 (Fig. 1b: EP 1) and at a pH-value of 4.7 (Fig. 1b: EP 2) – can be observed as well.

The reason for this result is that a part of the OH^- -ions of the sodium hydroxide solution are bound by carbon-dioxide producing carbonate and hydrogen carbonate. While the OH^- - and the CO_3^{2-} -ions can be determined at alkaline pH-value (EP1), the HCO_3^- - ions can be titrated only at weak acidic pH-value (EP2). Therefore samples containing sodium hydroxide solution should be titrated up to the second equivalent point at a temperature of 60°C.

In the following devised tests these chemicals were used:

- 0,1 m NaOH p.a. (Merck Co.),
- 0,05 m H_2SO_4 p.a. (Merck Co.),
- $CaCO_3$ p.a. (Riedel-de Haën Co.).

The titration has been done by an automatic titrator *Titrino*® of the Metrohm Co.. For weighing - an analytical balance MC BA 100 produced by the Satorius Co. was used. The test paper was a 20-year-old, acid-sized, wood-based paper. For preparation of an alkaline paper sample, the test paper was deacidified using the mass-deacidification treatment of the Deutsche Bibliothek[9]. The deacidification compound was magnesium methylate which was dissolved in hexamethyldisiloxan.

RESULTS AND DISCUSSION

Determination of the content of alkalis in paper

Three different tests for determination of the alkaline buffer were performed:

- Test 1: Extraction of paper with water, paper filtered off.
- Titration with 0.05 m H_2SO_4. Result, i.e. seeming alkaline buffer: 0,063 mmol/g.
- Test 2: Extraction of paper with10 ml 0.05 m H_2SO_4, paper filtered off.
- Back-titration with 0,1 m NaOH. Result, i.e. seeming alkaline buffer: 0.22 mmol/g.
- Test 3: Extraction of paper with 10 ml 0.05 m H_2SO_4. Titrated sample contains paper fibres.
- Back-titration with 0,1 m NaOH. Result, i.e. seeming alkaline buffer: 0.165 mmol/g.

Strikingly different quantities of alkalinity were found: In Test 2 the highest, in Test 1 the lowest. The reason of the apparently low alkalinity in Test 1 is the slight water-solubility of the magnesium compounds which were used during the deacidification process. Thus during water extraction only a very small amount of alkali was dissolved and the analytical result was accordingly distorted. A possible explanation for the different alkaline contents, which were found in Tests 2 and 3, is, that a part of the sulphuric acid is adsorbed on the paper fibre. Therefore after filtration (Test 2) a part of the acid remains in the filtration residue and cannot be determined during titration of the filtrate. This thus caused lower consumption of sodium hydroxide solution feign a higher alkaline content in paper. The attempt to extract the filtration residue a second time with water results in a negligibly low correction of the analytical result.

To clarify these considerations about the results of Tests 2 and 3 these experiments were repeated with acid paper:

- Test 4: Same procedure as for Test 2: Paper is filtered off.
- Result, i.e. acid sorbed by the paper: 0,07 mmol/g.
- Test 5: Same procedure as for Test 3: Titrated sample contains paper fibres.
- Result, i.e. acid sorbed by the paper: 0 mmol/g.

From these results it must be concluded that in the case of the distribution of an alkaline paper a 0.07 mmol/g higher alkaline content would be feigned. This difference corresponds to the divergence of the results between Test 2 and Test 3, where after filtration of the paper fibres a 0.055 mmol/g higher alkaline content was found than by titration of the sample with paper fibres. Therefore, when paper is extracted by acids, the following titration should take place in the presence of the paper, as suggested by ISO 10715, because the paper is able to bind acids by sorption. It is not possible to remove the adsorbed acid by a washing process, but it can be determined by direct titration. A reason for the observed sorption of acids on paper could be a beginning protonation of cellulose during extraction by acids. In the first step of this process the hydronium ion is bound to the oxygen atom of the glycosidic bond by a hydrogen bridge linkage. Therefore, it should be possible to titrate the bound acids quantitatively.

For determination of alkaline in paper the following analytical method was developed. At first the test paper is conditioned at 23°C and 50% RH. Then one gram of the chipped paper is extracted in 50ml distilled water for 12 hours at room temperature. During extraction the jar used is closed by a tube filled with CaO. To the extract, still containing the paper fibre, 10ml 0,05m H_2SO_4 are added and the extraction is continued for one hour. The extract, still containing the paper, is then titrated with 0,1m NaOH up to the second equivalent point (pH=7.6).

In Fig. 2a the titration curve of an alkaline paper is shown. For illustration the curve of the blank test (titration without paper) is shown in the diagrams as well.

For calculation of the content of alkalis the following equation is used (I).

$$\text{content of alkaline} = \frac{v_S \cdot f_S \cdot 0{,}1 - v_L \cdot f_L \cdot 0{,}1}{m} \text{ [mmol / g]} \qquad \text{(I)}$$

where:

v_S = volume of H_2SO_4 [ml]
f_S = titrimetric factor of H_2SO_4
v_L = volume of consumed NaOH [ml]
f_L = titrimetric factor of NaOH
m = weighed portion of paper [g]

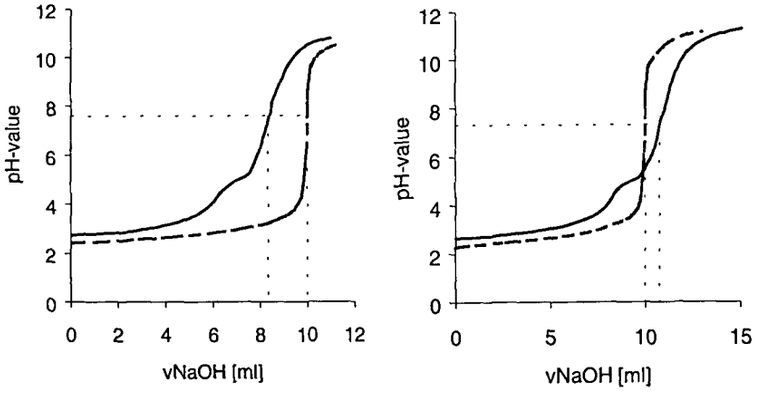

Fig. 2: Titration curve for determination of alkaline buffer in alkaline (a; left) and of acids in acidic test paper (b: right). —— Titration curve of the paper. – – – Titration curve of the blank test.

Determination of the content of acids in paper

In analogy to the experiments described above, three different tests for the determination of acids in paper were performed:

- Test 6: Extraction of paper with water and titration by 0.1 m NaOH. Paper is filtered off. Result, i.e. seeming acid content: 0.002 mmol/g.
- Test 7: Extraction of paper with 10 ml 0.1 m NaOH and back-titration by H_2SO_4.Paper is filtered off. Result, i.e. seeming acid content: 0.12 mmol/g
- Test 8: Extraction of paper with 10 ml 0.1 m NaOH and back-titration by H_2SO_4. Titrated sample contains paper fibres. Result, i.e. seeming acid content: 0.27 mmol/g

As the results show, very different quantities of acidity were found. Whereas in Test 6 nearly no acid was found, in Test 8 the highest content of acid was determined. The reason of the apparently low acidity in Test 6 is the low degree of hydrolysis of the weak acids in paper. Thus, during water extraction only a very small amount of acids was dissolved and the analytic result was accordingly distort.

In analogy to the experiments for determination of the alkaline buffer it was suspected that a part of the sodium hydroxide is sorbed on the paper fibre. Therefore, it was assumed that the analytical result is distort to a higher-seeming content of acid if the paper is filtered off before back-titration (Test 7). So the higher acid content in Test 8 in comparison to Test 7 was surprising.

To clarify these considerations about the results of Tests 7 and 8 these experiments were repeated with alkaline paper. During these experiments comparable content of acids were determined as in the acid paper. From these experiments it can be concluded that the results of Tests 7 and 8 have nothing to do with the real content of acids in the paper. The observed analytical results are the consequence of different, non-reversible, hydroxide-ion consuming side reactions between the sodium hydroxide and cellulose. This suggestion was based on the observation that the paper which was extracted in a sodium hydroxide solution was becoming frayed. This effect was intensified when a sodium hydroxide solution including paper (Test 8) was boiled. By lowering the concentration of NaOH it was possible to decrease the side reaction, but not to stop it. The pH-value, measured during extraction of paper with the sodium hydroxide solution, was about 12.1. Therefore an ion exchange H^+/Na^+ between the hydroxide groups of the cellulose and the sodium hydroxide is possible. But these exchanged H^+-ions have nothing to do with the acids in the paper.

Therefore, in the next test series it was attempted to extract the acids in the paper under milder conditions using $CaCO_3$. As a reference sample, the alkaline paper was investigated under comparable conditions.

- Test 9: Extraction of the acid paper by $CaCO_3$ (0.05g $CaCO_3$ suspended in 50 ml H_2O; pH: 8.8). Addition of 20 ml 0.05 m H_2SO_4 in order to dissolve surplus $CaCO_3$. Back-titration by 0,1 m NaOH. Titrated sample contains paper fibres. Result, i.e. acid content: 0.07 mmol/g
- Test 10: Same procedure with alkaline paper. Result, i.e. acid content: - 0.17 mmol/g

While in the acidic paper 0.07 mmol/g acid was found, in the alkaline paper 0.17 mmol/g alkaline buffer was determined, what means, so to say, "negative acid content". The alkaline content which was measured in Test 10 is comparable to the value determined in Test 3. It means that under these conditions side reactions between cellulose and $CaCO_3$ can be ignored. During extraction of the paper with $CaCO_3$-suspension only those acids of the paper were determined which would be neutralized during a conservation treatment with $CaCO_3$. In this respect, these method of determination of acids in paper is relevant to practice in paper deacidification.

For determination of acids in paper the following analytical method was developed. At first the test paper is conditioned at 23°C and 50% RH. Then one gram of the chipped paper is extracted in 50ml distilled water for 12 hours at room temperature. During extraction the jar used is closed by a tube filled with CaO. To the extract, still containing the paper fibre, 0.05g $CaCO_3$ are added and the extraction is continued for one hour. Finally to the extract 20ml 0,05m

H_2SO_4 are added. This mixture is shaken for 1 hour, then back-titrated with 0,1m NaOH up to the second equivalent point (pH=7.3).

In Fig. 2b the titration curve of an acid paper is shown. For illustration the curve of the blank test (titration without paper) is shown in the diagram as well. For calculation of the content of acids the following equation is used:

$$\text{content of acid} = \frac{2n_{CaCO_3} + v_b \cdot f_b \cdot 0{,}1 - v_a \cdot f_a \cdot 0{,}1}{m} \text{ [mmol / g]} \qquad \text{(II)}$$

where:

n_{CaCO_3} = amount of substance of $CaCO_3$ [mmol]
v_b = volume of consumed 0.1m NaOH [ml]
v_a = volume of 0.05m H_2SO_4 [ml]
f_a = titrimetric factor of 0.05m H_2SO_4
f_b = titrimetric factor of 0.1m NAOH
m = weighed portion of paper [g]

DETERMINATION OF THE ANALYTICAL ERRORS

To determine the analytical errors, 4 test series were performed, each containing 10 tests. In the first test series 10 ml 0.05 m H_2SO_4 was back-titrated with 0,1 m NaOH. As an average 10 ml NaOH were needed. The relative divergence of the single test results to the average was 0.15%. In the second series 0.05g $CaCO_3$ was dissolved in 20ml 0,05 m H_2SO_4 and the surplus of sulphuric acid was back-titrated with 0,1 m NaOH. On the average 10.04ml NaOH were needed. The relative divergence of the single measurements to the average was 0.3%. In two further test series the alkaline buffer in 1g alkaline test paper (experimental conditions like in Test 3) and the content of acids in 1g acidic test paper (experimental conditions like in Test 9) were determined. It became evident, that the titration curves become blurred by the presence of scraps of paper during titration. Therefore in comparison to the blank tests, the relative divergence of the titrated volume of each single experiment to the mean was increased to 0.6–0.8%. Therefore depending on content of alkali or acid in paper, the relative analytical error was 2–9%.

To minimize the error, the titration curve should be analyzed at the pH-value of the equivalent point of the respective blank test. The problem that the titration curve becomes blurred by scraps of paper could be avoided by using a colour indicator. But by analyzing aged paper samples it is nearly impossible to see the change of colour at the equivalent point, because the paper extract has a dirty-brown colour. Another possibility of reducing the analytical error could be to protect the pH-electrode mechanically from the scraps.

CONCLUSION

For the determination of acid or alkali in paper acid–base back-titration was investigated. The titration should takes place in the presence of the paper. Otherwise, the measurement becomes inaccurate because of the interaction of acid with paper during extraction. In the case of determination of acids in the paper, the paper should be extracted by a $CaCO_3$-suspension. After dissolving of the surplus of $CaCO_3$ by H_2SO_4, the acids contained in the paper are determined by back-titration of the H_2SO_4. Thus, only those acids were determined which would be neutralized during a conservation treatment with $CaCO_3$. In this respect, this method of determination of acids in paper is relevant to practice in paper deacidification.

During the determination of acids in the paper, the second equivalent point represents the summary content of acids. By separate evaluation of the equivalent points 1 and 2, it should be possible to distinguish between weak and strong acids in paper. It must be clarified in further investigations whether it is possible to quantify strong and weak acids separately.

Because the acidimetric determination of acids and alkalis is a destructive method of analysis, it can be used only for investigation of a test paper. Therefore, the aim for further investigation is to improve these methods to a micro-method, which needs only very small quantities of paper. In this way the acidimetric determination of acids and alkalis could become a quasi non-destructive analytical method.

ACKNOWLEDGEMENTS

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SUMMARIES

Determination of the Content of Alkalis and Acids in Paper

The content of acids and alkalis in paper should be determined by acid-base back-titration. However, during extraction of paper by NaOH or H_2SO_4 interaction with the cellulose takes place, which distort the subsequent back-titration. Therefore, when alkaline paper is extracted by acids, the subsequent titration should take place in the presence of the paper. After extraction of acidic paper with NaOH it is not possible to determine the acids by a subsequent back-titration. Therefore, the acidic paper should be extracted by a $CaCO_3$-suspension. Then the surplus of

$CaCO_3$ is dissolved by H_2SO_4. Finally, the acids of paper are determined by back-titration of the H_2SO_4.

Mesure de la teneur alcaline et acide du papier

La teneur alcaline et acide du papier est mesurée au moyen du procédé de retitration acide-base. Cependant au cours de l'extraction acide ou alcaline (par NaOH ou H_2SO_4) des réactions ont lieu entre le produit d'extraction et la cellulose, ce qui fausse la retritation subséquente. C'est pourquoi lorsque le papier alcalin est extrait par des acides la titration devrait avoir lieu en présence du papier. Après l'extraction du papier acide à l'aide d'une solution d'hydroxyde de sodium (soude caustique = NaOH) ou d'acide sulfurique (H_2SO_4) il n'est plus possible de mesurer la teneur des acides lors d'une retitration subséquente. C'est pourquoi l'extraction du papier acide devrait s'effectuer à l'aide d'une suspension de carbonate de calcium ($CaCO_3$). Le surplus de carbonate sera ainsi dissous dans une quantité définie d'acide sulfurique (H_2SO_4). Enfin on déterminera la teneur du papier en acides au moyen d'une retitration au H_2SO_4.

Die Messung des Alkali- und des Säuregehaltes in Papier

Der Säure- und der Alkaligehalt von Papier wird durch Säure-Base-Rücktitration gemessen. Beim sauren oder alkalischen Extrahieren (H_2SO_4 bzw. NaOH) laufen jedoch Reaktionen zwischen dem Extraktionsmittel und der Cellulose ab, welche die nachfolgende Rücktitrierung verfälschen. Deshalb sollte die Titration des Extraktes von alkalischen Papier in Anwesenheit des extrahierten Papiers erfolgen Nach der Extrahierung von saurem Papier mit Natronlauge ist es nicht möglich, den Säuregehalt durch nachfolgendes Rücktitrieren zu bestimmen. Deshalb sollte mit Calciumcarbonat-Suspension extrahiert werden. Das überschüssige Carbonat wird in einer definierten Menge Schwefelsäure gelöst, dann wird der Säuregehalt des Papiers durch Rücktitrieren mit Schwefelsäure bestimmt.

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The Ecology of the Fungal Fox Spots in a Book Published in 1854

by MARY-LOU E. FLORIAN & LESLEY MANNING

INTRODUCTION

This research project undertakes an extensive SEM analysis of fungal fox spots, mainly in one book published in 1854. The goal was to characterize the fungal infestations, identify the fungal species and determine the species distribution in the book, and to use this information to establish the fungal species origin and how the paper was contaminated.

The main book examined was:

- J. Bauer: Lives of the Brothers Humboldt, Alexander and William. New York: Harper and Brothers 1854.

It was unusual in that the rag paper pages up to page 96 were overall yellowed with a few fungal fox spots and the remaining pages were nearly white with many fungal fox spots. Analyses[1] of the papers showed the discoloured pages contained alum rosin and the white pages were untreated. A preliminary comparison of fungal fox spots in another book was undertaken:

- T. Snollett: *The History of England.* Vol. 1. London: T. Cadell and R. Baldwin 1785.

Both books had no heritage value and thus were considered research tools allowing destructive analyses.

The spots examined are fungal fox spots. These are evenly coloured rusty-red; they are irregular in shape, not circular; they do not have a central spot; they have the same surface texture as the adjacent un-foxed paper; they vary in size from just visible spots to large, diffused areas covering most of a page; they fluoresce under ultraviolet light with a yellow light; and most spots show migration of the stain through 1–3 successive pages. Except for the background iron normally present in paper[1], no additional iron was detected. Throughout this paper the term *spot*, pertains to this type.

The fungal origin of these spots is well established[1–5]. Several authors have shown the presence of fungal structures in these spots under light microscopy using histological preparations.

Beckwith et al.[2] obtained 55 fungal culture from scraping of fox spots in books. They stated their concern that these fungi may not necessarily be the causative fungi of the fox spots. They cultured dust from the library stacks and found many of the same species they found on the books. They suggested that these fungi may be picked up from the ventilation system and deposited on the books. There are many reports in the literature[6] that record a large number of different fungal species cultured from fox spots but the reports do not address the problem of proving that these are the causative fungal species of the fox spots. Because of this weakness, it was thought that by using Scanning Electron Microscopy, and observing directly the organism present in the fungal fox spots, it might be possible to identify the causative species located in the spot by their conidia and the conidiophore shape.

Beckwith et al.[2] observed that some spots contained fungal structures but did not produce fungal cultures, and assumed they were dead. Florian[7] reviews some mycological literature and shows that survivability of the conidia varies with the environmental conditions of storage. Under ideal storage conditions a few survived up to 22 years. Viability tests of the fungal structures in 145 year old spots from the *Bauer* book were undertaken.

Florian[1] 1996, suggests that the fox spots in old books may be caused by fungal contamination during the paper or book making process. Appling[8] found similar fungi and bacteria in pulp and paper. Florian and Dudley[9] and Valentine[10] have cultured and identified a number of species from contemporary paper used in conservation. Florian and Dudley[9] have shown that the amount and distribution of the species on one type of paper may suggest either contamination from the paper making process or surface contamination from adjacent mouldy material or the airspora some time after the paper was made.

Linterink et al.[11] observed that foxing stains of identical shape and approximate size were observed throughout the pages of some old books. They dismantled the books and returned the paper to the quire stage and found that identical shaped spots lined up on top of each other, proving their common origin. This suggests that the origin of the cause of the stains was from the book making process. They did not determine if these stains were fungal in origin. Florian[1] observed in an old book spots some which had not migrated and some which had migrated to adjacent pages suggesting that the fungal activity in these latter spots occurred after the book was assembled.

In this present SEM analysis the morphology of the fungal spots and the population of fungal species, their distribution in the book and their location on pages will be used to help determine how and when the paper was contaminated.

Fig. 1. A type 1 fungal fox spot with fragments of fuzzy hyphae and a few elliptical conidia and a fracture conidiophore.

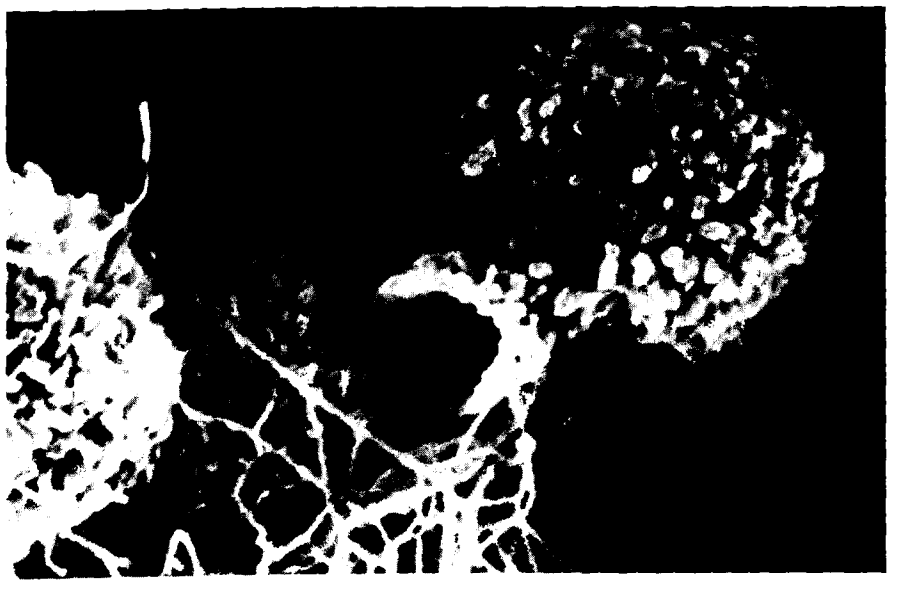

Fig. 2. Type 1 conidia entangled in hyphal mycofibrils (fuzz). The ornamentation of conidia is cerebrum-like ridges. The size averages around 5 x 5.5u. The shape is ellipti-cal or jug shaped with a prominent scar. The mycofibrils are single stranded and have a uni-form thick-ness throughout its length.

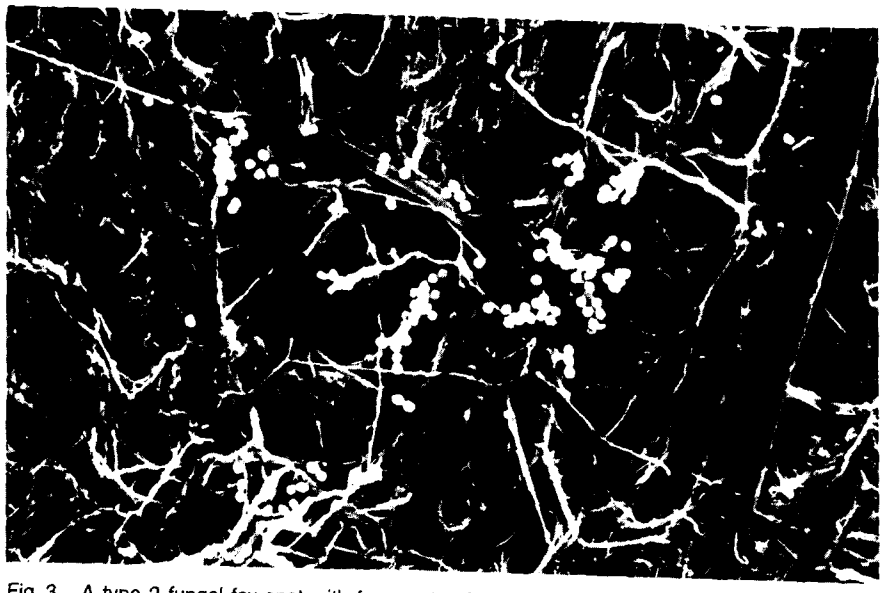

Fig. 3. A type 2 fungal fox spot with fragments of smooth hyphae, many spherical *Penicillium* conidia and a few fragments of conidiophores. In the right top corner a silk thread is seen as a tense, straight, small fiber.

Fig. 4. Type 2 spherical conidia, free and attached to a typical conidiophore. The ornamentation of the conidia is warty, with a prominent scar. The size varies with stage of development, those still attached to the conidiophore are the smallest. The average size of mature conidia is 2u–3u.

Fig. 5. Hyphae from a type 2 fungal fox spot. The hyphae are riddled with bacterial lytic holes.

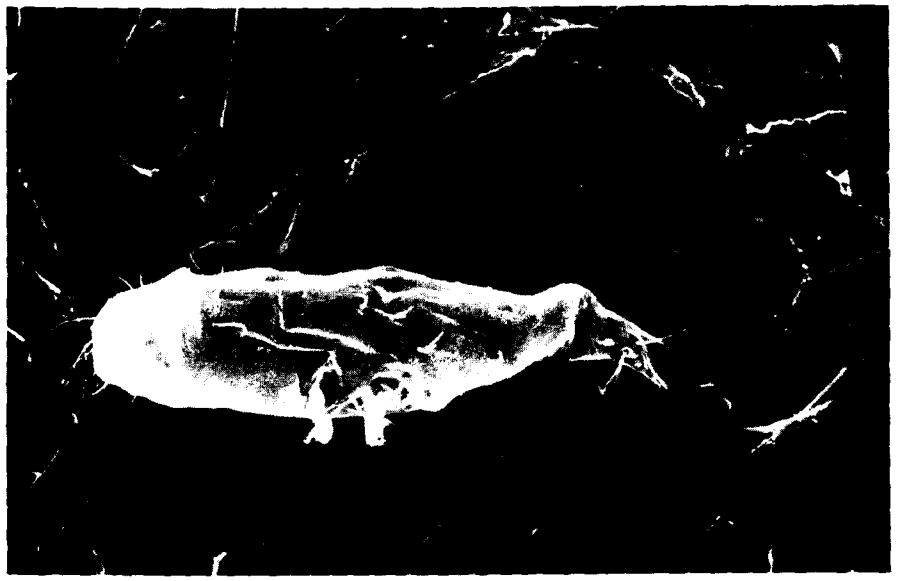

Fig. 6. A snout-nosed mite-like animal, now named *fox trotter*, from a fungal fox spot. It is 225u in length. There is a silk fiber attached to a setae on top of its snout. It has four legs. The snout is open on the ventral surface from the tip of the snout to the legs.

Fig. 7. A type 2 fungal spot located on the inner margin of the page against the spin. Type 2 conidia are interspersed in the debris. The large irregular surfaced spheres are faecal pellets. The structure in the lower right corner is the pebbled surface of a fractured egg shell. The egg and faecal pellets belong to *fox trotter.*

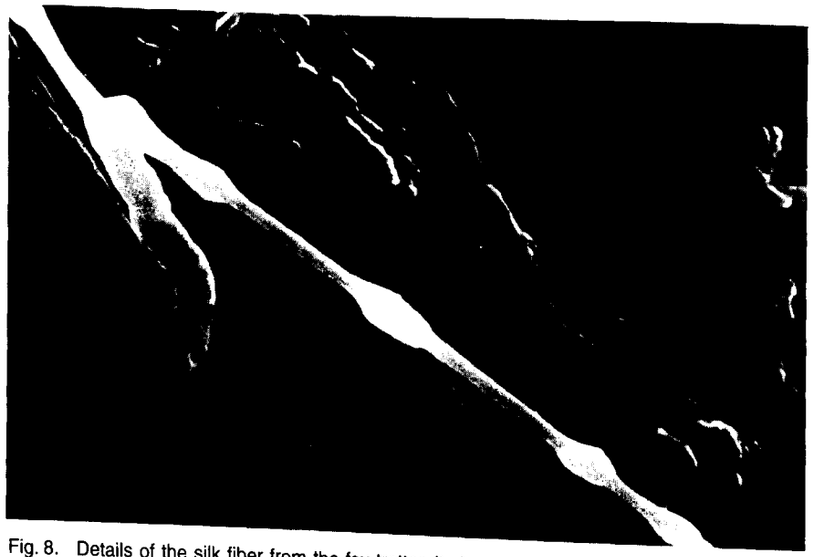

Fig. 8. Details of the silk fiber from the fox trotter. It shows the typical double strands of insect silk and the irregular thickness of the fiber, which is also show in Fig. 6.

METHODS AND MATERIALS

Viability test

Using aseptic technique, when possible, an area of a page, the size of a petri plate, was cut from nine pages (without alum rosin treatment) of the *Bauer* book. The 114 fungal fox spots on these pages were outlined with a graphite pencil. The marked paper was placed on sterile media in petri plates and incubated at room temperature (15–19° C). The media in the petri plates contained 3.9% potato dextrose agar acidified to pH 4–4.5 with sterile 0.1% aqueous solution of tartaric acid. The acidity prevents the growth of yeasts and bacteria.

Scanning Electron Microscopy (SEM) examination

The fungal fox spots had normally air dried thus no pre-treatment was considered necessary. Fungal fox spots and control, non-foxed paper, were cut from the pages using a razor blade or scalpel and with tweezers were placed on two-sided sticky tape already placed on aluminum SEM stubs. These samples were then coated with gold/palladium using a Technics Hummer V sputter coater. They were examined using a JEOL JSM-35C scanning electron microscope. Micrographs were taken on Polaroid positive/negative 665 film using 10KV to reduce surface charging and edge effects and at 15KV when higher resolution was required. The sampling depended upon the naturally occurring position of available spots, thus statistical analysis could not be considered. Thus the results show only a trend.

RESULTS AND DISCUSSION

Viability test results and discussion

The plates were observed continuously. After 72 hours there was no growth directly on any of the 114 outlined spots. There were 15 colonies of a blue-green fungus which caused the substrate to turn red. All were identical in colony colour, rate of growth and morphology. SEM analysis of the conidia and conidiophores showed that they were a *Penicillium* species. Three of these fungal colonies developed at the edge of three spots, eight developed at the edges of the paper and four in the middle of printed text. The conidia ornamentation of this

Penicillium species was different than the conidia in the fungal fox spots. The viable conidia could have come from airborne contaminants, poor aseptic technique or contemporary contamination within the book. The book has been extensively handled during the past three years, and could easily have become contaminated. This simple viability test shows definitively that the fungal structures in the fox spots were not viable.

SEM observations and discussion

Fungal spot description

Untreated rag paper. 75 fungal fox spots on 53 untreated rag paper pages in the *Bauer* book were scanned and 191 micrographs examined. Multiple spots on one page were taken from 11 pages. The position on the page, i.e., top, outer, bottom, and inner margin and on the text was recorded for all spots. The observations showed that the spots were basically of two morphological forms.

In Type 1 (T1; Fig. 1) the spot contained a few fragments of hyphae covered with fuzz and a few (less than ten in a 50x micrograph) isolated conidia. The conidia (Fig. 2) are jar shaped with low ridged ornamentation in a cerebellum pattern and the average size is 5.5 x 5 µ. The fuzz on the hyphae was observed restricted to the hyphae or in clumps surrounding and entangling hyphae and conidia. The hyphae are in fragments and in some cases they appeared brittle and fractured. The fungal structures are on top of the paper and there is no evidence of growth into the paper. The conidia are usually isolated not in clusters or chains.

Type 2 (T2; Fig. 3). The spot usually contained a large number (ten plus in a 50x micrograph) of conidia and a few isolated, often fractured, conidiophores (Fig. 4). There are only a few hyphae some of which appeared to grow into the paper and many with bacterial lytic holes (Fig. 5). The conidia are often in groups and chains. The conidia (Fig. 4) are near spherical spines with a prominent scar and have the average size of 2–3 µ. The size of conidia vary with stage of development, only conidia free from the conidiophore (Fig. 4) were measured. The presence of the bacterial lytic holes suggest that the fungus was growing in a wet environment prior to deposition on the paper. These hyphae were dead when deposited and the bacterial damage could not have occurred in the book.

Abbott[12] describes the Harper and Brothers Publishing procedures that would have been used on their *Bauer* book. The paper was dampened prior to printing using felts which could have been contaminated. Sharpley and King[13] show that

bacteria as well as fungi are on papermaking felts. The bacteria could have attacked the fungus in the wet felts and subsequently the fungus was deposited on the paper. After printing and drying the paper was pressed to make it flat. Many T2 conidia appear to be physically flattened.

There are a few isolated conidia of different ornamentation than T1 and T2, these are included in Type 3 (T3) spot.

There was considerable variation in amounts of fungal structures in all spots. The variation in amount depends on the position of the page in the three dimensional spot. Florian[1] has shown that with a spot which has migrated through three or four pages, the darkest spot shows the most fungal structures and is the point of contamination. The spots on the other pages have fewer fungal structures and in some cases there are no fungal structures, just the discoloration.

Identification

Conidiophores are necessary for genus determination. In *Aspergillus* the conidiophore has a distinct swollen head on which the conidia develop, whereas in *Penicillium* the conidia are developed on finger-like projections. Fig. 4 shows the type of conidiophore found related to the two types of conidia in the spots.

Conidia are identified by the type of conidia ornamentation, size and shape[14-18]. There are hundreds of species in both genera and only if the species under study has been included in the literature, which is sparse, can it be identified.

The causative fungi in T1 and T2 spots are two different species. Species identification is ongoing.

The following percent of different spot types in 75 spots distributed through out 53 pages in the book were found:

- T1: 53%
- T2: 37.5%
- T3: 9.5%

The 3 control areas showed no fungal structures.

The observations show clearly that the fungal species in Type 1 and Type 2 spots are the causative organisms of the fungal fox spots sampled.

Distribution on one page

Multiple spots on a single page showed a random distribution of T1 and T2 spots. Eleven pages with a total of 42 spots were observed:

- 7 pages with T1 and T2 spots,
- 2 pages with only T1;
- 2 pages with only T2.

The T1 and T2 spots were also shown to have a random distribution according to position on the page. All positions had approximately equal numbers of T1 and T2 spots with the exception of the top margin which had more T1. The sample size is small but the results on the distribution of the two spot types, T1 and T2 show a trend of random distribution on individual pages, position on the page, and on the pages through out the book.

The spots on the alum rosin coated paper were considerably fewer than on the untreated paper. They were smaller and near circular. On SEM observation, seven spots showed no fungal structures and two with only a few fragments of hyphae and conidia. The alum rosin coating looked like loose debris on the surface of the paper. A few hyphae-like structures appeared to be mixed into or below the coating.

Comparison with another book

The *Smollett* book was used for a preliminary comparison. 14 fungal fox spots from two pages were observed. There were two species, one was predominant. Their distribution was random on both pages.

Even though this is a preliminary study it is obvious that the two books have different species but the manner of contamination was the same. This type of analysis, using non-destructive sampling, could be very useful in authenticity or forensic studies.

The ecology

Hyphal mycofibrillar extensions (fuzz) was observed on hyphae in T1 spots, on single hyphae or surrounding and entangling hyphae and conidia (Fig. 2). The fuzz is made up a random meshwork of fibers, the average diameter is 0.08 μ. Because of the extensive covering of some spots, it was thought that it could be mite or booklice webbing.

Two snout nosed mite-like animals (Fig. 6) were found on two separate spots. They are not mites[19] and seem to be a new type of animal, for a lack of a better term, named *fox trotters.* Silk threads, faecal pellets and fractures egg shell (Fig. 1, 6, 7, 8) were associated with these animals and suggest a mini-ecosystem.

The silk threads associated with the *fox trotter* (Fig. 6 and 8) and located in spots (Fig. 1) are attached under tension to the substrate, the fuzz is not under tension. Unlike the fuzz, which is regular in diameter and single stranded, the silk threads show thickness irregularities and a double strand structure, due to paired spinerettes (Fig. 8), and are similar to mite silk[20].

Booklice are reported[21] to some times produce silk webbing. Because there was no reference to their silk structure in the literature, booklice were cultured and their silk observed under the SEM. The morphology was typical for silk. Thus the fuzz was not silk webbing. In mycological literature, only Locci[14], showed illustrations of the fuzz he called hyphal encrustment, and used this feature as an aid to identification of *Aspergillus* species.

There was also a body of literature on mycofibrillar extensions of hyphae which are on the nanometer scale. On discussing the fuzz with one of the authors[22] stated that the nanometer size fibrils can form cables and become much thicker. He also said the fuzz was formed on wood decay fungi hyphae when they become exposed at surfaces. This suggests an environmental response. He examined the fuzz in micrographs and said they were mycofibrils.

The role of the fuzz is not clear, it may act as a point of contact with substrates to maintain enzymes concentration, but because it is common on surface hyphae it may be a response to dehydration.

The silk, eggs and faecal pellets of the booklice were all measured for comparison with those associated with the *fox trotter.* They were not similar. To make a long study short, the silk threads, egg shells and faecal pellets belong to the fox trotter. There is no evidence of booklice in the spots.

CONCLUSIONS

The two species (T1 and T2) are the causative organisms of the fungal fox spots. Species identification using conidia ornamentations is possible and on going. The random distribution of the two species throughout the pages, on pages and in specific positions on pages, suggest a common contamination source for all pages. The fungal structures in the spots were not viable. Bacterial lytic holes in the hyphae of one species(T2) suggest that the hyphae were dead when deposited on the paper and came from a wet environment. Paper-making felts are suggested as a source. Mycofibrillar extensions (fuzz) on one species (T1) suggest that it came from a dried surface. The presence of a mite-like animal (now called a fox trotter) associated with silk, faecal pellets and egg shells suggest a complex ecosystem.

ACKNOWLEDGEMENTS

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SUMMARIES

The Ecology of the Fungal Fox Spots in a Book Published in 1854

A SEM analysis of fungal fox spots, in one book, dating 1854, was undertaken to characterize the fungal infestations, identify the causative fungal species and determine their distribution in the book, so as to help determine the species origin, source and method of contamination. Two species were the causative species. There was a random distribution of the two species on the 53 pages examined and with multiple spots and position on one page. The random distribution suggests contamination during the making of the book. One species had hyphae with bacterial lytic holes suggesting a wet environment origin and the other species had hyphal mycofibrils (fuzz) suggesting a dry environment origin. Viability tests showed the fungal structures were not viable. The presence of egg shells, faecal pellets, and silk threads in association with a mite-like animal illustrates a complex ecosystem.

L'écologie des taches de moisissure d'origine fongique dans un livre datant de 1854

On a soumis les taches de moisissure d'origine probablement fongique d'un livre datant de 1854 à une analyse microscopique avec des électrons afin de pouvoir caractériser les infestations fongiques, identifier les espèces de champignon en question et déterminer leur répartition dans le livre pour être en mesure de discerner l'origine, la cause et le moyen de contamination. On a trouvé deux espèces responsables de la contamination. Ces deux espèces étaient également réparties sur les 53 pages examinées dans des taches multiples à différents endroits. Cette répartition permet de supposer que la contamination remonte à l'époque de la confection du livre. Une des espèces trouvées comporte des caractéristiques qui permettent de conclure à une croissance dans un milieu humide, l'autre à une croissance dans un milieu sec. Des tests de viabilité ont démontré qu'aucune des deux formes de champignons trouvés n'était encore viable. La présence de restes de coquilles d'oeuf, d'excréments, et de fils de soie que l'on associe à un organisme vivant de type acarien, témoigne d'un écosystème complexe.

Die Ökologie von Stockflecken mikrobiologischen Ursprungs in einem Buch von 1854

Stockflecken von vermutlich mikrobiologischen Ursprungs in einen Buch von 1854 wurden einer elektronenmikroskopischen Untersuchung unterworfen, um ihren mikrobiologischen Charakter,

die Schimmelart und die Verteilung im Buch festzustellen, so daß die Ursache des Befalls erkannt werden kann. Es wurden zwei Spezies gefunden. Sie fanden sich annähernd gleichartig auf den 53 untersuchten Seiten des Buches, in vielfachen Flecken an unterschiedlichen Stellen. Die gleichartige Verteilung legt die Vermutung nahe, daß sie auf eine Kontamination bei der Buchherstellung zurückgehen. Eine der gefundenen Species wies Eigentümlichkeiten auf, die auf Wachstum in feuchter, die andere solche, die auf Wachstum in trockener Umgebung hinweisen. Keine der gefundenen Schimmelformen war noch lebensfähig. Reste von Eihüllen, von Kot und von Spinnfäden, die sich auf ein milbenähnliches Lebewesen zurückführen lassen, geben Hinweis auf ein komplexeres Ökosystem.

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Ageing of Laboratory Irongall Inks Studied by Reflectance Spectrometry

by M. CARME SISTACH, JOSEP M. GIBERT & ROGELIO AREAL

INTRODUCTION

Ancient recipes of irongall ink have been compiled in several bibliographical sources. Old recipes show us different ways to obtain gall-nut extracts; mention the solvents; and carefully explain the procedures used to make the ink. We checked two articles[1, 2] that compiled recipes from Mallorca dated between the XVth and XIXth centuries.

Three ingredients were consistent in all the recipes: nut-galls, vitriol and gum arabic; the amount of each ingredient and the procedure described were not always the same. Solvents used were water and/or wine. This one could add small amounts of alcohol and tannins to the ink. Gall extracts were obtained either by cold maceration or by boiling. Heat could be used to separately dissolve the components, and/or in a second step when the extracts and solutions were mixed together. A third very useful option was to warm the ink after all components were mixed together in a vessel. Solubility of iron(II) sulfate is three times higher in hot (48,6 g / 100 ml) than in cold water (15,65g / 100 ml). Solubility of gallic acid in hot water (3,45 g / 100 ml) is three times higher than in cold (1,15 g / 100 ml), in alcohol nearly fifteen times higher than in cold water (16,67 g / 100 ml). The amount of tannins extracted increases with temperature. As a result, quality of ink depends not only on the ratio of each ingredient, but also on the procedure used.

The most ancient recipe consulted[1], found in a document from 1461, tells us the amount of each ingredient and describes the process used to make the ink.

- Gall-nuts 2 ounces
- Vitriol or copperas 2 ounces
- Gum arabic 1 ounce
- Absinthe a little
- Water 24 ounces

Procedure: Soak the previously crushed gall-nuts, the vitriol and the gum arabic separately, each in 8 ounces of water, for 24 hours. Then, a little absinthe

should be added to the gallnut extract. Boil this solution gently. All of the extracts should be filtered. Then the filtrates should be mixed together in a vessel and, finally, boiled for a short time. – The recipe stated that this procedure yields a good writing ink.

Commercial ferrous sulfate, also known as copperas, green vitriol, iron vitriol, *vitriolum romanum* ($FeSO_4 \cdot 7\ H_2O$, 82%), was the best quality according to the majority of recipes, due to its higher purity. Many recipes detail that only the pure light green crystals can be used, and that the yellow-brown powder has to be rejected. Some recipes mention also blue vitriol ($CuSO_4$) or even rock alum. Other metallic cations can be found as impurities in natural vitriols (Fe^{3+}, Zn^{2+}, Mg^{2+})[3].

Gallotannins are the second essential ingredient of inks. They are found especially in Aleppo gallnuts gathered from the leaves of *Quercus infectoria*. Gallotannins are complex mixtures containing esters of glucose and digallic acid (mainly penta digalloyl glucose)[4]. Hydrolysis of these extracts yields gallic acid (3,4,5-trihydroxybenzoic acid).

Gum arabic is the third essential ingredient. It is an excretion of the bark of certain trees (*Acacia senegal, L.*). This polysaccharide contains units of (-)arabinose, (+)galactose, (-)rhamnose and (+)glucuronic acid. Its molecular weight ranges from 240.000 to 580.000, and acts as a protective colloid and thickener to prevent precipitation of the water insoluble blue-black ferrotannate complexes. Arabinofuranose hydrolyzes much more rapidly than pyranoside analogues[5], and further condensation to furfural derivatives, helps ink darkening.

Experimental

Laboratory ink

Two series of eight inks were prepared (A and B). The inks were grouped into four pairs with different ratios of iron-gallic acid. The ideal, i.e. the complex formation ratio would be 0,672 (molecular weight of gallic acid / molecular weight of ferrous sulfate). The second member of each pair contains gum arabic.

The A series was prepared with pure $FeSO_4 \cdot 7\ H_2O$, choosing the pale-green crystals and rejecting the yellow grains, which tend to contain Fe(III) ions as an impurity. Molecular weight 280,02, Fe 20,04 %.

The B series was prepared with ferrous sulfate oven-dried, and non-crystalline. Its orange colour denotes that it contains ferric ions as a result of air oxidation. Molecular weight is unknown, but determination of the total iron by standard methods gave a result of 22,4% Fe.

Table 1: Composition of inks, A series: Inks prepared with $FeSO_4\ H_2O$ (20,05% Fe)

	Gallic acid		$FeSO_4$		Gum arabic	Molar ratio	pH
	mg	mmol	mg	mmol	mg	Gallic acid / Fe	
1	0,0	0,000	200	0,714	0	0,000	3,7
2	0,0	0,000	200	0,714	500	0,000	4,0
3	0,5	0,003	220	0,786	0	0,003	3,4
4	0,5	0,003	220	0,786	500	0,000	3,9
5	5,5	0,029	22	0,079	0	0,372	3,1
6	5,5	0,029	22	0,079	500	0,372	3,1
7	11,0	0,058	220	0,786	0	0,074	2,8
8	11,0	0,058	220	0,786	500	0,074	3,5

Table 2: Composition of inks, B series: Inks prepared with $FeSO_4\ H_2O$ (22,4% Fe)

	Gallic acid		$FeSO_4$		Gum arabic	Molar ratio	pH
	mg	mmol	mg	mmol	mg	Gallic acid / Fe	
1	0,0	0,000	200	0,802	0	0,000	2,5
2	0,0	0,000	220	0,882	550	0,000	2,6
3	0,5	0,003	220	0,882	0	0,003	2,7
4	0,5	0,003	220	0,882	550	0,003	2,9
5	5,5	0,029	22	0,088	0	0,331	3,4
6	5,5	0,029	22	0,088	550	0,331	3,5
7	11,0	0,058	220	0,882	0	0,066	3,1
8	11,0	0,058	220	0,882	550	0,066	3,2

The other ingredients used were pure gallic acid ($C_7H_6O_5 \cdot H_2O$, molecular weight 188,14) and gum arabic powder.

Gallic acid was dissolved in water and diluted to 0,05 – 0,5 – 5 mg/ml. Amounts of $FeSO_4 \cdot 7\ H_2O$ for the A series and of impure iron sulfate for the B series: 220 mg – 200 mg – 20 mg. Aqueous solution of gum arabic: 110 mg/ml. The three ingredients were mixed to a final volume of 10 ml. The amounts present per 10 ml of each ink are listed in Table 1 and 2.

Each ink was applied with a brush to a uniform spot of about 4 cm in diameter on Whatman filter paper. Sheets were stored at 70°C and 35% RH for 7 and 27 days respectively.

Colour measurement

In spite of the fact that colours are sensory impressions of the mind, a quantitative description of them is necessary for their scientific investigation. In our particular case, the study of colours produced on a sheet of paper by the presence of

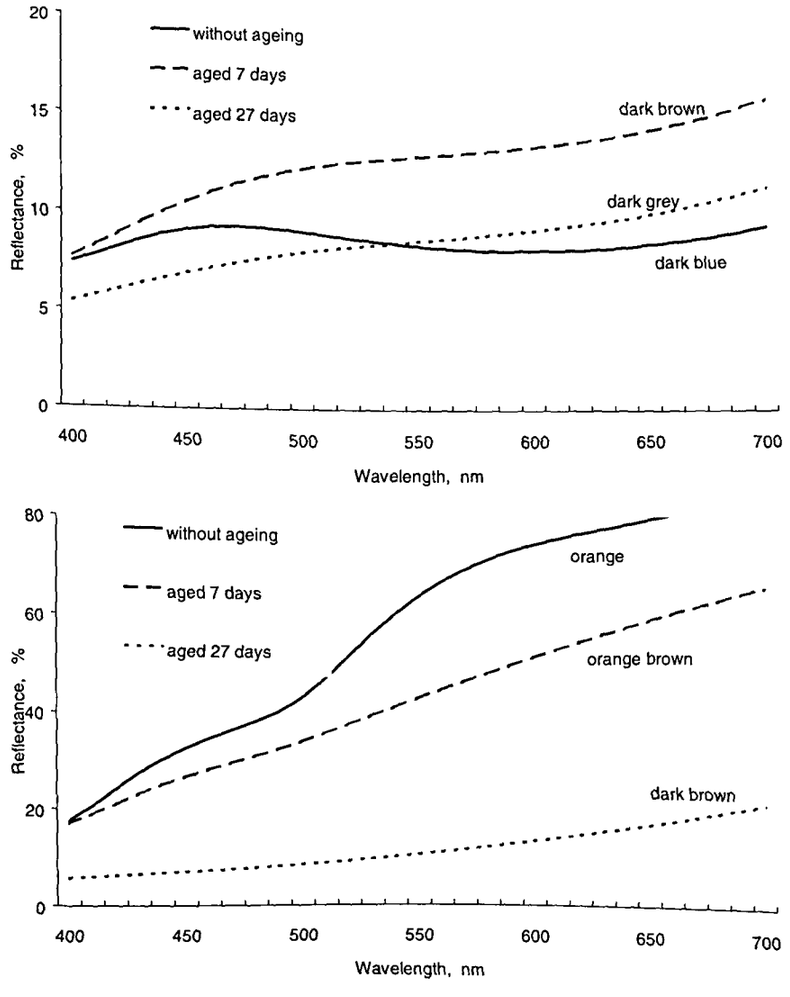


Fig. 1: Reflectance spectra of ink spots before and after ageing. Top: Ink no.5 (blue); iron-gallic complex. Bottom: Ink 2 (orange); only $FeSO_4$ (+ Fe_2O_3 hydrated)

several complex chromophoric structures, mainly insoluble, that is, of pigment type, made it necessary to measure colours directly by reflection, i.e., by measuring the light reflected by the coloured surface (reflectance) as a function of

Table 3: CIELAB coordinates (D65-10°) of the A series.

	unaged			aged 7 days			aged 27 days				
Ink n°	L	a	b	L	a	b	L	a	b	ΔE_1*	ΔE_2**
1	90,8	1,2	14,9	86,1	3,2	18,1	65,2	5,3	14,6	6,0	25,9
2	87,2	2,0	17,5	75,7	4,1	17,2	49,0	6,2	13,8	11,7	38,6
3	86,6	1,4	12,9	84,3	3,2	17,5	64,2	5,1	14,8	5,4	22,7
4	83,8	1,7	15,8	74,5	4,3	17,3	49,7	6,3	14,2	9,7	34,4
5	75,5	1,4	-3,8	78,1	1,2	2,9	77,9	3,0	9,7	7,2	13,8
6	74,6	1,1	-3,1	74,8	0,9	2,1	71,3	2,0	7,2	5,2	10,8
7	63,7	0,7	-4,5	66,1	0,7	3,3	57,3	4,4	11,8	8,2	17,9
8	62,6	0,7	-2,7	61,7	0,7	5,0	45,8	4,7	11,0	7,7	22,1

* aged 7 days vs unaged

** aged 27 days vs unaged

wavelength (400–700 nm). This is performed by using a spectrophotometer which illuminates the sample with a diffuse white illumination, imitating CIE standard illuminant D65: actual daylight, and measures the reflectance values relative to a reference white (cf. Fig. 1). The reflectance spectrum contains all the physical information about colour, but it is necessary to take into account two more elements in colour perception: illuminant and observer.

Reflectance data are used to calculate colorimetric CIE X,Y,Z values. The basis of the CIE System[6] is the fact that light reflected from any coloured surface can be visually matched by an additive mixture of red, green and blue lights in suitable amounts of each, called X, Y, Z tristimulus values. These values, which describe exactly any colour, can be derived from the percentage reflectance data at each wavelength by using the CIE standard methods. Today the so-called CIE Lab system is accepted as a universal standard. A simple mathematical formula transforms X, Y and Z values into three orthogonal coordinates L (lightness: vertical axis), a (red-green axis), and b (yellow-blue axis). The corresponding polar coordinates are $C = (a^2 + b^2)^{1/2}$ (chroma) and $H = \text{atan}(b/a)$ (hue angle).

The ink spots were measured with a *Spectraflash 300* spectrophotometer (*Datacolor*). Different calculated parameters were presented by the software included[7]. We only include in Tables 3 and 4 the CIE Lab coordinates for the D65-10° standard illuminant – observer combination. The last two columns of Tables 3 and 4 include also total colour difference ΔE. ΔE_1 means difference between "aged 7 days" and "not aged". ΔE_2 means difference between "aged 27 days" and "not aged". CIELAB colour difference is defined as follows:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

Table 4: CIELAB coordinates (D65-10°) of the B series.

	unaged			aged 7 days			aged 27 days				
Ink n°	L	a	b	L	a	b	L	a	b	ΔE_1*	ΔE_2**
1	76,2	15,2	45,1	68,9	10,2	28,3	58,9	9,5	27,7	19,0	25,2
2	82,1	6,4	31,9	71,6	5,9	21,7	39,3	6,1	12,0	15,0	47,6
3	60,9	21,7	46,7	52,6	15,0	33,8	60,9	6,9	19,0	16,7	31,5
4	73,2	9,7	38,2	55,7	5,8	22,0	41,8	8,4	17,7	24,2	37,5
5	42,8	-1,3	-1,2	44,8	-0,5	6,2	44,6	2,9	12,3	7,7	14,2
6	37,7	1,2	-4,5	37,9	0,9	-1,2	38,0	2,1	4,9	3,4	9,5
7	51,3	2,0	13,8	56,1	2,4	14,4	52,3	4,9	16,1	4,9	3,9
8	67,2	3,0	19,1	59,8	5,6	20,2	43,8	6,1	13,4	7,9	24,3

* aged 7 days vs unaged

** aged 27 days vs unaged

RESULTS

Changes in lightness

Inks with high iron content (1,2,3,4,7,8) show a stronger darkening after ageing than those having a gallic/iron ratio closer to the complex formation ratio (cf. p. xy) (ink 5 and 6). Both the A series and the B series show the same behaviour. The B inks are always darker than their respective A inks.

Presence of gum arabic causes some darkening in the course of accelerated ageing, which is clearly stated by comparing the decrease of lightness of the second members of each pair (2,4,6,8) against the decrease of lightness of the first members, without gum (1,3,5,7). This behaviour is more clearly marked after prolonged ageing (cf. Fig. 2).

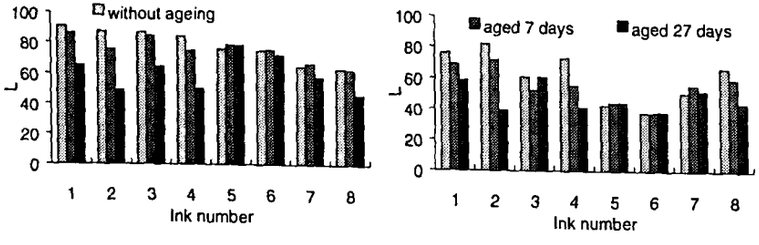


Fig. 2: Changes in lightness; left: A series (inks with Fe(II); right: B series (inks with Fe(II) and Fe(III).

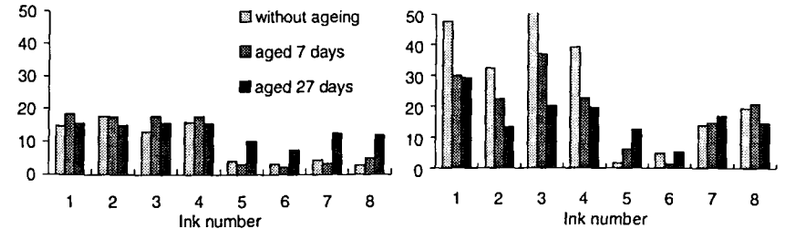


Fig. 3: Change in chroma; left: A series (inks with Fe(II); right: B series (inks with Fe(II) and Fe(III).

Changes in chroma

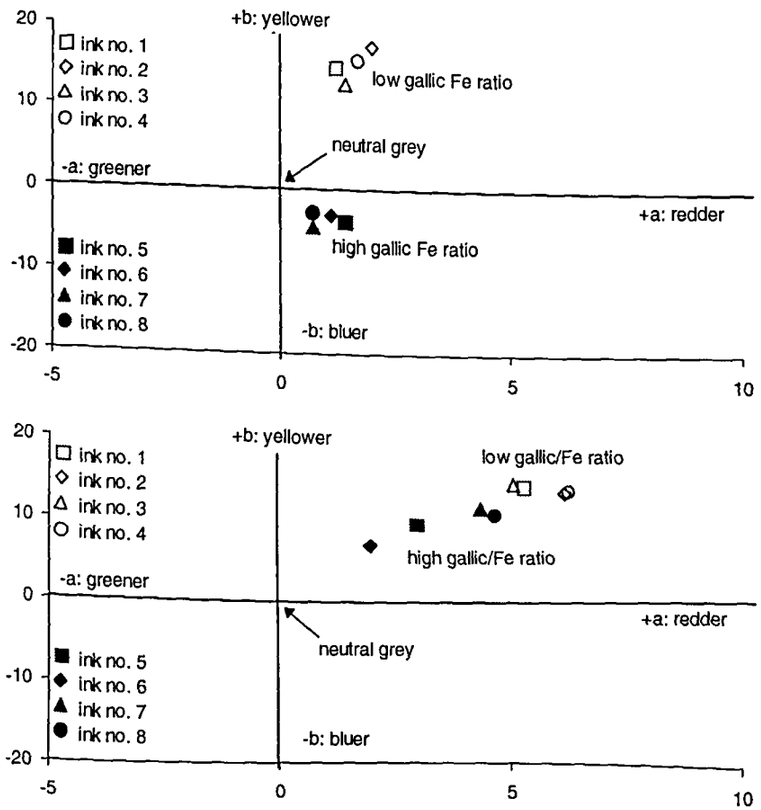
The A series shows overall low values of chroma (pale yellow to neutral or bluish grey shades) compared with the B series, because Fe(II) salts are less coloured than Fe(III) salts. The B series, especially 1, 2, 3, and 4, with low gallic content, shows initial bright orange shades, due to hydrated ferric oxide, but become duller (less saturated) due to the masking by the dark brown degradation compounds produced in the paper after ageing. In the B series chroma decreases in spots 1,2,3,4, but it increases in 5 and 7 (after the prolonged ageing also in 6), because the greyish initial shades turn brown and more chromatic. (See Fig. 3).

Changes in hue

CIELAB plane diagrams clearly show changes in hue. Inks with a higher gallic/iron ratio (5,6,7,8) have initially grey and blue shades (-b +a) and spots with an excess of iron (1,2,3,4) are yellow to orange (+a +b). Ageing approaches the two initial separated areas of hue, so the final hues of all aged spots fall in the area of browns, located in the quadrant +a +b. (Cf. Fig. 4).

Substrate degradation

Strong corrosion of cellulosic substrate is observed in the spots submitted to ageing. In the A series, visible corrosion is noticed only in the darkest spots: 8 and 7. Aged spots of the B series are more corroded than those of A series. The samples are now stored in the dark for further investigations.



g. 4: CIELab diagrams of the A series test inks, unaged (top) and after 27 days of accelered ageing (below).

Discussion

Influence of iron gallic ink. Colour of the complex and its changes during ageing

It is known that diluted solutions of commercial tannic acid (gallotannin) forms with ferric ion blue colours at acidic pH range. A diluted solution, pH 4, of the 1:1 complex iron-gallic acid shows an absorbance maximum at 620 nm. This dark blue colour of Fe-gallic complex is explained[3] by the charge transfer from the aromatic nuclei in gallic molecule (I) to the Fe(III) central ion, thus generating a conjugated double bond system responsible for energy absorption in the visible range (cf. Fig. 6: II → III). As it has been colorimetrically checked above,

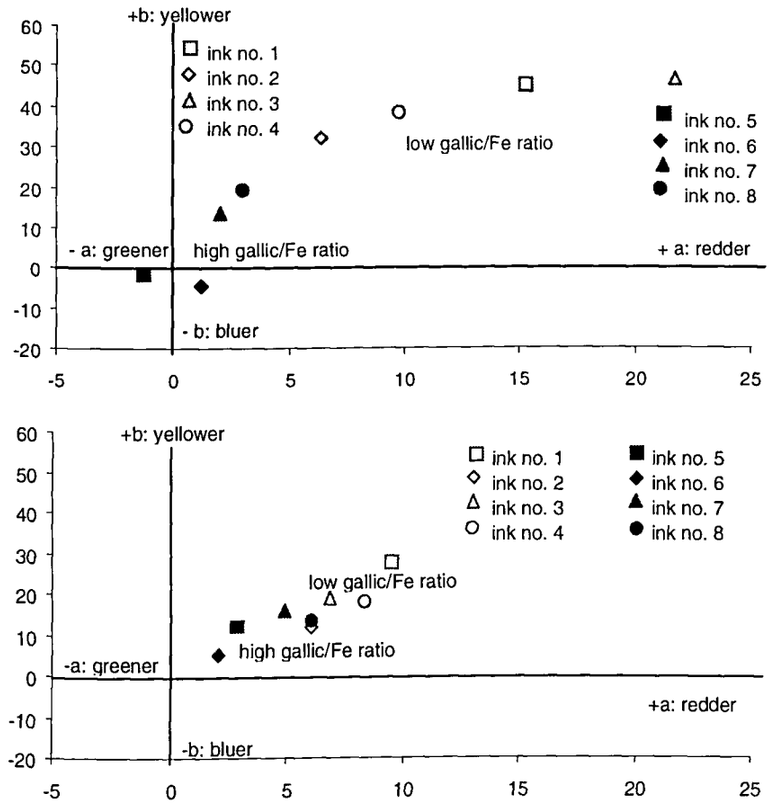


Fig. 5: CIELab diagrams of the B series test inks, unaged (top) and after 27 days of accelerated ageing (below).

this blue shade changes to dark brown or black. In our case, accelerated ageing at 70°C and 35% RH contributes to an increase in acidity under the ink spot, so the complex becomes unstable. Decomposition of the initial blue complex gives brown coloured quinone structures. Up to now, any interaction with cellulose has been taken into account.

Another possible explanation is that the iron-gallic acid complex, together with hydrogen peroxide, constitutes a redox system similar to that proposed by Hamilton in his explanation of the radical hydroxylation of aromatics[8, 9]. The peroxide activated compound (Fig. 6: IV) loses water and is transformed into a quinone-like structure (Fig. 6: V) capable of abstracting hydrogens from cellu-

lose (VI) yielding radicals (VII). These radicals finally become oxidized cellulose, containing chromophoric carbonyl groups (VIII). In this redox system active radicals are continuously generated by the interaction between iron, gallic acid, cellulose and peroxides (see Fig. 6). We call this hypothesis *Fenton-Hamilton mechanism.*

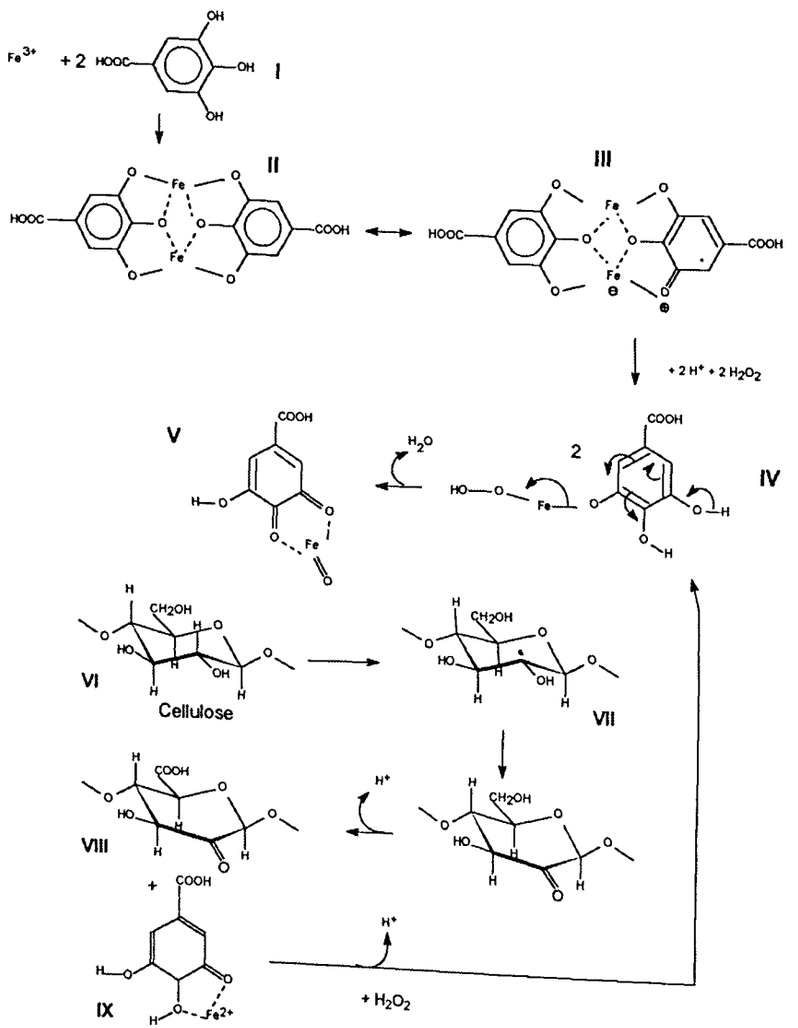


Fig. 6: Suggested mechanism for the reaction between iron-gallic complex and cellulose

Another hypothesis we suggest relates the observed changes of colour to the polyphenol structures of gallotannates: Organic autoxidation[10] means slow oxidation by free oxygen (of air) at moderate temperatures. Catalysts such as metallic oxides and organic peroxides initiate this. Autoxidation can be inhibited by phenols and other oxidizable compounds present in vegetal tissues.

A simple scheme of autoxidation radical processes is:

- Catalyst → R· initiation of chain
- R· + O_2 → R-O-O· propagation of chain
- R-O-O· + R-H → R-O-O-H + R·
- 2 R-O-O· → products, X
- R· + R-O-O· → products, Y termination of chain
- 2R· → products, Z

Radicals formed by autoxidation can be captured by polyphenolic compounds like gallic acid and its derivatives, which are oxidized to compounds of quinonoid structure. If a large enough amount of polyphenols is available, organic matter R-H is protected against autoxidation. But since polyphenolic antioxidants can be exhausted (read destruction of iron-gallic complex), the autoxidation processes can further continue, accelerated by free ferrous and ferric ions.

Quinones formed by oxidation, when they are irradiated by light, are converted into oxygenated diradicals, which are able to absorb hydrogens from any kind of substrate. Reaction of oxygen and semiquinone radicals and alcoholic groups leads to the formation of hydrogen peroxide. This reaffirms also the Fenton's hypothesis.

All these reactions proceed slowly at room temperature, but are accelerated in the climatic chamber.

Colours due to degradation products of cellulose and gum arabic caused by oxidation and hydrolysis: Fenton's mechanism

Previous studies[11, 12] noted that many of the ancient recipes of irongall inks contain much more Fe(II) sulfate than needed. Not all the iron excess is Fe(III). Some Fe(II) ions are present in spite of oxidation processes, due to reducing species on the paper. Cellulose corrosion is thus explained by a mechanism similar to that explained for Fenton's reagent[13] (ferrous sulfate plus hydrogen peroxide) in pulp bleaching[14]. Some hydrogen peroxide is produced in situ by autoxidation in presence of Fe(II) via a radical mechanism. Fenton's reagent produces very

reactive hydroxyl radicals[15, 16], which oxidize hydroxyl groups of cellulose[17] and of gum arabic into carbonyl (cf. Fig. 7).

It is known that ·OH radicals attack cellulose in a non-selective way, so the following processes are possible:

- hydrolytic cleavage in carbon C1, with subsequent oxidation of the remaining aldehyde group to carboxyl, giving gluconic acids;
- hydrolytic cleavage in carbon C4 giving glucoside fragments,
- oxidation of carbons C2, C3, to give keto groups,
- oxidation of C^6 to give aldehyde groups and then to glucuronic acids.

This has been shown[18] in analyzing the degradation products of methyl β-D-glucopyranoside, a model compound of cellulose, oxidized with Fenton's reagent. The residual oxidized cellulose and other fragments from hydrolysis tend to degrade more readily by heat and acids than the initial cellulose.

By the same Hamilton reagent mentioned above[9], carboxylic groups from previously oxidized cellulose can change to peroxy acids[19]. These peroxyacids yield more ·OH radicals, which contributes to increase the number of carbonyl groups in cellulose.

Many of the oxidation processes already described begin, continue and stop by radical mechanisms, but it is also true that paper spotted with iron-gall ink in a wet atmosphere is an aqueous system. Therefore cellulose must withstand an acidic environment. At high temperatures, dehydration reactions on protonated hydroxyl groups from glucose and other monosaccharides are possible, giving

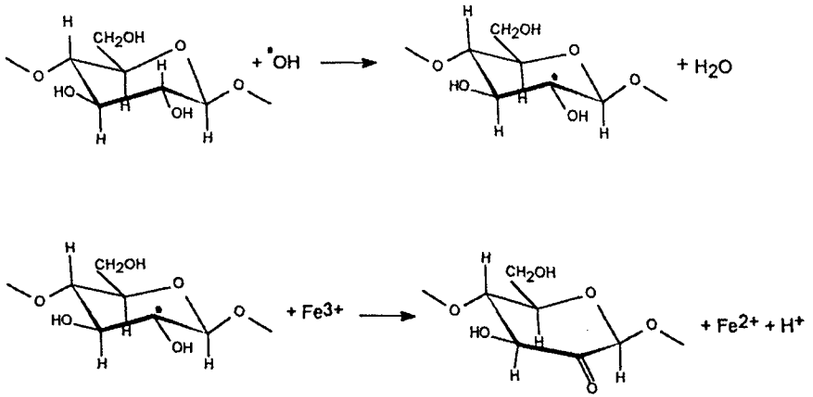


Fig. 7: Formation of carbonyl groups in cellulose by oxidation with OH radicals, supplied by Fenton's reagent.

furfural derivatives[14], compounds of aldehydic nature which tend to condense giving dark coloured products (cf. Fig. 8).

CONCLUSIONS

- Ferrous and ferric ions yield different initial colour to the ink, but final colours are quite similar, showing that new chromophoric groups appear in cellulose by their catalytic influence.
- Blue colour of ink (iron-gallic complex) changes to brown and black after ageing. Browning and darkening can be caused by oxidation of ink components, giving quinonoid structures, and also by degradation products of cellulose and/or gum arabic.
- Since arabinose units oxidize more readily than glucose, inks containing gum arabic always become darker than those prepared without it.
- Spots of inks containing gum arabic are more uniform due to the better ink stabilization. This fact can also increase their darker appearance.
- Changes in colour can be accurately studied by reflectance spectrometry, so that quantitative information can be correlated with chemical hypothesis.
- The main hypothesis in order to explain colour, its changes, and cellulose degradation are:

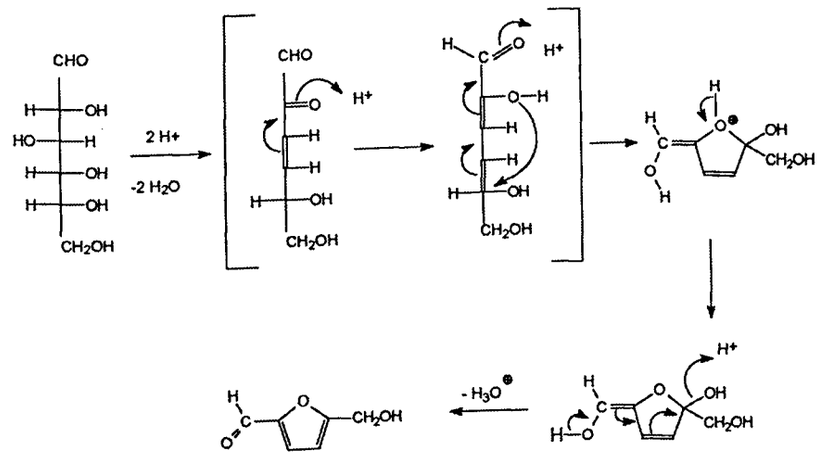


Fig. 8: Formation of 5-(hydroxymethyl)-2-furaldehyde by acid-catalyzed condensation of glucose (•-D-glucopyranose).

- Autoxidation of cellulose with atmospheric oxygen, catalyzed with Fe^{2+} and Fe^{3+} ions, with formation of reactive intermediates, such as peroxides, hydroperoxides and radicals.
- Autoxidation of gallotannates with atmospheric oxygen and other oxidants present gives quinones susceptible to photochemical activation.
- Fenton's reaction, between Fe^{2+} and hydrogen peroxide formed by autoxidation, with formation of very active hydroxyl radicals.
- Oxidation of cellulose by hydroxyl radicals, with formation of carbonyl and carboxyl groups.
- Fenton-Hamilton mechanism explaining the role of iron-gallic complex as the hydroxyl radical conveyor in cellulose oxidation.
- Acid hydrolysis of cellulose and acid condensation of hydrolytic fragments.
- Some of the hypothesis proposed need to be confirmed experimentally in further studies, by means of analytical analysis of ink degraded paper. Other hypotheses are well sustained by numerous bibliographic data.

Acknowledgements

This work has been carried out as part of the project PETRI 95-0081-OP financially supported by the *Comisión Interministerial de Ciencia y Tecnología (CICYT)* of the Government of Spain. We thank also Mrs. Janet Coulomb for the revision of text.

Summaries

Ageing of Laboratory Irongall Inks Studied by Reflectance Spectrometry

This study tackles changes in colour of irongall inks over time. Different chemical processes, in which ink composition has a major influence, cause colour change. Two series of inks were prepared, one using ferrous sulfate partially oxidized, and another using pure ferrous sulfate heptahydrated; pure gallic acid and gum arabic. The inks were applied on Whatman filter paper, and then aged in a climatic chamber.

The colour of ink spots was measured with a spectrophotometer. Changes in lightness, chroma and hue were related with ink composition. All inks become darker and browner after ageing, including those not containing gallic acid. Inks prepared with an iron/gallic ratio nearer to that needed for the complex formation are the darkest ones initially and show the slightest change in colour. Gum arabic containing inks darken more than inks without it. Strong corrosion was observed in the aged dark spots.

Le vieillissement de l'encre gallique ferrée étudié sur des échantillons de laboratoire au moyen de la spectrométrie de réflexion

Cette étude traite du changement de la couleur des encres galliques ferrées qui intervient à long terme ou après la procédure du vieillissement accéléré. Ce sont divers processus chimiques dépendant fortement de la composition de l'encre qui sont responsables du changement de la couleur. On a préparé deux groupes d'échantillons d'encre, l'un utilisant du sulfate de fer partiellement oxydé, et l'autre utilisant du sulfate de fer pur heptahydraté, de l'acide gallique pur et de la gomme arabique. On a appliqué ces échantillons d'encre sur du papier filtre de Whatman et ensuite on les a soumis au vieillissement accéléré dans une pièce climatisée.

On a mesuré la couleur des taches d'encre à l'aide d'un spectrophotomètre. Les modifications intervenues dans la clarté, le ton et l'intensité de la couleur ont été analysées en fonction de la composition de l'encre. Toutes les encres deviennent plus foncées, plus brunes après le vieillissement, même celles qui ne contiennent pas d'acide gallique. Les encres dont le rapport des constituants en fer et en acide gallique est proche du rapport aliquote requis pour la formation du complexe sont les plus foncées dès leur fabrication et présentent lors du vieillissement le changement de couleur le plus léger. Les encres contenant de la gomme arabique foncent davantage que celles qui en sont dépourvues. On a observé que lors du vieillissement les taches d'encre foncées causaient une forte dégradation de la substance du papier.

Die Alterung Eisengallustinte im Lichte der Reflexionsspektrometrie, untersucht anhand von Laborproben

Es wurde die Farbveränderung untersucht, die nach längerer Zeit bzw. bei beschleunigter Alterung an Eisengallustinte auftritt. Die Ursache hierfür sind verschiedene chemische Prozesse, deren Ablauf stark von der Zusammensetzung der Tinte abhängt. Es wurden Probetinten aus Eisensulfat, reiner Gallussäure und Gummi arabicum angefertigt, und zwar in zwei Gruppen: die eine mit teilweise oxidiertem (Fe[II/III]), die andere mit reinem Eisensulfat (Fe[II]). Die Tinten wurden auf Whatman Filtrierpapier aufgestrichen und dann beschleunigt gealtert.

Die Farbe der Tintenaufstriche wurden spektrophotometrisch gemessen. Veränderungen in Helligkeit, Farbton und -intensität wurden in Bezug die Tintenzusammensetzung untersucht. Alle Tinten werden im Laufe der Alterung dunkler und stärker braun, auch die, welche keine Gallussäure enthalten. Tinten, in denen das Verhältnis der Eisen- und der Gallussäurekomponente nahe bei dem für die Komplexbildung notwendigen aliquoten Verhältnis liegt, sind gleich nach der Herstellung am dunkelsten und zeigen bei der Alterung die geringste Farbveränderung. Gummi arabicum verstärkt das Dunklerwerden. Bei der Alterung bewirkten die dunkelfarbigen Tintenaufstriche starke Zersetzung der Papiersubstanz.

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Ink Corrosion
Aqueous and Non-Aqueous Treatment of Paper Objects – State of the Art

by BIRGIT REISSLAND

INTRODUCTION

A questionnaire sent to paper conservation studios all over the world by van Gulik and Kersten Pampiglione[1] and a recent opinion poll of Dutch paper conservators, clearly demonstrated that paper conservators are still uncertain about which treatment they should apply to treat ink corrosion. This might be due to the fact that unsatisfactory results were obtained from previous and existing treatments, and that the degradation process is chemically complicated and still under investigation. However, the main factors causing ink decay are now known. In light of this theoretical knowledge the efficacy of current conservation practices can be re-assessed.

Preventive conservation plays a key role in delaying further decay. When active conservation measures are indeed necessary, ink-corroded artifacts present the conservator with two main tasks: first, the degradation process caused by sulphuric acid and iron(II)ions must be arrested, and secondly mechanical strengthening of the degraded support is required.

This article will focus on aqueous and non-aqueous treatments commonly used to retard ink corrosion. The positive influences of these treatments and their risks will be discussed based on the results of previously published studies and on the author's practical experiences.

DEGRADATION PROCESS

Ink corrosion is caused by the degradative effect of the applied media on the support material. In order to select a treatment for an ink-corroded object it is essential to understand the chemical degradation process. Recent investigation[2] proved, once again, that iron-gall inks containing surplus iron(II)sulphate accelerate cellulose degradation[3]. In principle two main degradation processes are in-

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Fig. 1: Detail of a document (18th cent.) damaged by corrosive ink.

volved; hydrolysis (catalyzed by acid) and oxidation (rapidly catalyzed by transition metal ions such as iron(II)ions). Both reactions result in the increased decay of cellulose[4,5]. In addition, oxidation also causes discoloration of the support material: First the paper starts to fluoresce under UV; increased degradation causes brown discoloration*. To arrest the degradation process, both chemical reactions have to be blocked. It must be emphasized that ink corrosion will continue if the catalytic activity of free iron(II) and iron(III)ions as well as acid is not stopped completely.

Treatments used for ink corrosion – Overview

All active treatments cause irreversible changes to the original substance. A comparison of the perceived benefits and the possible risks for the object is always advisable. In the case of ink corrosion, the conservator is confronted with the decision to use either an aqueous or a non-aqueous treatment. Major advantages and disadvantages depend on the solvent used (water or organic solvent). In the

* Based on visual assessment, a condition rating system was developed in order to facilitate decision-making concerning conservation measures.

case of ink corrosion, both reactive components (iron(II)ions and acid) are water soluble. The influences of described treatment methods on the degradation process will be outlined and the risks and benefits of each are summarized.

Aqueous treatments

Aqueous treatments are commonly used methods in paper conservation. Their positive influences on aged papers are well-known. Water-soluble products are washed out, the fibre-to-fibre bonding is reactivated and the papers appear more flexible. Aqueous treatment of bound artifacts is usually only possible if the leaves are separated.

For ink-corroded artifacts, paper conservators often hesitate to use aqueous treatments. This is quite reasonable, as several disadvantages must be considered. Alterations in the appearance of the support and the media may occur. The change in paper tone might alter the contrast between the ink and the support. Water-soluble ink compounds dissolve during aqueous treatment ("bleeding") and may cause brown discoloration of the surrounding areas. Some soluble compounds might fluoresce and can therefore be detected. However, some might not be visible, for example in the case of water-soluble iron(II)ions. The undetected iron(II)ions migrating within the paper, may allow degradation to spread throughout the whole artifact. Water penetration properties vary with the extent of paper degradation: dark brown discoloured areas are hydrophobic, light brown discoloured or fluorescing areas are hydrophilic. Due to variations in the water absorption tensions are created, degraded cellulose breaks and loss of substance might occur[6,7].

Aqueous treatments involve water, mixtures of water and alcohol, aqueous deacidification methods, chelating agents and ammonium caseinate (cf. Fig. 2).

Water

Many paper conservators prefer to treat the ink corroded artifact in water prior to aqueous deacidification treatments. Washing in water will remove many soluble compounds, but the degradation process will only be inhibited, if all the iron ions are inactivated or removed, and all the acid is neutralized.

Distilled/demineralized water

Purified waters are more effective at dissolving water-soluble products like iron(II)ions than solutions containing salts. However, they also remove the alka-

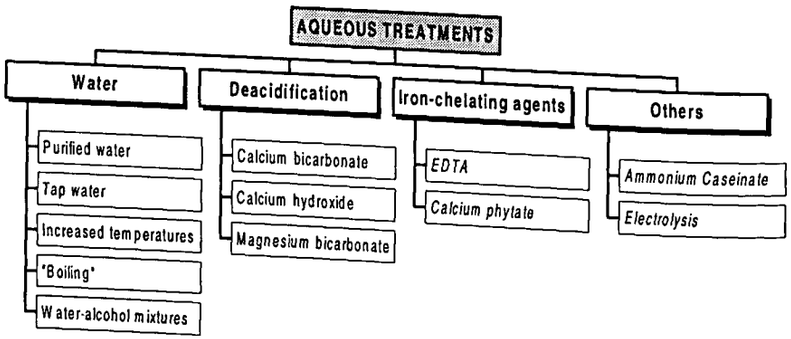

Fig. 2: Overview of aqueous treatments commonly used or proposed in the case of ink corrosion

line reserve that paper naturally contains, decreasing its natural protection against acid-catalyzed hydrolysis[8].

Brannahl[9] investigated the influence of water of different quality on original ink-corroded papers. From pH measurements he concluded that demineralized water removed acid. Heller et al.[10] determined a decrease in the iron(II)ion content of papers and inks. Kolbe[11] noticed an increased 'bleeding' effect using demineralized water in comparison to salt-containing aqueous solutions on original.

- Benefit: considerable dissolving properties
- Risk: increased bleeding of inks, removal of alkaline reserve

Tap water

Tap water contains salts and other contaminants. Therefore it will dissolve a smaller number of compounds. Its calcium carbonate content can protect the paper against loss of its natural alkaline reserve. However, contaminants such as chlorine, iron and copper ions could accelerate the degradation process. Testing the effects of wash water quality on the ageing characteristics of paper, Tang and Jones[8] achieved best results using Washington tap water. However, the variability and unreliability of tap water qualities prevented them from recommending it as the preferred type for aqueous treatments.

- Benefit: increased calcium-carbonate content, less "bleeding" than with demine-ralized water.
- Risk: contaminants can accelerate degradation.

Increased temperatures

In 1996 research was carried out in Göttingen, Germany, to determine the influence of a temperature increase on immersed iron-gall ink written manuscripts. The manuscripts were immersed at room temperature and at 35°C for 20 minutes. After drying, neither the surface pH nor the appearance of the inks and papers differed. It was concluded that an increase in temperature had no significant influence on the washing property[12].

"Boiling"

A more controversially discussed method involves the treatment of ink-corroded papers in boiling water. One of the first studios to apply this method was the Vatican library in Rome. Nowadays the "boiling" method is internationally used in several conservation studios.

Investigation of this method resulted in contradictory results. Brannahl[9] obtained a negative influence on iron-gall inks and the paper as *strong tears and blurring out of ink particles* were observed. In contrast, Heller et al.[11] stated that *the ink during the boiling-process occasionally is bleeding less than in cold water* and the paper showed a remarkable increase in flexibility. A temperature increase will accelerate the rate of chemical reactions and causes an increase of solubilities (except that of calcium carbonate). Consequently, the dissolution of soluble compounds will be enhanced and exaggerated movement of molecules occurs. The latter might lead to destruction of crystalline structures as a result of which brittle areas become more flexible after treatment. Investigations carried out by Biggs[13] on historical hand-made laid papers proved that the folding endurance increased after "boiling" treatments of different duration. The best results were obtained after 15 minutes immersion at ca. 100°C. The boiling process is always accompanied with conspicuous water movement. Protection of objects (e.g. Hollitex-envelopes) is therefore essential. The authors' preliminary experiences have shown that shrinkage of treated objects occurs. The influence of higher temperatures on the gelatine surface size is as yet, undetermined.

- Benefit: reaction time speeds up, increased solubility, increased paper flexibility, faster drying.
- Risk: reaction time speeds up, increased solubility, change in object dimensions, loss of substance caused by water movement.

Water-alcohol mixtures (ethanol, isopropanol)

Due to its surface-active properties, the addition of alcohol causes better wettability of hydrophobic, highly ink-corroded areas, and limits the access of water.

Alcohol appears to limit paper swelling. In addition the penetration is more homogeneous and the drying process is faster. Moreover, the migration of water soluble ink compounds is reduced. Recent investigations[14] have shown that the higher the ethanol content of the used aqueous solution, the more water-soluble iron(II)ions remain in the paper, risking continued degradation.

As inks from the 18th century onwards might contain alcohol-soluble dyes (e.g. aniline dyes), testing of alcohol soluble compounds is necessary.

- Benefit: excellent penetration, short drying process.
- Risk: iron(II)ions remain in the paper, alcohol-soluble dyes dissolve.

Aqueous deacidification

In the case of ink corrosion, acid hydrolysis is caused by sulphuric acid. To delay further degradation, the acid has to be neutralized so that its catalytic effect is inhibited. This is possible by applying deacidification solutions. Additionally, this procedure allows precipitation of an alkaline reserve, realising a long-term protection against acid catalyzed hydrolysis.

By using Russel photography, Daniels[15] proved that some deacidification agents (e.g. sodium bicarbonate, barium hydroxide and calcium hydroxide) were effective antioxidants to inhibit autoxidation of different papers, while water washing produced no significant changes. Anyway, a single deacidification treatment is not sufficient to prevent ink corrosion because the iron(II) catalyzed oxidation is only blocked temporarily[3, 16]. During the deacidification process, the reactive iron(II)ions are oxidized to water-insoluble iron(III)oxydhydrate (rust). Iron(III)ions can not catalyze oxidation. However, iron(III)ions are reduced to reactive iron(II)ions under conditions present in degraded papers (reducing endgroups on the cellulose produced by acid hydrolysis).

It seems that the ink complex is decomposed under highly alkaline, as well as acid, conditions[17]. To avoid changes in ink colour, the pH range during and after the treatment should be adjusted to between pH ca. 5.0–8.5.

Calcium bicarbonate

Well preserved historical papers include a high calcium-carbonate content, a "natural" alkaline reserve. Under room conditions calcium carbonate has a low solubility in water (0.06 g/l)[16]. This can be increased to a maximum value of 1.086 g/l, if carbon dioxide is added. When the solution is saturated with CO_2, its pH decreases to a value of 5.88. The situation inside the paper changes during treatment and especially during the drying process. This behaviour is often underestimated. During drying of the object, the pH increases to a maximum of 8.1 (CO_2 evaporation), surplus calcium carbonate or calcium sulphate are precipitated. In opposite to inks and papers deacidified with magnesium bicarbonate solutions, those deacidified with calcium bicarbonate distinctly have less changed ink-colour after treatment and paper-colour after artificial ageing[18].

- Benefit: no colour change of inks and papers.
- Risk: insufficient alkaline reserve.

Calcium hydroxide solutions

Calcium-hydroxide solutions often are used under the false assumption that the calcium content of the solution increases with highly alkaline pH values. In fact, the opposite occurs, at a pH level of 10.0, calcium hydroxide solutions contain the lowest calcium concentration in solution (pH 10 = 0.14 g/l). Moreover, fibres can swell under highly alkaline conditions. This may also change ink colour due to the initially high alkaline pH levels. Tensile strength determination by Sistach[19] resulted in better physical and mechanical properties of papers deacidified using a mixture of calcium/magnesium bicarbonate (5:1) in comparison to papers which were deacidified with calcium hydroxide (pH 10–12.34).

- Risk: colour change of inks and swelling of fibres because of highly alkaline pH-levels, no alkaline reserve.

Magnesium bicarbonate

Magnesium carbonate is more water-soluble than calcium carbonate, even at room temperature (0.93 g/l). Therefore, a significantly higher alkaline reserve can be precipitated in the paper. In an aqueous solution saturated with CO_2, 18.3 g of magnesium carbonate are dissolved per litre (mainly as bicarbonate). The pH of this solution is 7.07. After drying, the pH reaches a value of 9.9. Therefore, acid inks and papers have to sustain high pH variations.

On some occasions it was noted that magnesium inhibited the catalytic effect of transition metal ions during the oxidative bleaching process[20]. Nevertheless, it has to be considered, that this was tested only at high alkaline pH values (pH 12) during the pulping process. To what extent calcium salts will have such an effect is not known.

After artificial ageing, papers deacidified with magnesium bicarbonate showed a significant yellowing[18, 21]. This effect was not observed, or at least in a significantly smaller amount[22], with papers that were deacidified with calcium bicarbonate. The discoloration may be due to the highly alkaline pH levels that are

reached. Hey[23] also observed yellow brown "foxing" stains on magnesium bicarbonate deacidified papers after artificial ageing.

- Benefit: high content of alkaline reserve.
- Risk: changes in ink and paper colour due to alkaline pH levels.

Iron-chelating agents

If an iron gall ink contains excess iron(II)sulphate, not all of the iron ions are bound in the ink complex, but some remain in the paper as iron(II) or iron(III)ions. Iron(II)ions catalyze oxidation of the cellulose. Iron(III)ions may be reduced to iron(II)ions. One method used to prevent oxidation involves to complex the metal ions with a chelate. The chosen chelate has to fulfill the following criteria: its chelating property must be less strong than that of the tannins in the ink complex, it has to form a complex with iron(II) and iron(III)ions, and the colour of the reaction product must not disturb the aesthetic integrity of the artifact. However, even metal-ions bound in a complex might still catalyze cellulose oxidation. This depends on the chelate chosen. If a suitable chelate is used, iron(II) catalyzed oxidation is prevented. Excess chelate remains in the paper as an "antioxidant reserve", providing a long-term protection against oxidation. Acid catalyzed hydrolysis is only delayed.

EDTA (salts of ethylene diamine tetraacetic acid)

EDTA is a widely used chelating agent in conservation. It binds with both, iron(II) and iron(III)ions. Several investigations have shown that EDTA is not able to inhibit the oxidation process of cellulose. On the contrary: it can even be accelerated[20, 24, 25].

- Risk: oxidation increased.

Calcium phytate

Neevel[5] proposed the use of phytates as antioxidants to treat ink corrosion. Phytates, calcium salts of myo inositol hexakisphosphate, are natural antioxidants found in the seeds of plants. They are not detrimental to human health and are used by the food industry and medicine. Phytates are one of the few chelates that inhibit the iron(II) catalyzed oxidation of cellulose[26]. Additionally an "antioxidant reserve" is created by surplus calcium phytate that remains in the paper. Complexes formed with iron(II) and iron(III) ions are white. Recent investigations prove that ink corrosion is delayed to a remarkable extent if calcium phytate treatment is followed by a deacidification treatment using calcium bicarbonate[16]. Since the pH of calcium-phytate solution is acidic it has to be adjusted to pH 5.5–6.0 by the addition of ammonia. The use of calcium phytate in combination with calcium bicarbonate is simple and can be performed in any paper conservation studio[6, 7].

- Benefit: oxidation inhibited, long-term effect.
- Risk: precipitation of white crystals (iron phytate) on the surface.

Aqueous treatment using ammonium caseinate

A study to compare different treatments[25], proved that the application of ammonium caseinate treatments delayed ink corrosion. The mechanism is still under investigation. This treatment offers an interesting advantage in a mechanical reinforcement of friable objects. During the treatment high temperatures are reached (ca. 60°C). Probably caseinate, being a protein, offers complexing as well as neutralising properties. Artificial ageing caused browning of the paper comparable to browning caused by treatments using a saturated solution of magnesium bicarbonate[27]. The browning could be an effect of the Maillard reaction (reaction of carbohydrates and proteins).

- Benefit: mechanical strengthening.
- Risk: high temperatures during application (60°C).

Non-Aqueous Treatments

Since aqueous treatments bear the risk of spreading the ink-corrosion process, frequently the use of non-aqueous treatments is preferred. Furthermore aqueous treatments can often not be applied because of the presence of water-soluble media, or due to the binding structure of an artifact.

Non-aqueous methods have the advantage that water-soluble products are not dissolved and do not migrate within the paper. In addition, the swelling of paper fibres is minimized.

The benefits of non-aqueous treatments are accompanied by a number of disadvantages. It is not possible to remove degradation products. Neither an increase in flexibility nor a reorganisation of fibres is achieved. Friable brittle papers receive no mechanical reinforcement. Degradation products might be soluble to a certain extent in the organic solvent. Attention has to be drawn to the retention time of the solvent as well as its requirements concerning storage and health.

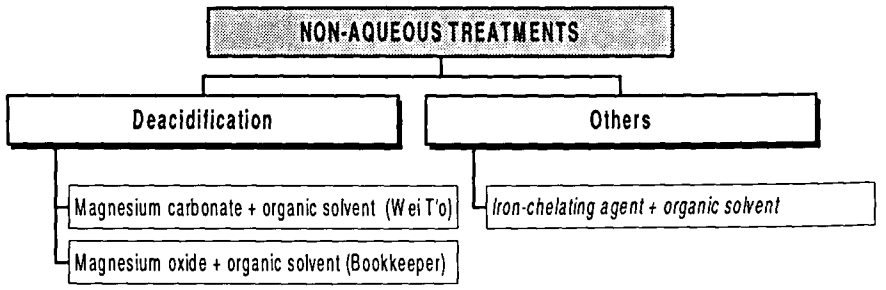

Fig. 3: Overview of non-aqueous treatments commonly used or proposed in the case of ink corrosion.

In the case of ink corrosion some non-aqueous deacidification methods are used (cf. Fig. 3). The use of iron-chelating agents (like calcium phytate) in organic solvents is still under investigation.

Non-aqueous deacidification

Non-aqueous deacidification can neutralize acid and precipitate an alkaline reserve in the papers. Therefore it arrests acid catalyzed hydrolysis, one primary degradation process in the case of ink corrosion. Due to the alkaline reserve a long-term protection against acid catalyzed hydrolysis can be achieved. On the other hand degradation due to oxidation alone is delayed. Oxidized cellulose is susceptible to alkaline hydrolysis. Often after evaporation of the organic solvent, highly alkaline pH values are reached, accelerating the degradation[21].

Methyl magnesium carbonate in organic solvent (Wei T'o)

Wei T'o was developed at the beginning of the 1970's at the University of Chicago. It should be noted, that the brand name Wei T'o includes several different products (Wei T'o No. 2: Methoxy-magnesium-mehtyl-carbonate = MMMC; No. 3/4: Ethoxy-magnesium-ethyl-carbonate; No. 10: Magnesium-methyl-carbonate = MMC; No. 11/12 Magnesium-ethyl-carbonate).

Hey[23] drew attention to the bad penetration of MMC and recommended immersion or double-side spray application. She warned that uneven application might cause only partial neutralisation and deposition of alkaline reserve. The amount of solvent applied is not easy to control. Addition of solvent can reduce the high concentration of the initial solution. Wächter[28] treated a drawing by Vincent van Gogh using MMMC. He stated that MMMC *inhibits the degradative effect of the iron and therefore delays its destructive effect.* Further investigation[25]

proved that MMMC did not improve the ageing behaviour of ink-corroded papers to a sufficient extent. Highly alkaline pH levels of 10.1 were reached. Besides, Hill[29] and Heller[11] described treatments using Wei T'o. Colour changes of inks or papers that could be expected due to the highly alkaline pH ranges were not discussed by any of the authors except Hey, who observed a conversion of magnesium carbonate "gritting" into dark foxing stains after ageing at 90°C and 50% RH.

- Benefit: sufficient alkaline reserve.
- Risk: colour change of inks and paper, uneven application.

Dispersed magnesium oxide

This method, the Bookkeeper process, was developed at the beginning of the 1980's. Initially CFC 113 was used as liquid which serves as the carrier for magnesium oxide in the suspension. The process has been converted to CFC-free carriers; recently another company (Libertec, Nurenberg, Germany) has changed to air. The efficiency of the process with respect to treating ink corrosion appears to be unpublished. It is comparable to Wei T'o in that an even application (brushing or spray) is difficult to achieve. Possibly white magnesium oxide will precipitate on the surface; with the Libertec variant this is the case inevitably. High pH values might cause discoloration of inks and paper.

- Benefit: sufficient alkaline reserve.
- Risk: colour change of inks and paper, uneven application.

CONCLUSION

Currently used conservation measures vary in their effectiveness with respect to delaying the ink-corrosion processes. For each artifact a method must be chosen which is appropriate to its nature and its problems. Every treatment always combines a number of benefits as well as risks. If the ink corrosion process should be retarded, the effect of both catalytic active components must be blocked. Therefore removal of all iron(II) and iron(III)ions outside the ink complex, and the neutralisation of the acid must be guaranteed.

Recent investigations have shown, that the combination of an aqueous chelating agent (calcium phytate) with an aqueous deacidification method (calcium bicarbonate) gives positive results. The addition of ethanol offers a faster and uniform penetration of the aqueous treatment solution[18]. At the Netherlands Institute for Cultural Heritage a standard method has been developed which allows the comparison of treatments with regard to their effectiveness to arrest ink corrosion.

ACKNOWLEDGEMENTS

This investigation is part of the Ink-Corrosion Project of the Netherlands Institute for Cultural Heritage. The author would like to express her gratitude to the members of the Nederlands Ink-Corrosion Group for the fruitful discussions we had on the subject.

SUMMARIES

Ink Corrosion. Aqueous and non-aqueous treatment of paper objects - State of the art

Paper conservators are still uncertain about the treatment they should apply on ink corroded objects. This might be due to unsatisfactory results obtained by previous treatments, as well as the fact that the degradation process is chemically complicated and still under investigation. However, the main factors that cause ink decay are known today, and so more suitable conservation measures can be chosen. This article is discussing commonly applied aqueous and non-aqueous treatments. Also the positive influences of these treatments and their risks are discussed, based on the results of previously published studies, as well as on the author's practical experiences.

Corrosion de l'encre. Traitement aqueux et non-aqueux d'objets en papier. Etat actuel de la technique

Les professionnels de la conservation du papier ne savent toujours pas avec certitude quel est le traitement à appliquer aux objets en papier corrodés par l'encre. Ceci est probablement dû tant aux résultats insatisfaisants obtenus par les traitements appliqués jusqu'à présent qu'au fait que les processus chimiques de dégradation sont compliqués et qu'ils font toujours l'objet de la recherche scientifique. Aujourd'hui les principaux facteurs responsables de la dégradation de l'encre sont cependant connus et il est donc possible de choisir des méthodes de conservation mieux appropriées. Cet article exposera les traitements aqueux et non-aqueux utilisés habituellement. On exposera les effets positifs de ces traitements ainsi que les risques qu'ils comportent à partir de résultats d'études publiées antérieurement ainsi qu'en se référant à l'expérience personnelle de l'auteur.

Tintenfraß. Wäßrige und nichtwäßrige Behandlung von Papierobjekten - state of the art

Papierrestauratoren sind noch immer unsicher, wie sie tintenfraßgeschädigte Papierobjekte behandeln sollen. Das dürfte ebenso auf die unbefriedigenden Ergebnisse der bisherigen Behandlungsmethoden zurückzuführen sein wie darauf, daß die chemischen Abbauprozesse, kompliziert und stets Gegenstand der Forschung sind. Die wesentlichen Ursachen des Tintenfraßes sind heute jedoch bekannt, und es ist daher möglich, entsprechende Gegenmaßnahmen zu ergreifen. Dieser Aufsatz beschreibt die üblichen wäßrigen und nichtwäßrigen Behandlungen. Aufgrund

veröffentlichter Untersuchungen sowie persönlicher Erfahrung werden ihre positiven Wirkungen und ihre Risiken diskutiert.

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Aqueous Conservation Treatment of 20th Century Papers Containing Water-Sensitive Inks and Dyes

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INTRODUCTION

Aqueous immersion treatments of archival records are fundamental measures enabling the optimal cleaning and stabilization of paper documents. Water-sensitive dyes on these documents can cause serious problems and prevent the application of aqueous media in restoration treatment. This study focuses on the protection of modern inks, occurring for example in records, maps or books of the 20th century, against any destructive action of water which is used for traditional aqueous paper conservation techniques.

MODERN INK DYESTUFFS

Dyestuffs for modern inks, formerly called aniline inks, displaced the permanent iron gall inks since the latter half of the nineteenth century. At first, the new dyes were used as additives to iron gall inks to make the characters visible at once. Some important dyes are listed below (See Table 1). The violet ink dye Basic Violet 3 has an outstanding role for copying pencils and stamping inks from about 1870 to now. The listed dyes are relatively small organic molecules containing chemical groups which make them soluble in water. Therefore, they are not permanent and keep their water-solubility with ageing.

In inks, aqueous solutions of dyes are present with small amounts of gum arabic and surfactants as additives. In addition, most dye solutions are set strongly acidic (pH 2-3) to prevent fading of the writing. Fading of inks, especially of blue inks, in alkaline media is caused by the carbinol-formation, which is a reversible loss of the colour (hue).

Stamping inks are divided into oil-free and oil-based ones. Oil-free stamping inks consist of solutions of anionic or cationic dyes in mixtures of water, glycerol

Table 1: Some important ink dyes, their occurrence and solubility (++ very soluble, + soluble, - slightly soluble)

	Methyl violet	Methylene blue	Ink blue	Eosin
Colour	violet	greenish blue	deep blue	yellowish red
Colour Index	Basic Violet 1	Basic Blue 9	Acid Blue 93	Acid Red 87
Discovered	1861	1867		1873
Chem. nature	Cationic	Cationic	Anionic	Anionic
Chem. name	Triaryl methane	Phenothiazine	Triaryl methane	Xanthene
Solubility*	w+ e++ g+ a -	w+ e++	w++ e++	w++ e++
Use	stamping inks, copying-ink pencils, writing inks	stamping inks, copying-ink pencils	writing inks	writing inks coloured pencils

* w water e ethanol g glycerol a acetone ++ very soluble + soluble - slightly soluble

or glycols and alcohols. Oil-free stamping inks are – depending on the dyestuff – more or less readily water-soluble. Oil-based stamping inks for metal stamps are water-resistant. They contain fatty acids and oils and are coloured with pigments or fat-soluble dyes.

Lead, coloured and copying pencils comprise a lead embedded in a wooden sleeve. The dyes are: graphite for lead pencils, organic pigments for coloured pencils, and anionic or cationic dyes for coloured copying pencils. Whereas lead pencils leads contain a ceramic binder, both natural and synthetic water-soluble and water-insoluble polymers can be used for coloured and copying pencils. According to that, coloured pencils are sometimes not completely water-resistant, whereas copying pencils are readily water-soluble on principle.

POSSIBILITIES OF FIXATION

Fixation of water-soluble dyes on paper can be performed in several ways. One possibility is the formation of a film which prevents the access of water and solvents to the dye. The treated areas in the paper are also protected against the cleaning action of water (cf. Fig. 1a). Thus, in the case of an extensive text this method is contradictory to the intended treatment.

Film-forming fixatives tested on "dummies" in the context of this work are gelatine in water, Paraloid B72 in toluene, paraffin in hexane and the volatile consolidant cyclododecane. The successful application of gelatine is very restricted, and paraffin is hard to remove without residues. Paraloid B72 has to be applied in very high concentrations of 30 to 40% in toluene. It forms relatively

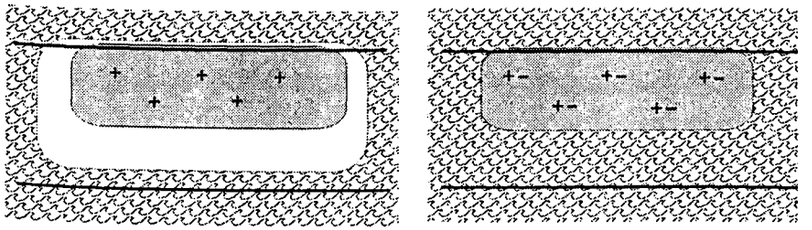

Fig. 1: Fixation of a water-soluble dyestuff, a) by film-forming fixatives, b) by ionic fixatives, both immersed in water (▒▒▒)The film-forming compound is including the dyestuff, making the surrounding paper (═) inaccessable to water.

flexible, glossy films and gives satisfying fixing results in many cases. For the removal of the Paraloid film, however, the use of large amounts of highly toxic solvents like toluene or xylene is necessary since many ink dyes are soluble in alternative solvents like ethyl acetate or acetone. If film-forming fixatives are used, the volatile consolidant cyclododecane proved to be the most suitable one. A major decisive factor for a good success is a suitable application technique, which is described later.

WATER PROTECTION BY IONIC FIXATIVES

A completely different way of fixation is the transformation of the dye into a water-insoluble form by contact with an ionic fixative[1, 2, 3] (cf. Fig. 1b). Apart from some red and green inks, all dyes can be fixed safely by this method. The paper remains completely accessible to water.

Modern inks dyes are ionic substances which are soluble in water in form of anions (anionic or acidic dyes) or cations (cationic or basic dyes). If an oppositely charged polyionic substance is added to the dye, it can be precipitated in form of a complex, with no or only restricted solubility in water.

For fixation, an aqueous solution of the fixative is brought in contact with the dye, either by immersion or by local application with a minimal amount of fixative solution. The dye-fixative-complex is formed immediately without change of the hue of the dye. The formed complex is resistant against water, but not against strongly alkaline solutions and solvents such as ethanol. Ionic fixatives are designed for applications comprising a washing process after treatment. Especially cationic fixatives have a low ageing performance. Acid degradation products can attack the cellulose chain molecules[4].

The fixatives are commercial products for textile finishing, some of them applicable for dyestuffs on paper. It is crucial to differentiate between anionic dyes which need cationic fixatives, and cationic dyes which need anionic fixatives.

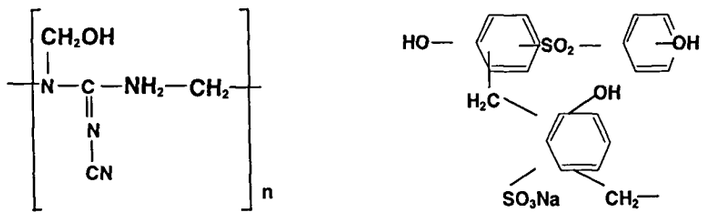

Fig. 2: Cationic (a) and anionic (b) fixatives. a: Condensation products of cyanamide derivatives, such as dicyandiamide, with formaldehyde; b: aromatic sulfonates with phenolic hydroxyl groups.

Suitable cationic fixatives are condensed productes derived from dicyandiamide and formaldehyde (Fig. 2a). Suitable products are Rewin EL®, Stabifix OF® or Sandofix WE®.

Anionic fixatives are needed for the fixation of cationic dyestuffs. The most common cationic dyestuff is methyl violet which can be found in stamping inks, copying pencils and typewriter ribbons. Higher molecular aromatic sulfonates with phenolic hydroxyl groups proved to be suitable anionic fixatives (Fig. 2b). The preferred product is Mesitol NBS® (Bayer).

Slightly anionic dyestuffs such as eosine or naphthaline green form only weak electrostatic interactions with cationic fixatives. As a consequence, the resulting dyestuff-fixative-complex is not completely water-insoluble, but hardly soluble. In this case it is favourable to combine the cationic fixative with the anionic one to neutralize part of its positive charge. This effect is produced when a small amount of Mesitol NBS is added with vigorous stirring to the cationic fixative. A fine polymer-suspension is generated giving much better protection for the critical red and green dyestuffs.

During preliminary tests, the stamping ink methyl violet has been fixed by Mesitol NBS and cyclododecane (Fig. 3). The fixation is of similar quality, however, application of cyclododecane is more time consuming.

Cyclododecane, a volatile fixative

Cyclododecane, $C_{12}H_{24}$, a nonpolar, ring-shaped, saturated hydrocarbon, has been introduced in conservation of paintings, mural paintings, and stone serving as a volatile fixative by Hangleiter et al.[5]. Applied on water-sensitive surfaces, the

* Suppliers located in Germany for any material mentioned in this report can be obtained by the authors.

Fig. 3: Fixation of the stamping ink methylviolet on natural aged rag paper. a) Untreated. b) After immersion in water (20 min). c) After fixation by cyclododecane (solution in petroleum solvent 100/140, both sides) and immersion in water (20 min). d) After fixation by Me-sitol NBS 6% (brush, both sides) and immersion in water (20 min)

white, crystalline solid can serve as a temporary protection against water because it is extremely hydrophobic. Due to its low melting point (60°C) it can be evenly distributed as a thin layer which is afterwards slowly sublimating without leaving any residues. A 0.03 mm layer of cyclododecane disappears within 24 hours. It can also be applied dissolved, for instance, in petroleum ether, the solvent evaporating and leaving the solid fixative. There is always enough time for the aqueous treatment, because sublimation is slow enough. Investigations on application of cyclododecane in paper conservation have been reported in detail by Bandow[6].

The conservation of a 20th century, water-sensitive document – a case study

The archive of Heidelberg University, the oldest university in Germany (founded in 1386), is keeping some 10,000 staff dossiers. Among this huge number, there are not only records of far bygone centuries of special interest for historians and scientists, but also modern dossiers, especially from the time before and during the time of the NS regime. Since paper from this period is known to be of very poor quality, there is a serious conservation problem. The archive has chosen the dossier of Emil Julius Gumbel (1891–1966) to be conserved in an optimal way to survive as a testimony for the development of nationalistic and antisemitic tendencies at the University in the twenties.

Gumbel, who was born in Munich as a son of Jewish parents, was teaching mathematics and economics as a professor of Heidelberg University from 1922 to 1932 when he was rejected from his duties after many years of quarrels initiated by nationalistic students and the similarly orientated direction of the univer-

sity. Gumbel used to include pacifist remarks in his lectures which seemed to be intolerable at that time in Heidelberg. After his rejection, he emigrated and went on lecturing in France, England, and the United States. He died in New York. His dossier includes documents from the period 1922–1964.

Description of object and damages

The file consists of 122 single paper sheets (groundwood-containing writing and copying paper) with formats between ISO A5 and A4 and a quality varying from very poor to good. The sheets were protected at the front and the back by two file covers of red board; the complete file was sewed only at the upper left corner which is the traditional way of record sewing in that region of Germany. Many of the papers were brittle and heavily yellowed; the mean pH value of the sheets was 3.9. The paper showed typical degradation by lignin and, moreover, tears and losses. On 42 sheets, former repairs with self-adhesive tape had caused severe damages in the region of the sewing and at the edges. Two stages of degradation of these papers could be identified: Either the tape carrier had become loose the adhesive having migrated into the paper rendering it brownish and transparent, or carrier and adhesive had not separated yet, only the paper beneath had become yellow, and inks and colours had darkened.

The whole file contains numerous stamps, inks, and coloured pencils, as well as coloured type writing. The stamps are violet, green, red, or blue. The inks are violet, black, blue, or bluish-green. For paginating in the upper right corner, a red coloured pencil has been used. On some sheets, marks of a blue coloured pencil can be found, copying-ink pencil on others.

Conservation concept

The file is a typical example for a 20th century record; countless files of similar condition can be found in archives worldwide. The paper of this file shows a lot of tape repairs, what, fortunately, is not always the case, but typical for those intensively used. To remove them, what is necessary for conservation, means laborious work for numerous conservators.

For most of these records, only microfilming or/and mass deacidification and stabilization can be afforded. Up to the present day, there is no mass treatment available, which gives enough consolidation to papers with a condition described above without any risks for the colours. Since 1997, the Archiv Center in Bückeburg (Lower Saxonia, Germany) has been running a conservation machine de-

acidifying and stabilizing single paper sheets with an aqueous treatment[7]. It is self-evident that a mass treatment of this kind is only suitable for papers which are not yet very badly damaged. For the fixation of modern inks and stamps, the ionic fixatives mentioned in the theoretical part of this contribution, are applied during the Bückeburg process, especially the standard suspension of anionic and cationic reagents. After the fixation, most of the inks and colours withstand the aqueous treatment unchanged, sometimes with slight alterations like small halos or migration to the verso side. Some few colours, especially some reds, unfortunately, remain water-soluble. For the great mass of records to be conserved, the Bückeburg method is an excellent possibility to provide washing, deacidifying, and resizing of weakened records at very competitive prices with a rather small risk of alteration.

In the case of this file, however, the keeper of the archive wanted to preserve it in an optimal way without any risk for the colours and asked for a full restoration including complete removal of the tape residues. Soon after the first testing it became clear that the treatment would be very time consuming, because on every page colours are present which proved to be water-soluble. Nevertheless, it was decided to perform an aqueous treatment to eliminate the acid, dirt, and all by-products of degradation, and to be able to resize with Tylose and to carry out traditional repairs using Japanese tissue and starch.

The goal of this conservation project was to test if it is possible to treat a manifold of water-sensitive modern inks and colours with a traditional wet process without doing any harm to them. The object had been judged to be valuable enough for individual treatment. It provided the occasion to investigate the range of application of several new fixatives which have been described above.

In order to protect the document against new damage caused by readers, it was microfilmed after conservation. At the Institute for Preservation of Archives and Library Material, all documents which needed conservation involving great expense are microfilmed, so that the original document has the chance to remain in the stacks when a reader asks for it.

Conservation treatment

Preparatory work

The record was collated and partly paginated. The sewing was opened, and the board covers were removed so that the sheets could be isolated. The paper was dry cleaned using eraser powder (Lyons Dry-Cleaning-Pad) and an eraser (Läufer Plast-0120) in order to remove surface dirt.

Tape removal

First, the tape carriers were removed, either mechanically (advanced tape degradation) or by local application of a hot air stream. In this latter case, the adhesive showed some swelling, and could be scraped off easily by means of a blunt scalpel just after taking off the carrier. The remaining adhesive had to be treated with a solvent in all cases. Ethyl acetate proved to be most efficient. From some areas, the adhesive could be eliminated by touching them with a cotton-wool swab soaked with ethyl acetate, rotating the swab tip over the paper. For the obstinate residues, a poultice was used, consisting of *Attapulgit*, a magnesium-aluminium-silicate, moistened with ethyl acetate:

On the desk, a dry layer of *Attapulgit* is spread which must be larger than the adhesive containing area to be treated. On top of this layer a thin sheet of Hollytex® (polyester non-woven) is placed, then the object, and another Hollytex. On the top, some *Attapulgit* moistened with ethyl acetate is distributed over the adhesive containing paper sections. In order to intensify the poultice effect and to prevent evaporation of the solvent, the *Attapulgit* is covered by glass plates. The work shall be performed under the protection of a fume-hood. The poultice shall remain for several hours as described, but must be monitored regularly. This procedure can be repeated; in some cases it was necessary to apply five poultices one after another. However, this technique is not as time-consuming as the treatment on a suction-table, because this latter means to be always present in order to add the solvent continuously.

With the help of the poultices, all adhesive residues could be eliminated successfully. The whole step of tape removal needed some 85 hours working time, that means two hours for one single sheet of paper.

Identification of colours

In order to find out whether an ink, coloured pencil, stamp or type writing is cationic or anionic, the so-called microtest was performed. Under the microscope, the colours have been tested by touching them with a tiny amount of Mesitol NBS or Rewin EL applied with a very fine brush or a glass capillary. If the colour is bleeding in contact with Mesitol NBS and remains stable with Rewin EL, it contains an anionic dyestuff. In the opposite case, it contains a cationic dyestuff. Often, the colours are migrating so slowly that it is more difficult to realize the movement under the microscope than with the naked eye. Therefore it is necessary to monitor both results of observation.

Violet inks, violet stamps and copying-ink pencil proved to be cationic. Blue, bluish-green and black inks, red and green stamps, and red and blue coloured

pencils were anionic. It might be interesting that there have been much more anionic dyestuffs than cationic ones used. Unfortunately, every single page had been marked with a cationic, violet owner's stamp of the archive which had to be fixated separately, even if all other colours on the page proved to be anionic.

Preparation and application of ionic fixatives – locally or by immersion

The anionic reagent Mesitol NBS was used to protect the cationic dyestuffs of the violet inks, stamps and copying pencil, the cationic reagent Rewin EL was used with the anionic colours (all but violet).

Mesitol was prepared as a 3%-solution for the application at the suction-table and for the immersion treatment. The powder was slowly spread in deionized water under continuous stirring (best with a magnetic stirrer), because it tends to clot. Rewin EL which is a liquid was diluted for both applications to a final concentration of 3.5% in deionised water. Stirring is also recommended.

For local application, a thin blotter was placed on a suction-table; on the blotter, the object was laid with the face down. With a fine brush, the suitable fixative was spread on the rear side of the ink or stamp. The liquid remaining on the paper was removed immediately with a blotter in order to prevent discolouring of the area, a danger noticed especially with the brownish Mesitol. The object was then covered by a blotter, so that it could not be damaged by dirt or dust from the air by suction which was put on until the complexing agent had completely absorbed into the paper. The application was repeated up to three times. From time to time, it was necessary to change the position of the object on the blotter to obtain optimal suction. The front side was treated accordingly (Fig. 4).

The suction-table treatment proved to be the most suitable and safe method to apply the complexing agent precisely and carefully to small, definite areas like, for instance, single characters. Since the first coat was laid from the rear, the dye-stuff could immediately migrate into the blotter beneath, if the colour, unexpectedly, tended to bleed in spite of previous testing.

Nevertheless, in some cases, an immersion of the whole sheet seemed to be the better choice: firstly, because it is done much quicker, especially in the case of large areas with ink as, e.g., complete hand-written letters or water-sensitive type-writing, secondly, the application of Rewin, performed at the suction-table as described above, sometimes caused dark edges or discoloured spots, a phenomenon which appeared irregularly and could not yet be explained. Four pages with blue and black anionic ink were immersed in a 3.5%-solution of Rewin EL, after the cationic colours appearing on the same pages (for instance, the ubiquitous owner's stamp and date stamps) had been fixated by Mesitol NBS at the

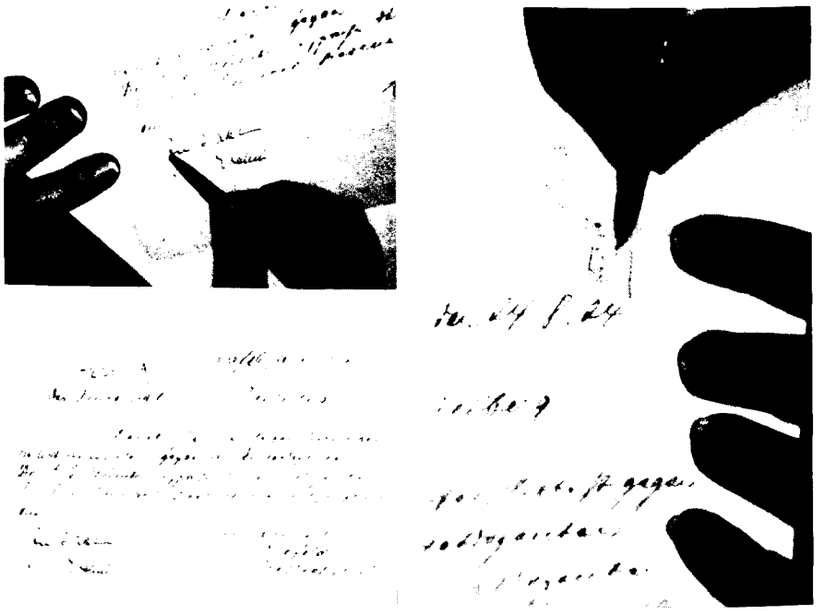

Fig. 4: Local application of ionic fixatives. a) Protection of violet cationic dyes with Mesitol NBS. b) Protection of red anionic dyes with Rewin EL. c) Paper after aqueous conservation treatment

suction table, as described above. Two pages with cationic ink or type writing were immersed, accordingly, in a 1%-solution of Mesitol NBS, the anionic colours (e.g. red pagination) having protected before by suction-table application of Rewin EL. The duration of the bath was 2–3 minutes in all cases.

Combination of both ionic fixatives in a suspension

In the Bückeburg mass conservation process[7] the anionic and cationic colours have to be fixed simultaneously by a single treatment step. The only possibility to avoid pretesting and local application of the fixatives is to combine the fixatives in a suspension. The suspension containing 1.2% Mesitol NBS and 6% Rewin EL has been developed to give the maximum of protection to the majority of colours occcuring on common record. The percentage of Mesitol is lower than that of Rewin, because on records mainly anionic colours are found. In addition, this composition provides the best protection for critical red and green inks. A disadvantage of the suspension is its muddy, white-brownish colour,

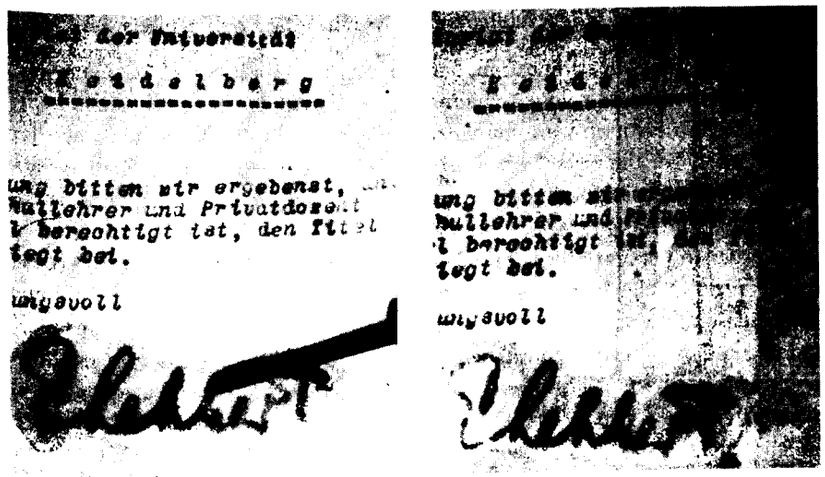

Fig. 5: Cyclododecane, a volatile fixative. a) Application of cyclododecane melt. b) Paper shortly after aqueous conservation treatment.

which impedes observation of the object and the characters to be protected during treatment.

The suspension is prepared by adding equal parts of a 2.4% solution of Mesitol NBS to a 12% solution of Rewin EL under vigorous stirring. Before use, the suspension has to be stirred again. On 15 well-tested papers, the suspension was applied, however, after individual protection of the cationic colours. The objects were immersed in the suspension for 3–4 minutes.

Local fixation with cyclododecane

Cyclododecane was applied on 13 pages which could not be protected by ionic fixatives: they either showed bleeding with both oppositely charged reagents, or differently charged inks were found at the same spot, or the inks had been applied too intensely (mostly copying-ink pencil).

Under a fume-hood a layer of cyclododecane melt was applied on both sides of the object. In a small ceramic bowl, two tablespoonfuls of granulate were melted at 60°C. With a brush, the fluid was spread on the paper and worked-in with a heat spatula. The melt must penetrate the paper completely. To prevent hardening of the brush, it is recommended to dip it from time to time into pure petroleum solvent (100–140). After application of cyclododecane, the paper could be wetted immediately (Fig.5).

Aqueous treatment and filling of losses

Aqueous cleaning, deacidification, and resizing were performed the same way, whichever method of colour fixation had been used before. The papers being kept under observation were immersed horizontally in deionised cold water for 3–4 minutes. For the papers which had been immersed totally in a fixative solution or in the suspension, the bath was repeated several times with fresh deionized water.

In order to prevent formation of puddles and bleeding of colours during the drying process, the papers were shortly predried on a suction table, colours downside on a thick blotting paper. In case of cyclododecane fixation, this technique could only be applied on the non-fixated areas, because around the hydrophobic areas, the paper showed tensions and wrinkling under the influence of suction.

All papers were then air-dried horizontally on sieve frames. Afterwards, they were immersed for 3–4 minutes into a second cold bath providing an alkaline reserve consisting of calcium and magnesium bicarbonates. This buffering bath containing approximately 19 mmol/l Mg^{2+} and 1.5 mmol/l Ca^{2+} was prepared using a water circulation system[8] with dolomite mineral. After the bath, the papers were pre-dried and dried as described above. Resizing was performed with a 1%-solution of Tylose MH 300, prepared with the same water as used for the buffering bath applied with a broad Japanese brush.. Afterwards, tears were repaired with Japanese paper 5 g/m^2 or 11 g/m^2; losses were filled with Japanese paper 18 g/m^2, all applied using wheat starch. In order to achieve the typical smoothness of the paper surface, all papers were quickly sprayed with water (enriched with earth alkaline carbonates as described), before they were pressed between Hollytex and blotters. For the final drying, the papers were pressed only between blotters.

Storage

In order to achieve optimal physical protection of the object, it was decided not to reconstruct the sewing, but to keep the single sheets unbound. All sheets were encapsulated in polyester sleeves, which are open on two sides.

Experiences from the case study

Following the concept of optimal protection, after the microtest of every single paper sheet it became evident that the treatment had to be performed in a very

individual manner due to the many different inks and colours that had been used. Nearly all 122 sheets had to be treated with more than one fixative. Most frequently, both Mesitol and Rewin were applied locally, each at the corresponding inks. The different fixatives were used as follows:

Mesitol NBS (3%) and Rewin EL (3.5%), both locally	78 sheets
Mesitol NBS (3%) locally, and immersion in standard suspension	17 sheets
Mesitol NBS (3%) locally, and immersion in Rewin EL (3.5%)	4 sheets
Rewin EL (3.5%) locally, and immersion in Mesitol NBS (3%)	4 sheets
Mesitol NBS (3%) locally	2 sheets
Rewin EL (3.5%) locally	2 sheets
Cyclododecane melt,	
mostly combined with local application of Mesitol and Rewin	13 sheets
no fixation necessary	2 sheets
Total	122 sheets

Only by this very time-consuming individual procedure could it be guaranteed that all colours remained stable during the wet treatment performed after the fixation. The protection proved to be reliable if some aspects were considered:

- Mesitol NBS, which is coloured, can cause discoloration of the paper; therefore, if applied locally, excess solution has to be prevented from remaining on the object for more than a few seconds. That is why the use of the suction table is highly recommended.
- Rewin EL is able to "cationize" the paper so that it can attract dirt from outside or from degradation products rinsed out during wet treatment. This negative effect was observed in a few cases. Perhaps an even more sophisticated method of Rewin application than that one described above can be developed.
- The standard suspension showed the least satisfying results in this case study. In spite of the relatively high proportion of Rewin, even the anionic (fixated) inks showed bleeding during immersion in water and migrated into the blotter on the suction table. Therefore, for objects with large areas of cationic inks, fixation in a bath of pure Mesitol (3%) was preferred. Moreover, the observation of the papers was impeded due to the opaque white-brownish colour of the suspension.

- Stamps and colours that had been reduced with water and ethanol (1:1) at the suction table – what is a very common method to prevent bleeding in contact with water – could no longer be fixated with the described fixatives.
- In addition, all areas that had come in contact with ethylacetate during the tape removal treatment, could no longer be protected with the ionic fixatives. So, it has to be considered that any use of organic solvents (including ethanol) impedes the impact of Mesitol and Rewin which need the high polarity of pure water to be attached to the water-soluble organic dyestuffs forming water-insoluble complexes.
- As to the application of cyclododecane, it has to be realized that these areas, having been rendered hydrophobic, consequently could not be wetted anymore and therefore could not be deacidified by the aqueous treatment. In some cases discoloured edges, tensions, and wrinkles have been observed, especially when large areas had been treated. Sometimes the papers regained smoothness after light re-moistening.
- The brush for the application of the cyclododecane melt has to be cleaned very thoroughly with petroleum solvent. Residues of the solvent can damage sensitive colours when the brush comes in contact with them. It is recommended to use several brushes simultaneously, so that there is always a clean, dry brush available.
- During careful application of the melt into the paper using the heat spatula a temperature of about 60°C has to be kept. This may result in irreversible deformations, if the process is not performed carefully enough, or if the paper is too thin and sensitive.

On the whole, the fixation was successful, and all paper sheets could be treated in the traditional aqueous immersion baths followed by wet resizing and repairs with wheat starch. The pH value of the paper rose from about 3.5–4.0 to 7.0–7.5. The papers looked clean, brighter, and felt much more flexible and stronger than before treatment. Combined with the complete removal of the self-adhesive tapes, the restoration seems to have improved the condition of the object much more than ever expected. However, it has to be realized, that the restoration needed a lot of time: 86 hours for the tape removal alone, 86 hours for the tests and the fixation, and 61 hours for the aqueous treatment and repairs. 20 hours have to be added for preparatory works, encapsulation, and documentation, so that the total time is about 250 hours for 122 sheets, that means, approximately, two hours per sheet. For a conservator of graphic art, that seems to be not too much, but for a conservator of records, it is a horrendous expense.

OUTLOOK

After the successful application of the new fixatives on highly sensitive objects it seems to be very necessary to improve the tested techniques for a quicker treatment, possibly on the cost of slight concessions to the optical appearance, so that "normal" documents, not only those of outstanding value, can be treated within reasonable time: objects that, for what reason ever, cannot be treated in a mechanized mass process. Obviously, it is possible to reduce the risk of bleeding even by complete immersion of an object with various inks. Some papers can be treated with one substance without previous testing of the inks.

CONCLUSION

As a result we can state: using the recently suggested types of ionic fixatives, Rewin EL (cationic) and Mesitol NBS (anionic), together with the volatile fixative cyclododecane it is possible to prepare even the most heterogeneous modern record consisting of water-sensitive modern inks, coloured pencils and stamps, for aqueous cleaning and deacidification or applying water-containing adhesives. The application is easy, does not need expensive equipment, and is free from hazardous solvents. We succeeded in treating every sheet individually with a variety of methods. This is time consuming and, considering the usual amount of modern files, quite expensive. Further studies will concentrate on the possibilities to reduce the time needed in a variety of techniques in order to accelerate the treatment.

ACKNOWLEDGEMENTS

The authors, a conservation scientist, a preservation manager, and a paper conservator, are very grateful to the University Archive of Heidelberg as owner of the record, and to the *Landesarchivdirektion* Baden-Württemberg for the opportunity to test new conservation techniques on an object which deserves optimal treatment. They also would like to thank two colleagues from *the Institut für Erhaltung von Archiv- und Bibliotheksgut*: Cornelia Bandow has given assistance and useful hints concerning the application of cyclododecane, and Samy Virmoux has carried out the removal of tapes and their residues. We are also very grateful to Wilfried Feindt of the *Niedersächsisches Staatsarchiv* Bückeburg for his demonstrations and valuable information on the whole subject.

SUMMARIES

Aqueous Conservation Treatment of 20th Century Papers Containing Water-Sensitive Inks and Dyes

Water-sensitive modern dyes used for writing or marking on records can be transferred into a water-proof condition by use of ionic fixatives. Thus, aqueous restoration techniques like washing or resizing can be applied even on documents with large areas of modern inks, stamps or copying-ink pencils. The volatile fixative cyclododecane is used for local water-protection of small endangered areas. The application of the fixatives Rewin EL™, Mesitol NBS™, and cyclododecane is described at the example of the conservation of a complex 20th century record, thereby avoiding any diffusion of a multitude of different inks and colours found on every single sheet of paper.

Traitement aqueux de conservation du papier datant du 20ème Siècle et contenant des encres et des colorants sensibles à l'eau.

Les colorants modernes sensibles à l'eau tels que ceux que l'on utilise pour écrire et faire des inscriptions dans les registres peuvent devenir résistants à l'eau par un traitement avec des fixateurs ioniques. Ainsi des traitements aqueux de restauration, tels que le lavage ou le recollage, pourront être appliqués même à des documents comportant de grandes parties écrites avec ces encres, tampons et stylo-couleurs modernes. Pour la protection de plus petites surfaces menacées par l'eau on a testé un fixateur volatil, le cyclododécane. On décrit l'application des fixateurs Rewin EL, Mesitol NBS et cyclododécane par exemple dans la conservation d'une liasse complexe de documents datant du 20ème siècle qui a permis d'éviter toute bavure des nombreuses sortes d'encres et de couleurs que comportait chaque feuille de papier.

Wäßrige Behandlung von Papier aus dem 20 Jahrhundert mit wasserempfindlichen Tinten und Farben

Wasserempfindliche moderne Farbstoffe, die zum Schreiben und zum Markieren verwendet werden, können durch ionische Fixierstoffe wasserfest gemacht werden. Auf diese Weise können wäßrige restauratorische Behandlungen wie Wässern und Nachleimen auch auf Stücke mit großen Partien angewandt werden, die in denen solche modernen Schreibstoffe (Tinte, Kopierstift) enthalten sind. Das flüchtige Fixiermittel Cyclododecan wurde erprobt zum Schutz von kleinen wassergefährdeten Bereichen. Am Beispiel eines komplex zusammengesetzten Aktenkonvolutes aus dem 20. Jh. wird die Anwendung von Rewin EL®, Mesitol NBS® und Cyclododecan beschrieben, welche jedwedes Auslaufen einer der sehr zahlreichen verschiedenen Tinten und Farben verhinderte, die jedes einzelne dieser Stücke aufwies.

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What Fiber for Paper Strengthening?

by HELMUT BANSA & RITSUKO ISHII

Introduction

To give a sheet of paper, used as information carrier, it be a picture or a text, decayed by chemical or microbiological processes, back the mechanical strength that it needs to be used in the intended way, is among the most often demanded duties of a paper restorer. If the paper is so weak that it really cannot withstand the stress of careful handling – touching with hands, lifting, turning over – then this strengthening can only be done by combining it with another sheet-shaped object[1]. Any other method that are currently done in practice or that are under research – bathing in or brushing on the solution of a film-forming compound, graft polymerization, crosslinking, tying a molecular string along the cellulose molecular chain – does not give enough strength, if the sheet in question has suffered decay in such an amount that it can no longer be handled.

This combining the weakened sheet with a strengthening one can be done in different ways. A very interesting procedure is making the second, the strengthening sheet out of fiber especially prepared for its purpose instead of using a preproduced one[2]. At best this papermaking is done in the leafcasting machine, and if an apt program[3] for computing the amount of fiber and the other ingredients necessary for precise leafcasting is available, then this strengthening paper can be custom-made very precisely for the requirements of the specific paper to be to strengthened. The simplest way to do this strengthening is just to reduce the suction in the leafcasting machine as soon as the primary aim of leafcasting, i.e. to substitute lost parts in a sheet of paper, has been achieved, but still leaving a certain amount of suspension containing a precisely defined amount of fiber just above the object. The suction must be reduced to be distinctly lower than the weight of the fiber resting in the water, so that these fibers will deposit all over the leafcasting area, thus forming a tissue that is covering the object, hence strengthening its weak parts. Where this strengthening tissue is not needed and where the fiber (or the tissue resp.) would impair the aesthetic quality of the object, masks (wax paper, Hollytex™) may be positioned. A more precise result – precise computing provided – is obtained if the strengthening tissue is made in a a separate procedure, and this technique also allows to use different fiber: such

type that renders a better strengthening effect than the fiber used for filling in missing parts, i.e. usually a mixture of chemical pulp and cotton, of shorter and longer fibers. Such a strengthening tissue is usually put on both sides of an object, aa was done with all samples of the research project reported here.

Japanese Fiber

Frank Mowery[4] was the first restorer to use the strongest fiber known in papermaking for paper restoration. He used Japanese fiber instead of the paper made of it, i.e. Japanese tissue. The problem with the Japanese fiber is that it must be processed to become paper imediately after having been cooked in alkali and beaten; if it becomes dry, it must be cooked and beaten again. If it is necessary to define a certain amount of fiber in order to process it to become a tissue of defined grammage, this must be done with wet fiber. We have found the following relation:

10 g *shirokawa = white bark,* i.e. inner bark (from which the outside dark-coloured and wood-like layer has already been removed)

soaked for 12 h in cold water,

boiled for 150 min in aqueous soda ash solution 2.7 % (135 g $Na_2CO_3 \cdot 10\ H_2O$ in 5 l water),

slowly cooled down,

rinsed in cold water,

beaten for 10 min with a square-cut wooden club on a stone support, will become

32 g wet fiber mass, from which

7.29 g paper can be made.

The difference, i.e. 2.61 g or ca. 27 % of the *shirokawa*, are hemicelluloses dissolved during the boiling process and removed together with the boiling lye. We found no significant difference in these relations between the two kinds of fiber, i.e. *kozo* and *mitsumata.* If the water of the lye evaporates and the dry residue is dissolved in 17.5% NaOH, i.e. submitted to the alkali-solubility-test[5], a part of it, ca. 11% in relation to the dry *shirokawa,* is not dissolved again and must therefore be defined as being α-cellulose: one of lower quality, i.e. shorter chains, not soluble in cold strong alkali, but only during longer alkaline boiling. Another fraction, computed into relation of dry *shirokawa* ca. 7%, can be defined as β-, the rest (ca. 9% of dry *shirokawa*) as γ-cellulose.

Long fiber as that of Japanese origin, as well as flax and hemp, can only be processed to become paper if a polyelectrolyte (natural: neri = polygalacturone acid; synthetic: polyacrylamide) is present in the suspension. Empirically we found the following:

32 g wet fiber mass (cf. above) should be suspended by slight stirring by hand
8000 ml water together with
0,4 g polyacrylamide.

The PAcA type we use upon advice of the Kochi Pulp and Paper Institute in Japan is named as "PAM-P", a product of Sumitomo Seika Chemicals, Osaka (Japan). We found it to be useful, but we did not check whether it is the most apt type. The 0,4 g are dissolved in 100 ml warm water (truly: 4 g/1000 ml, 90% used otherwise). PAcA is also added to the process water for normal leafcasting: 10 ppm. We made rough preliminary tests with accelerated ageing, three times doubling this normal amount of PAcA in the process water (20, 40, 80 ppm) and found no negative influence of this additive on the ageing behaviour of the paper. For processing long fiber the PAcA is not only added to the fiber suspension prepared for use as described, but also the concentration in the machine is doubled: 20 ppm. For long fiber the suspension in the machine must be as thin as possible, i.e. the fiber suspension prepared for use as described must be evenly distributed in the biggest possible amount of processing water that is pumped into the machine part above the sieve. This amount is depending on the machine type; in the machine that is to our disposal it is 60 l; it can be called the "active process water", in contrast to the water in the lower part of the machine, in our machine another 140 l. 10 ppm PAcA in the total process water (60 + 140 = 200 l) means 2 g, 20 ppm means 4 g.

That very amount of the Japanese fiber suspension prepared as described (7.29 g dry fiber in 8000 ml water containing 0.4 g PAcA) which is, exactly computed by the leafcasting program, necessary for a specific process, must be added to the "active" process water only after having already been pumped into the upper part of the leafcasting machine. The fiber itself must not be pumped, as it normally done for leafcasting: too much of it would stick in the pump. Japanese fiber suspension must be mixed in by slowly pouring it into the stream coming out of the pump hose and distributed evenly using an apt instrument.

Other Fiber

Because the procedure with Japanese fiber is rather laborious and because in many cases with the fiber normally used for leafcasting a good strengthening effect can be achieved we wanted to find out in what case the "normal" leafcasting fiber is enough and in what other Japanese fiber is necessary. In the workshop from where this report originates "normal" leafcasting fiber is a mixture of bleached white cotton, unbleached linters of natural colour and chemical pulp dyed to several tints of yellow, brown, orange, blue and grey (black). Preliminary tests were done in search for a fiber not only of better strength but also not requiring laborious preparation. We found flax fiber, the same as used industrially for tea bags, and we included this product for our tests. It was supplied by Schoeller & Hoesch GmbH Papierfabrik, Gernsbach (Baden, Germany) via Walter Klug & Co., Immenstadt (Württemberg, Germany). Specifications are as follows:

- length of fiber: min. 1.2, max. 7.6 mm, avg. 4.8 mm
- thickness: min 15–30 µm
- Schopper Riegler freeness: 10

Processing flax fiber in the leafcasting machine is comparable to processing Japanese fiber. It is advisable not to begin with dry fiber as it is done with the mixture for normal leafcasting, but with a pre-prepared suspension: 5 g/1000 ml + 10 ml PAcA solution 4g/1000 ml, i.e.

5 g fibre,
40 mg PAcA,
1010 ml water.

Pulping the dry flax fiber can be done in a mixer. The PAcA is dissolved separately. As with Japanese fiber the suspension must not be pumped. Again as with Japanese fiber the amount of PAcA in the process water must be doubled (20 ppm).

We found, again by mere experience, that the minimum grammage of a strengthening tissue from whatever fiber is 1.7. Therefore this is the "normal" measure for which the leafcasting program is computing how much suspension of the selected kind is necessary for a strengthening tissue of the size in question. During input the computer is asking whether that grammage shall be increased by multiplying by 1.5, 2 or such factors required.

Experiment

Treatment

In order to find out what fiber is the most apt in different cases, five paper were chosen to be strengthened by four kinds of fiber: *kozo*, *mitsumata*, flax, chemical

pulp, each by a single (1.7 g) and a double (3.4 g) tissue. As treating paper in the leafcasting machine normally requires the paper to be washed and as washing can have a significant influence on the physical properties chosen for describing the quality of a process, we also included simple washing into the treatments to

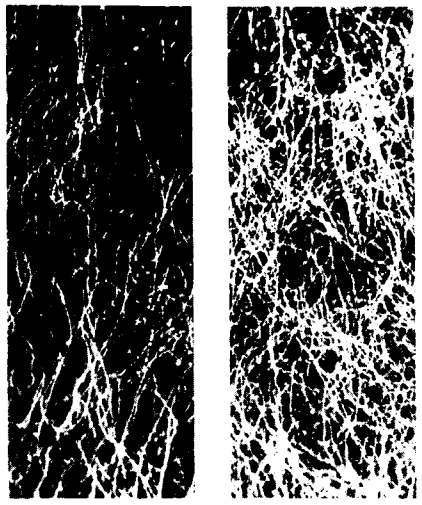

Fig. 1: Single and double tissue of *kozo*

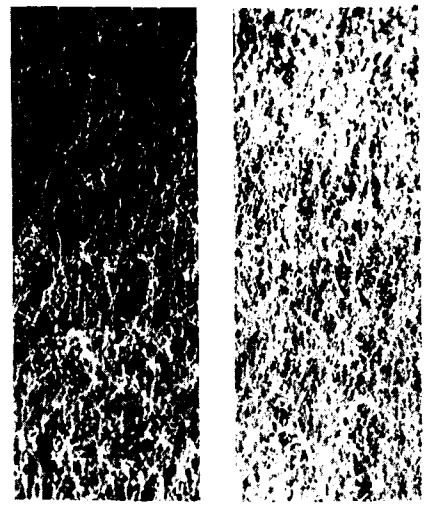

Fig. 2: Single and double tissue of *mitsumata*

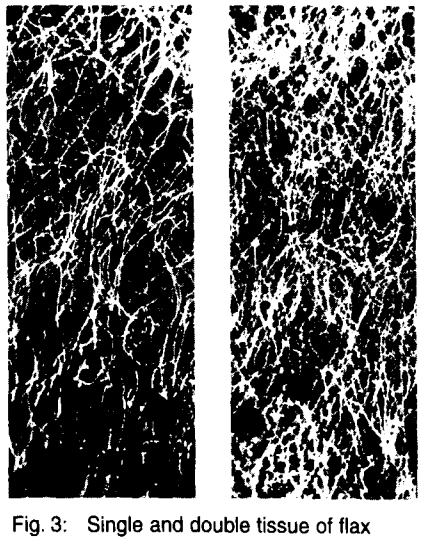

Fig. 3: Single and double tissue of flax

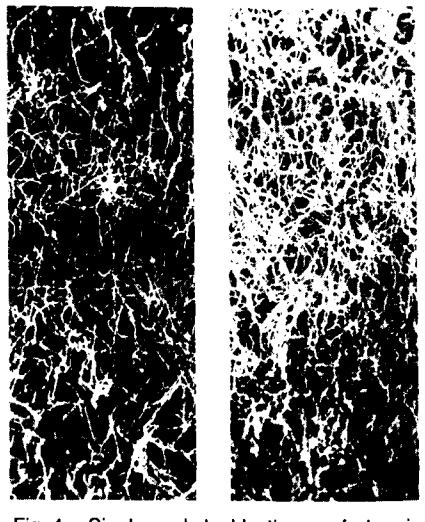

Fig. 4: Single and double tissue of chemical pulp

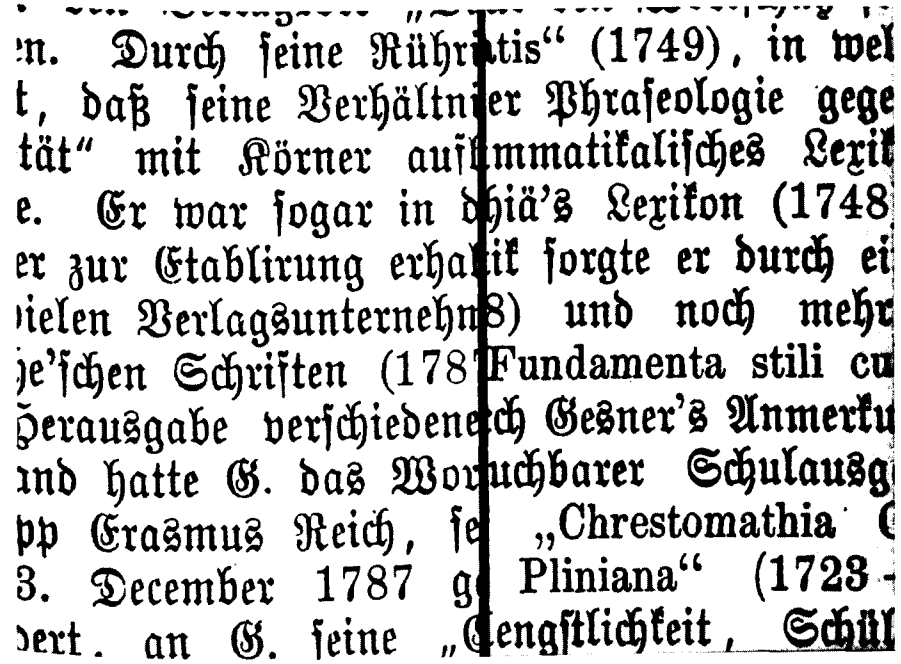

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Fig. 5: Brittle Paper, untreated, washed, single letter.

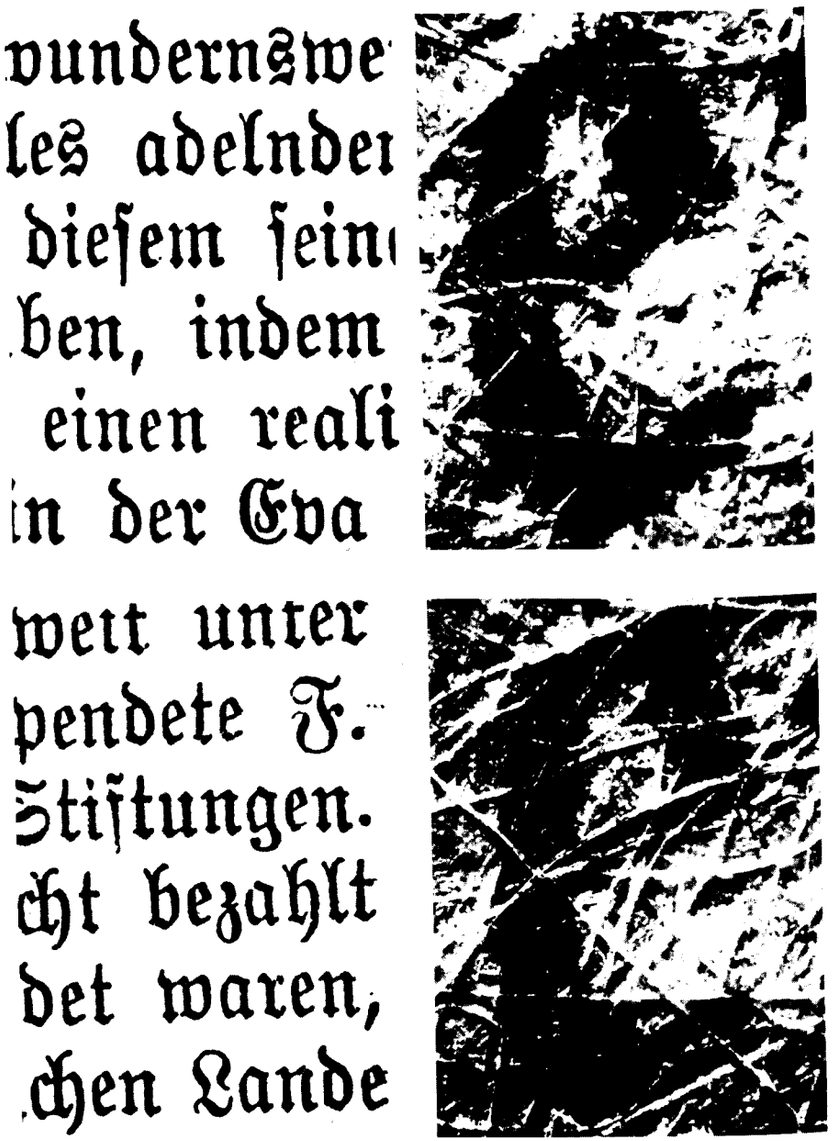

Fig. 6: Brittle Paper, single tissue (top), double tissue (bottom) of *kozo*..

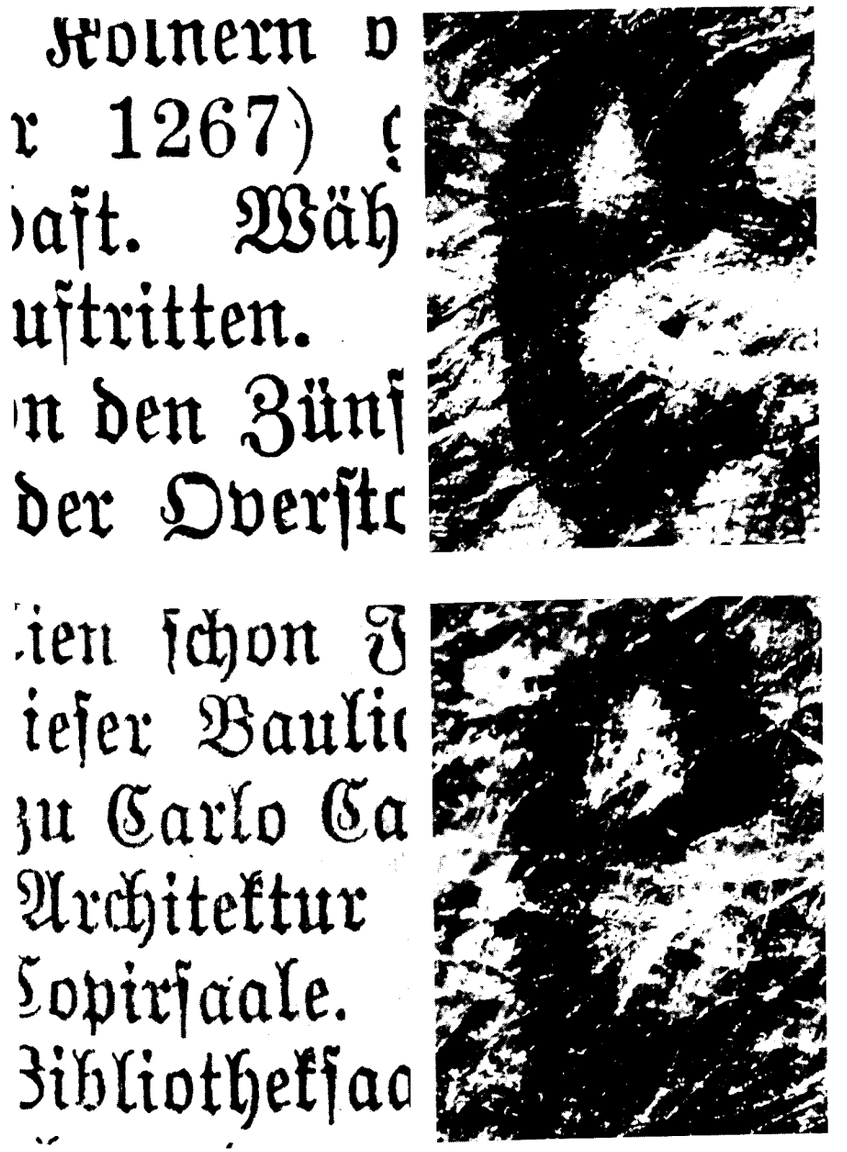

Fig. 7: Brittle Paper, single tissue (top) amd double tissue (bottom) of *mitsumata*.

Fig. 8: Brittle Paper, single tissue (top) and double tissue (bottom) of flax.

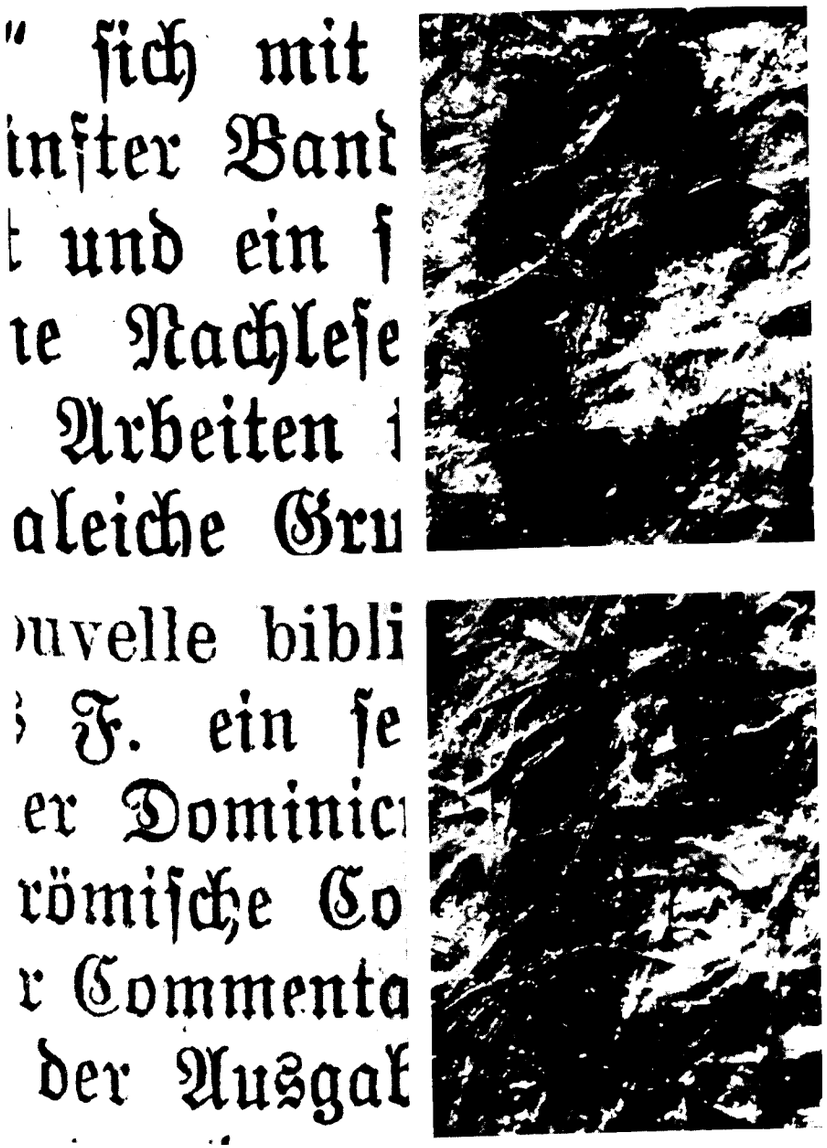

Fig. 9: Brittle Paper, single tissue (top) and double tissue (bottom) of chemical pulp.

be checked. As any paper is to be pasted before the tissue is positioned onto it wet-on-wet, simple pasting is also included. The paste is milk-thin, following the Far-Eastern manner: 15 g wheat starch / 1200 ml.

Altogether there were 10, or, including the control, 11 treatments:

- ctr control; no treatment
- Wa washed
- Pa pasted after washing
- K1 strengthened by a single tissue of *kozo* fiber after washing and pasting
- K2 strengthened by a double tissue of *kozo* fiber after washing and pasting
- M1 strengthened by a single tissue of *mitsumata* fiber after washing and pasting
- M2 strengthened by a double tissue of *mitsumata* fiber after washing and pasting
- F1 strengthened by a single tissue of flax fiber after washing and pasting
- F2 strengthened by a double tissue of flax fiber after washing and pasting
- Ch1 strengthened by a single tissue of chemical pulp fiber after washing and pasting
- Ch2 strengthened by a double tissue of chemical pulp fiber after washing and pasting

All samples with tissue recto and verso.

Papers

Following the principle that results from conservation research usable can be valid for practical conservation only if the research is done not only with modern objects, chosen because they are of well defined and reproducible quality, but also with real, i.e. old and/or damaged ones, the tests were done not only with filter paper, but also with two heavily decayed papers from the 19th century. During the experiment it became evident that the main advantage of the leafcasting-tissue-technique is not so much with modern machine-made paper that has not only lost its mechanical strength as result of acid-catalyzed hydrolysis, but also become hard and brittle as a result of crosslinking. The main object of this technique rather is historic rag paper damaged by mould, and as it was not possible to provide a paper damaged by mould in such an even way that mechanical strength tests could provide reproducible results, it was tried to prepare by

Table 1: The papers

	Origin	Fiber	g/m²	ash (%)
Brittle	Allgemeine Deutsche Biographie 9. Leipzig: Duncker & Humblot 1879.	ca. 50% chemical pulp ca. 20% groundwood ca. 30% rag (cotton)	69	12.02
Very brittle	The Indian Law Report; Calcutta series 27. Alipore (West Bengal): Government Pr. 1903.	chemical pulp, partly from rice straw	83	17.14
Rag	Multz, Jacob Bernhard: Reprae-senatio Maiestais Imperatoriae. Öt-tingen (Bavaria): 1690	Flax or hemp	57	3.15
Filter	Product of J.Binzer Papierfabrik GmbH, Hatzfeld (Lower Saxonia, Germany)	ca. 70% chemical pulp ca. 30% rag (cotton)	59	0.19
Weakened Filter	Filter paper put for 20 min 10% HCl at 50°C, then for 20 min in 3% $KMnO_4$ at room temperature, finally for ca. 3 min in 3% $Na_2S_2O_5$ until the brown colour of manganese dixide disappeared	same as Filter	61	0.26

chemical treatment a material exhibiting comparable mechanical properties. We were aware that this is not really imitating mould-damaged paper. Even if the product was too weak to be handled when it was wet it gave significantly better strength numbers than those to be expected with heavily mould damaged paper. But it was so weak that it could hardly be put out of the last preparation bath and not submitted to the washing procedure of the experiment. A fifth paper chosen for the experiment was a well preserved historical rag paper without damage. The main reason was that a good conservation technique should show a result – an improvement, of course – only on damaged objects; undamaged ones or undamaged parts should stay unchanged. It seemed interesting to see what fiber would be nearest to this ideal.

The papers used for the experiment are given in Table 1.

Mechanical Strength

For checking the mechanical strength achieved by the different treatments the following parameters were checked:

Fig. 10: Microscopic picture 1:90 of the Brittle, the Very Brittle and the Weakened Filter Paper.

- Tensile strength after one defined fold, what is best apt to describe the usability of old paper[6]. As the "control" samples of the "Brittle" paper gave only tensile strength numbers below the limit of the testing machine and as for computing the increase achieved by the different treatments in relation to the state before a number higher than 0 is necessary, the lowest number found during the whole testing procedure – 10–12 samples for each average number – was taken arbitrarily whenever tensile post fold was not measurable. This number is 0,09 N. It was taken even for "Very brittle" –"Control", "Washed", and "Paste", where the test strips (15 mm) broke already during folding.
- Tearing resistance[7]. This test might be apt to describe the strength a sheet of paper needs to be used as information carrier. Its disadvantage is that quite a lot of paper is needed: more than often can be provided of old paper. This was the case with the "Very brittle" paper; tear resistance for ctrl, Wa and Pa could not be tested.
- Tensile strength[8] is easily to be tested, but the numbers are giving little information regarding the usability of a paper as information carrier. Even an extremely brittle paper can have a considerablly high tensile strength[9]: higher than a flexible paper that can be used without restriction.
- The MIT fold test[10] is not apt for measuring mechanical strength in paper conservation research[11], for several reasons: it is too strong to describe the quality of paper that has suffered already some decay and too sensitive towards decay processes that have little influence on the usability; with the most often very uneven historic and /or decayed papers the results fall in a too wide range. Nevertheless we tried to included this test in our experimentbe-

Table 2: Mechanical strength numbers

	ctr	Wa	Pa	K1	K2	M1	M2	F1	F2	Ch1	Ch2
Tensile post fold (N)											
Brittle	0,09	0,09	0,09	5,56	3,44	1,48	6,37	4,37	7,51	0,62	2,70
Very brittle	0,09	0,09	0,09	0,09	2,69	0,09	1,00	0,09	0,89	0,09	0,09
Rag	6,70	4,95	9,33	15,39	21,13	13,99	19,70	16,81	21,23	14,61	14,20
Filter	6,42	6,28	14,56	21,13	22,46	24,09	28,58	20,19	22,12	14,55	17,83
Weakened filter	3,44		4,95	13,46	15,90	10,13	18,03	11,00	10,51	11,91	13,46
Tear resistance (mN)											
Brittle	6,61	6,85	6,91	25,36	42,79	17,36	30,73	22,00	29,27	11,58	22,67
Very brittle				26,79	39,64	15,07	25,47	14,13	26,80	11,27	15,73
Rag	50,36	42,36	51,09	53,45	56,36	47,82	52,20	53,00	54,55	46,64	42,00
Filter	37,64	36,91	62,36	76,18	84,91	74,18	82,00	75,00	76,55	62,18	71,82
Weakened filter	22,00		24,18	35,82	33,82	25,27	34,00	28,20	31,45	27,82	33,64
Tensile strength (N)											
Brittle	13,08	14,17	15,12	20,03	23,23	23,05	31,34	25,37	25,79	22,03	24,57
Very brittle	9,83	6,55	15,42	11,38	8,59	9,93	14,53	11,68	13,76	11,21	10,54
Rag	11,91	8,12	14,20	22,49	25,36	25,52	26,35	24,31	26,66	22,03	18,06
Filter	6,58	6,46	14,19	20,47	23,18	25,26	26,52	22,72	22,96	13,03	19,88
Weakened filter	4,25		8,68	20,39	20,39	11,94	25,74	15,67	19,88	15,79	15,26
Folding endurance (number)											
Brittle											
Very brittle											
Rag											
Filter*	5	9	28	144	159	142	208	146	122	58	149
Weakened filter**	4		11	29	131	12	124	20	106	65	115

* load 500g

** load 200 g

cause it is the most often used one in paper conservation research. For the "Brittle" and the "Very brittle" paper MIT fold numbers were below measurability. For the "Rag" samples we abstained from them because they are too diverse. The "Weakened filter" was too weak to be tested with the load demanded in the relevant instructions, i.e. 500g; so it had to be reduced to 200g. Folding endurance in the correct way was checked only for "Filter".

Mechanical test numbers are given in Table 2 and Fig 11–15.

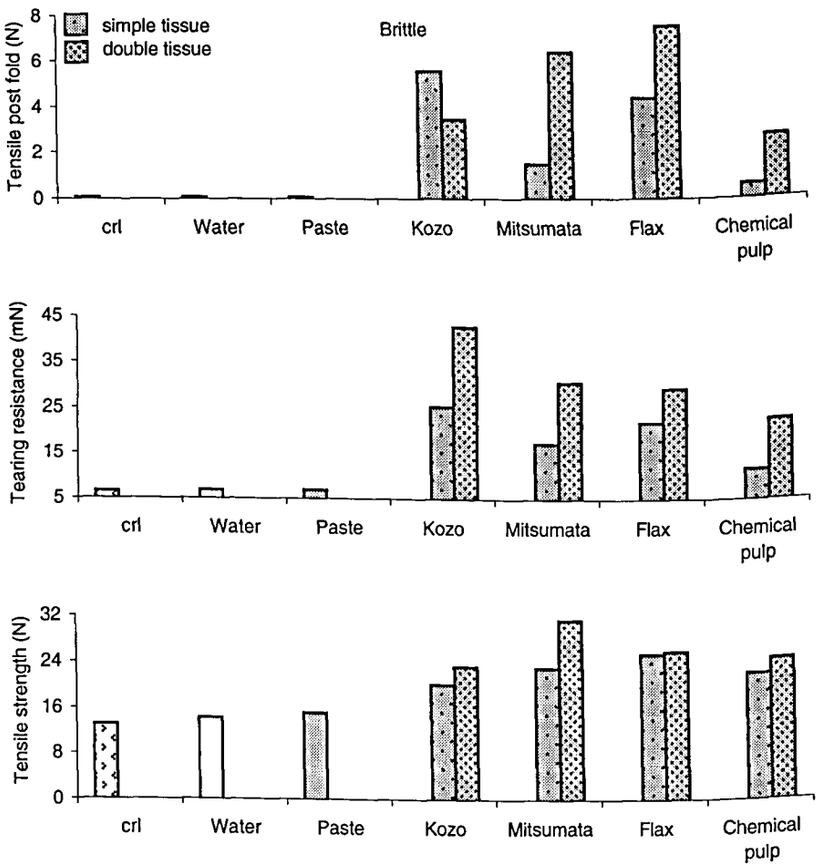

Fig. 11: Mechanical strength of the Brittle paper.

Sensory Quality

The ideal conservation treatment is a one that is affecting only that very aspect of an object that is to be improved, because it prevents the object to be used properly, while any other condition, mainly those forming the aesthetic quality of the object, i.e. those to be perceived by the human sense organs, stay unchanged. They may be called the sensory qualities. As it was the aim of the experiment reported here not just to find out what of the methods under reseach is giving the best mechanical strength, but, more generally, what is the "best", those sensory qualities were included. Numbers to be checked by an instrument can,

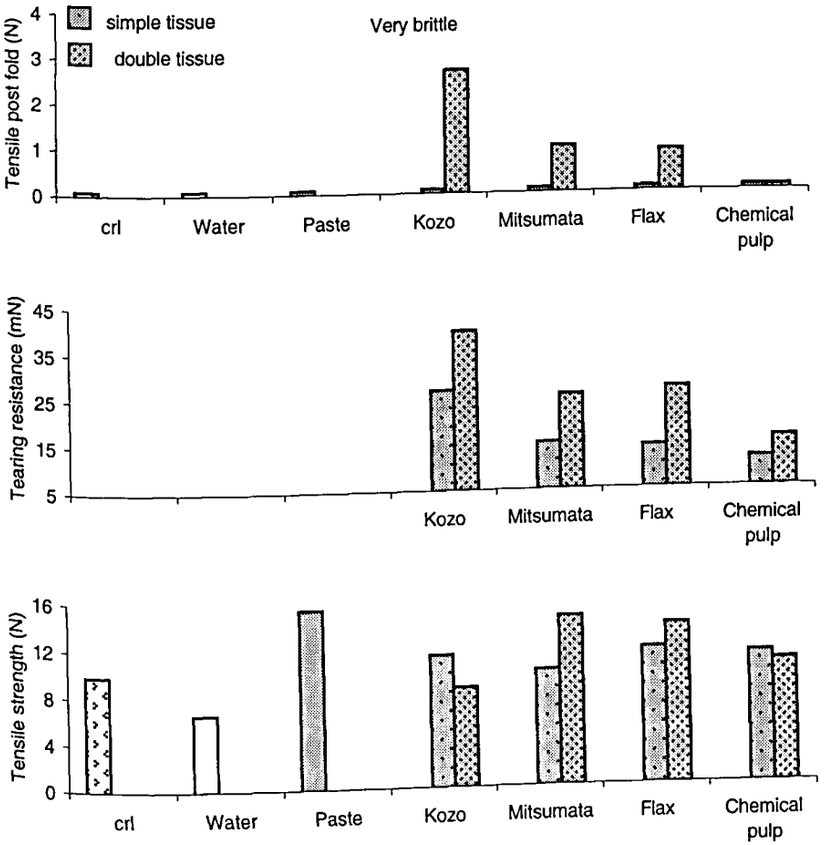

Fig. 12: Mechanical strength of the Very brittle paper.

of course, never describe exactly the aesthetic appearance of an object. But they can introduce some objectivity to this field so widely open to taste and partiality.

We checked thickness, stiffness[12] and the three colour elements of the CIELAB system. The results are given in Table 3.

EVALUATION

On order to put the mechanical strength increase achieved by the different treatments in correlation to the change in sensory qualities inevitably associated to

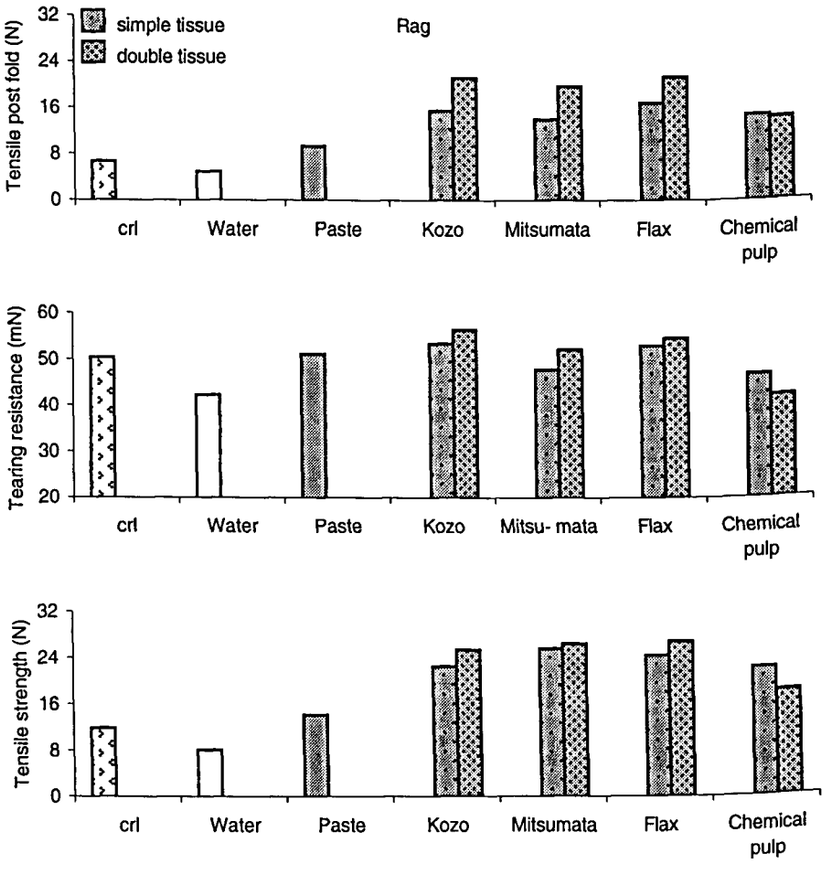

Fig. 13: Mechanical strength of the Rag paper.

them the quality numbers of a certain treatment were compared to the relevant quality number of the untreated sample and reduced by 1:

$$\frac{m_{treated}}{m_{untreated}} - 1 \quad \text{and} \quad \frac{s_{treated}}{s_{untreated}} - 1 \qquad \text{where:}$$

m = mechanical strength number
s = sensory quality number.

The result is characterizing the change achieved by the relevant treatment: >0 meaning increase, <0 meaning decrease. For the sensory tests the absolute values

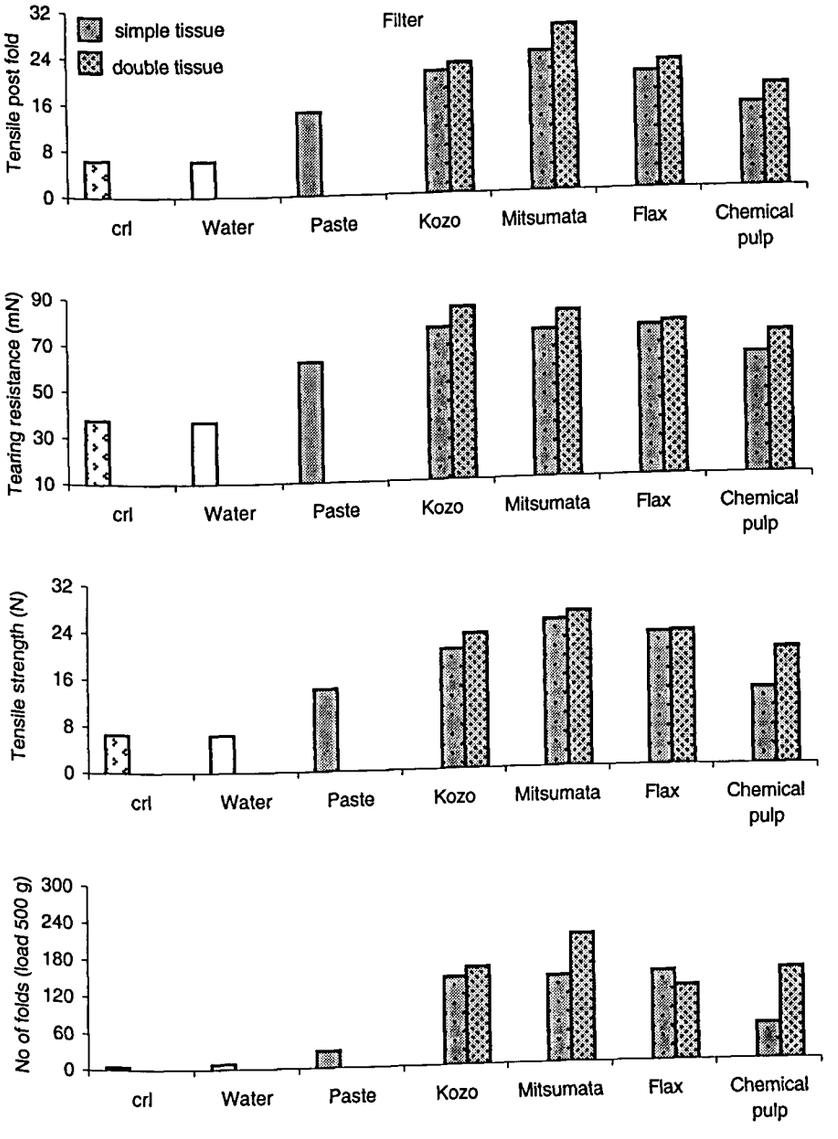

Fig. 14: Mechanical strength of the Filter paper.

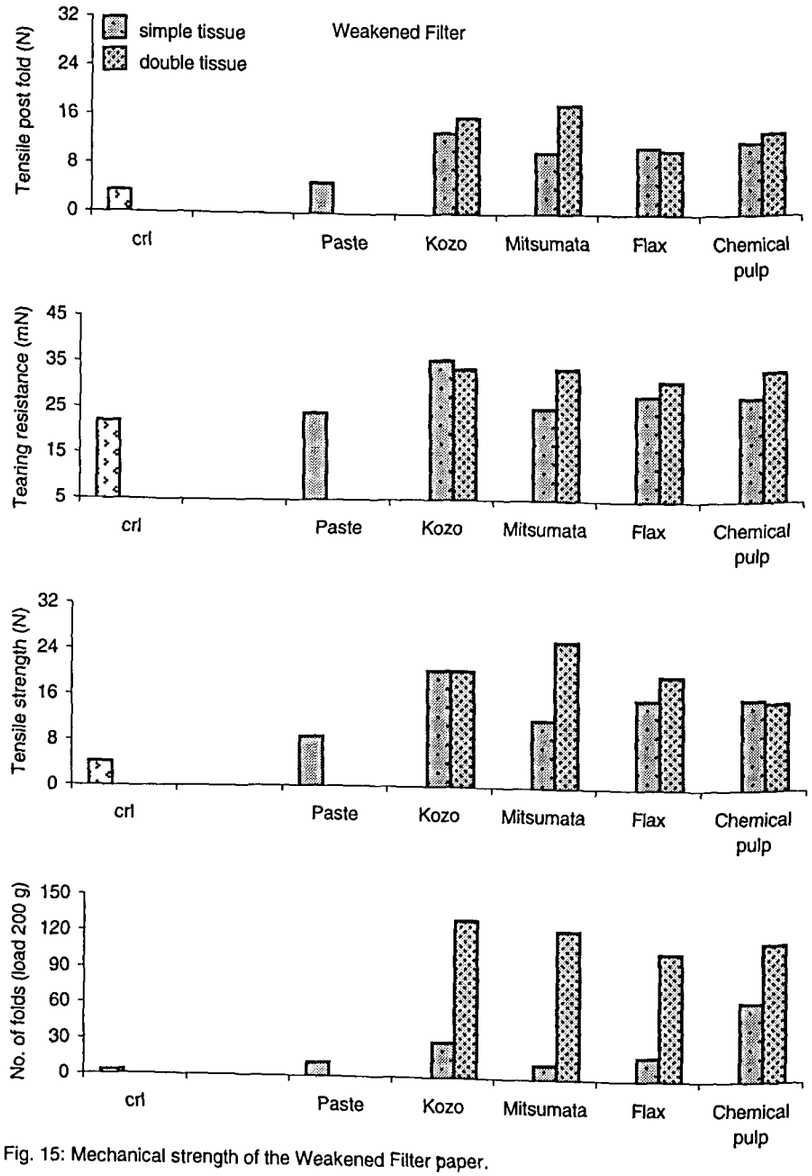

Fig. 15: Mechanical strength of the Weakened Filter paper.

Table 3: Sensory numbers

	ctr	Wa	Pa	K1	K2	M1	M2	F1	F2	Ch1	Ch2
Thickness (mm)											
Brittle	55	60	58	75	83	75	72	64	78	64	67
Very brittly	85	79	87	103	106	93	97	90	99	98	93
Rag	124	132	126	119	125	111	120	122	124	126	113
Filter	151	157	165	106	113	104	111	106	106	110	113
Weakened filter	153		160	143	105	111	105	110	108	108	114
Stiffness (N • mm)											
Brittle	0,31	0,30	0,30	0,50	0,64	0,52	0,54	0,51	0,57	0,39	0,45
Very brittly	2,13	1,86	1,51	2,05	2,31	1,33	1,86	1,32	1,55	1,80	1,42
Rag	0,67	0,74	1,40	1,35	1,69	1,37	1,36	1,31	1,55	0,79	0,60
Filter	1,26	1,06	2,29	1,22	1,88	1,24	1,43	1,23	1,42	1,08	1,14
Weakened filter	0,96		1,91	1,86	1,06	0,70	1,38	0,57	0,70	0,69	0,59
CIE*L											
Brittle	75,66	77,47	73,12	76,51	76,16	77,54	76,75	74,80	73,46	74,52	74,76
Very brittly	73,23	75,22	73,58	73,11	72,91	72,78	73,19	73,22	74,67	73,19	73,31
Rag	89,06	89,04	88,78	88,92	88,75	88,56	87,48	88,69	88,87	88,66	88,78
Filter	93,79	94,01	93,70	93,18	93,33	92,95	92,85	93,14	93,16	93,58	93,70
Weakened filter	94,40		94,16	94,36	93,91	93,70	93,35	94,04	93,84	94,21	94,37
CIE*a											
Brittle	4,71	4,20	4,99	4,51	4,40	5,49	4,07	4,79	5,11	5,02	4,84
Very brittly	4,08	3,60	4,14	4,09	3,77	3,82	4,13	4,05	3,60	4,17	4,11
Rag	0,71	0,88	0,75	0,71	0,83	0,77	1,08	0,75	0,79	0,74	0,82
Filter	-0,23	-0,26	-0,20	-0,16	-0,13	-0,08	0,02	-0,18	-0,12	-0,16	-0,18
Weakened filter	-0,30		-0,32	-0,22	-0,19	-0,26	-0,15	-0,25	-0,26	-0,33	-0,30
CIE*b											
Brittle	20,41	19,51	20,74	19,77	19,16	22,45	18,22	19,97	19,40	21,00	20,70
Very brittly	17,86	17,37	18,18	17,44	16,92	17,08	16,53	17,06	16,45	17,94	17,54
Rag	11,57	12,83	11,73	11,20	11,67	11,44	12,11	11,77	11,82	12,06	11,85
Filter	5,67	4,86	5,50	6,17	6,26	6,69	7,17	6,06	6,18	5,71	5,62
Weakened filter	3,97		4,25	4,52	5,28	5,42	6,25	4,65	5,12	4,79	4,50

of the subtraction are pertaining, because any change is to be rated in the same way, it might mean "less" or "more". If the change indices of the mechanical strength numbers are put into relation to the change indices of the sensory quality numbers, either be subtraction or by division, a single number characterizing the overall quality of a treatment in relation to another one is found. It might be called the quality index. If the average of all sensory change indices is subtracted

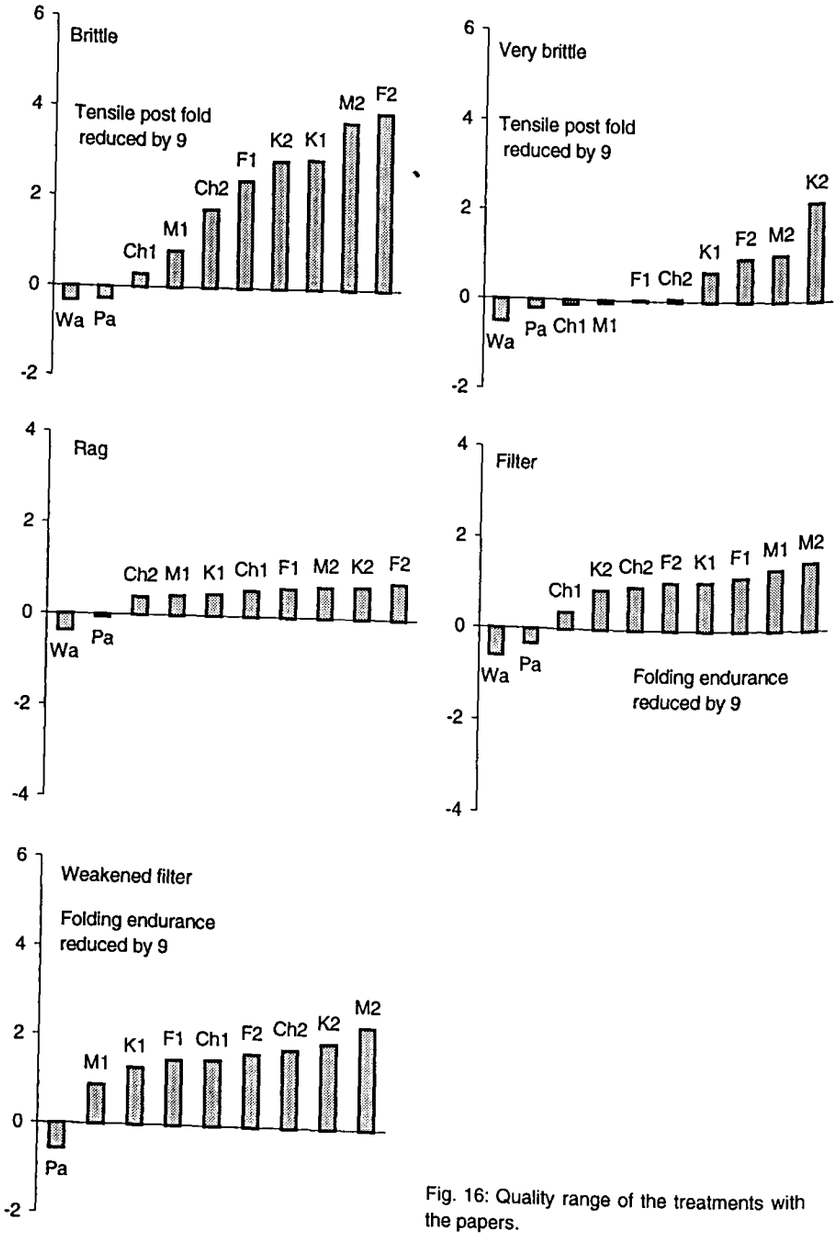

Fig. 16: Quality range of the treatments with the papers.

from the average of all mechanical change indices, 0 is indicating the uselessness of a treatment, positive numbers its positive, negative numbers its negative effect, and the higher the number the better the effect. All these are only relative, a comparison of different treatments.

In mathematic language the formula to evaluate the quality index by subtraction is as follows:

$$\frac{1}{a}\sum_{i=1}^{a}(m_i^{(t)}-1) - \frac{1}{b}\sum_{i=1}^{b}|s_i^{(t)}-1| \qquad \text{where:}$$

m = mechanical strength tests relations, i.e. $value_{treated}$ divided by $value_{untreated}$
s = sensory test relations, i.e. $value_{treated}$ divided by $value_{untreated}$
a = number of mechanical strength tests
b = number of sensory quality tests
t = treatment.

Fig. 16 is giving the quality indices of different treatments with regard to the different papers as range numbers to each other.

RESULT AND DISCUSSION

From tensile post fold, tearing resistance and tensile strength of filter paper (Fig. 14) it becomes evident that any tissue is giving mechanical strength to the paper, the double one more than the single. For this platitude it would not have been necessary to do the tests. More interesting is that, regarding filter paper, *mitsumata* is giving slightly better results, whereas common opinion attributes the better mechanical strength to *kozo*, as supported by some – not all – results with other papers. Obviously different kind of damage is met differently by specific qualities of the different fiber.

Really surprising is the fact that sometimes the single tissue is giving better strength than the double: most often *kozo* (Brittle tensile post fold; Weakened filter tearing resistance, Very Brittle tensile strength). An explanation may be the uneveness of the *kozo* double tissue (cf. Fig. 1), which prevents exact measuring. The same phenomenon with folding endurance for flax tissue on Filter is to be explained with the inaccuracy of the fold test. All mechanical strength tests with flax on Filter gave little differences between single and double tissue. The specific quality of the flax fiber used for this experiment – long and strong, but little fiber-to-fiber bond compared to Japanese fiber – is not an advantage with the good, undamaged Filter.

A result important for practice is that with paper that has suffered decay not only by depolymerization in the course of acid catalyzed hydrolysis, what makes

it weak, but also by crosslinking in whatever chemical course, what makes it hard and rigid, cannot be restored to have the mechanical strength necessary to be used as information carrier. If, based on previous research[6], we assume that the minimum strength for this purpose is 4 N for tensile strength post fold and 30 mN for tearing resistance, we must state that these two numbers have not been reached for the Very brittle paper by any treatment. If such a paper, a paper in the final state of chemical decay, is to be restored by the tissue method, then *kozo* must be used, and the tissue must have a grammage near to that of preproduced Japanese tissue, i.e. 4–6. If it is really necessary to restore such an information carrier in its original format, i.e. in the case of high intrinsic value, it might be better to do it by paper splitting accepting the big change in sensory qualities inevitably connected with this method[1].

A paper having suffered the same kind of decay, i.e. weakening combined with hardening, but not yet reached the final state, what is the case with the Brittle paper, can sucessfully be restored to a state involving usability by a double tissue of any long fiber, *kozo* and *mitsumata* as well as flax. Quite surprising is the fact that this last fiber is giving very good results: if we were not afraid to overinterpret the results of our strength measuring we would say: the best. The specific quality of Japanese fiber, i.e. not only to be long and strong, but also to have a very good fiber-to-fiber bond is not an advantage in this case. Chemical pulp, consisting of shorter fibres and having a fibre-to-fibre bonding capacity comparable to flax is not giving enough strength to a paper damaged as described.

From practical application we knew that mould-damaged paper even in a highly advanced state can be restored by the leafcasting tissue method with surprisingly good result. For this research we tried to imitate such a paper by artificially promoting hydrolysis and oxidation of filter paper. Any of the tissues gave this paper, the Weakened filter as we called it, good strength, while it was below usability limit before treatment. The surprising fact is the little difference between Japanese fiber, flax and even chemical pulp. If we look at the quality range numbers, a superiority of the Japanese fiber becomes evident with the double tissue, *mitsumata* being the best. The double *mitsumata* tissue, however, provokes the greatest paleness of a black background (cf. Fig. 2b) and thus also on the script (Fig. 7c). With the single tissue *kozo* is the best, followed by chemical pulp, while *mitsumata* is at the low end of the range chain.

Relying on the principle that a good conservation technique should show the aspired result only on damaged objects or on its damaged parts while it leaves undamaged ones or undamaged parts unchanged, the very good quality of any variant of the tissue technique can be stated: the Rag paper of the experiment had suffered very little change, and the differences between the different fibers are smaller than worth to be mentioned. This phenomenon is of practical use in

the case of good old rag paper partly damaged by mould. In such a case the undamaged parts will be covered by masks. There will always be a border area where a strengthening tissue would not be necessary. But as it is not changing the appearance of the object, this does not matter.

CONCLUSION

We conclude from our experiment that the tissue method is very well apt for strengthening damaged paper, mainly such one that has become weak and limp, as it is the case with mould damage. Paper embrittled by crosslinking of its cellulose can be strengthened by this method only in a middle state of damage; in the final state – the paper breaks already when it is bended – only a thicker tissue of *kozo* may be useful; such a thicker *kozo* tissue, however, tends to be uneven (cf. Fig. 1). It might be advisable to mix *kozo* and *mitsumata,* at least for the double tissue, so that the unevenness of the first and the tendency to reduce the contrast between black script and white paper of the other (Fig. 7c) will not become too evident. Quite often it is not neccessary to use Japanese fiber laboriously prepared. Good flax fiber may give the same strength, even if the tissue itself, not connected to a damaged paper, is by far weaker than a tissue of same grammage made of Japanese fiber. The capacity of the flax fiber used for the experiment to form fiber-to-fiber bonds could be increased by further beating; it freeness value is only 10. But this would presumably reduce length and thickness and thus the strength of the fiber. Sometimes even chemical pulp fiber, which is demanding the least effort to be prepared and used, is giving enough strength to a damaged sheet of paper. The decision what fiber is the most apt in the strain between least possible effort and best possible result is a matter of individual decision for a well experienced restorer.

ACKNOWLEDGEMENTS

We want to express our thanks to the students of the course 1997/2000 of the *Staatliche Fachakademie zur Ausbildung von Restauratoren für Bibliotheks- und Archivgut* in Munich, who, as part of their being educated how to do and how to understand scientific research, under supervision of the co-author performed a great lot of the mechanical strength and sensory quality tests. Thanks are also to be said to Monika Dreher, who did the chemical tests and preparations necessary for the project.

SUMMARIES

What Fiber for Paper Strengthening?

Overall covering with a thin fiber tissue made in the leafcasting machine is a very effective method to strengthen paper weakened by chemical or biological decay. Recently it has been suggested to use Japanese fiber for paper restoration, what can be adopted also for leafcasting. As Japanese fiber is quite laboriously to be prepared, it seemed advisable to assess their benefit in relation to the expenditure they need.

Different kinds of paper, representing different states of strength as found in library, archive and museum objects, were treated according to the leafcasting-tissue-method, using *kozo, mitsumata,* flax and chemical pulp fiber. Several mechanical strength parameters (tensile strength after one defined fold, tearing resistance, etc.) were checked to assess the benefit, several sensory quality representing parameters (colour, thickness, stiffness) were checked to assess possible negative side effects. The two groups of tests parameters – mechanical strength and sensory quality – were combined by subtraction, what allowed to assess the entire result of a method.

As main result it is stated that the leafcasting-tissue-method is very well apt for mould-damaged paper. For paper not only weakened by acid catalyzed hydrolysis of its cellulose, but also enbrittled by crosslinking, the method is useful only in the middle, not in the final state of decay. Flax is giving nearly the same strengthening effect as Japanese fiber, even if a stand-alone tissue of flax is by far weaker than a tissue of same thickness made of Japanese fiber.

Quelles fibres choisir pour renforcer la durabilité du papier?

La méthode qui consiste à recouvrir le papier d'une mince gaine de tissu fibreux obtenu par laminage s'est avérée être très efficace pour renforcer le papier ayant souffert de détérioration chimique ou biologique. Récemment il a été recommandé d'utiliser des fibres de japon pour la restauration du papier, ce que l'on peut transposer également à la méthode de gainage précitée. Etant donné que la préparation des fibres japon est très laborieuse il est conseillé de considérer l'avantage de leur utilisation par rapport aux efforts investis.

Différentes sortes de papier qui présentent le degré de résistance que l'on trouve dans le papier des bibliothèques, des archives et des musées ont été recouvertes de gaines de différentes fibres : *kozo, mitsumata,* lin et cellulose. Plusieurs paramètres de résistance mécanique (la résistance à la traction après un pliage déterminé, la rigidité flexionnelle et autres) ont été testés afin de pouvoir mesurer l'avantage de plusieurs paramètres représentant des qualités sensorielles (couleur, épaisseur, rigidité) ainsi que d'évaluer les effets secondaires éventuellement négatifs. Les deux groupes de paramètres testés (qualité de résistance mécanique et qualité sensorielle) ont été combinés par soustraction, ce qui a donné un résultat qui permet d'évaluer l'effet global de la méthode.

Il faut constater comme résultat principal que la méthode de gainage par une mince couche de fibre est parfaitement adaptée pour la restauration de papier endommagé par des champignons. En ce qui concerne le papier dont la cellulose n'a pas été atteinte seulement par une hydrolyse catalysée à l'acide mais qui a également été fragilisé par des processus de liaison croisés la méthode est adaptée, mais seulement à un stade intermédiaire et pas au stade final de dégradation. On peut obtenir avec le lin des effets de renforcement quasi-identiques à ceux des fibres de papier japon même si le tissu de lin en-soi est loin d'être aussi résistant à épaisseur égale que le papier japon.

Welche Fasern sind für das Festigen von Papier am besten geeignet?

Das Festigen von Papier durch ein im Anfasergerät hergestelltes dünnes Faservlies ist eine sehr wirksame Methode zum Restaurieren von Papier, das durch chemischen oder biologischen Abbau geschädigt ist. Kürzlich wurde empfohlen, in der Papierrestaurierung Japanfasern zu verwenden. Das läßt sich auch auf das Anfasern übertragen. Da Japanfasern einen beträchtlichen Vorbereitungsaufwand erfordern, erschien es ratsam, eine Vorstellung von ihren Vorteil im Vergleich zum Aufwand zu entwickeln.

Verschiedene Papiere, die den Festigkeitszustand von Papier in Bibliotheks-, Archiv- und Museumsgut repräsentieren, wurden mit verschiedenen Fasern übervliest: *Kozo, Mitsumata,* Flachs und Zellstoff. Mechanische Festigkeitswerte (Bruchkraft nach Falzung, Durchreißwiderstand, u.a.) wurden gemessen um den Nutzen, sinnlich wahrnehmbare Parameter (Farbe, Dicke, Biegesteifigkeit) wurden gemessene um denkbare negative Nebenwirkungen einzuschätzen. Die beiden Gruppen von Meßparametern (Festigkeit und sensorische Werte) wurden durch Subtraktion verbunden, was eine Zahl ergab, die eine Einschätzung der Gesamtwirkung einer Behandlung erlaubt.

Als Hauptergebnis ist festzustellen, daß das Übervliesen zur Restaurierung von schimmelgeschädigtem Papier sehr gut geeignet ist, für Papier, das nicht nur durch säurekatalysierte Hydrolyse seiner Cellulose geschwächt, sondern durch Vernetzungsvorgänge in ihr auch steif und hart geworden ist, aber nur wenn der Abbauvorgang noch nicht das Endstadium erreicht hat. Mit Flachs ist fast die gleiche Festigungswirkung zu erreichen wie mit Japanfasern, auch wenn ein freihängendes Vlies aus Flachs bei weitem nicht so fest ist wie eines der gleichen Dicke aus Japanfasern.

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The Development of a Ready-For-Use Poultice For Local Removal of Starch Paste by Enzymatic Action

by INGRID SCHWARZ, AGNES BLÜHER, GERHARD BANIK, ELISABETH THOBOIS & KARL-HEINZ MAURER

INTRODUCTION

Starch paste was used for mounting together paper objects. It usually can be removed by humidification that causes swelling of the paste to a viscosity that makes detachment of the mounted items possible. The use of alum and animal glue as additives to the paste causes higher adhesive power and embrittlement. It can still swell to a certain extent but due to rather high residual viscosity it cannot be removed without loss of paper. Starch digesting enzymes – amylases – are very useful for decomposing such modified starch paste. Hatton[1] and Chapman[2] describe the application of enzyme-containing gels for this purpose; the application of gels has the advantageous effect that the starch molecule is broken down to smaller water-soluble units thus allowing the detachment of the mounted item is possible with a smaller amount of moisture.

For the detachment of works of graphic art from albums in the Graphic Collection *Albertina* in Vienna mounted with modified starch paste hardly sweling, an enzyme gel of special composition has been developed[3, 4]. Additives to the gel composition make it possible to reduce the enzyme concentration in the gel considerably so that only minimal residues of the enzyme remain in the paper. The transfer of the enzyme to the adhesive point or the mounting adhesive is possible with an extremely small amount of moisture. After local application of the gel, residues consisting mainly of decomposition products of starch can be removed by means of moist cotton swabs. Washing after treatment is not necessary.

As it is difficult to produce the gel and as its efficacy will last only for limited time the idea arose[5] to develop a ready-for-use poultice and a technique for its effective use. After having investigated the behaviour of modified starch paste a number of poultice materials and the application techniques for poultices have

been tested. A number of test samples have been analyzed for the amount of residual enzyme and detergent before and after accelerated ageing. The goal of the research was to develop a technique for routine application. The poultice developed in this way has been used not only for objects in the *Albertina*, but also for objects of other collections: *Kupferstichkabinett* of the *Hamburger Kunsthalle, Kupferstichkabinett Dresden, Goethe- und Schiller-Archiv* of the foundation *Weimarer Klassik*. Thus the method was developed to an optimum.

Damage

Huge amounts of objects mounted by means of starch paste are to be found in every graphic collection, archive and library. Wheat starch paste was considered a suitable mounting adhesive because of its well-known adhesive power and its permanent elasticity. A further advantage of the starch paste is easy removability which can be realized by swelling using moisture even after centuries of natural ageing. Removal of adhesive joints is always necessary if an antiquated mounting has to be changed.

Pure starch paste keeps well only for a limited period. Therefore, as early as in the beginning of the 19th century several additives were used to achieve a better durability. Alum, $KAl(SO_4)_2 \cdot 12\ H_2O$ can prolong the durability of starch paste for several weeks or even months. Depending on its amount, the pH of the paste is reduced to < 5; its receptivity to water after drying is reduced as well; it becomes brittle and hard to swell. To improve the adhesive strength, proteinous substances are added. Animal glue is hardened by alum thus reducing even more the ability of the paste to swell.

Those recipes are not recommended for mounting valuable objects[6]. If the humidity in the surrounding air is changing, the reduced swelling ability of hardened paste can result in damage. An originally unsized paper becomes to a certain extent locally sized within the area where the hardened paste is applied, which results in tension, formation of folds (cf. Fig. 1), cockling and creases (Fig. 2).

Starch paste

The main component of the paste used for mounting is starch, a polysaccharide photosynthesized by green plants. The macromolecules are built up of α-D-glucopyranose. Every two of these units are combined by exuding one molecule water. In contrast to cellulose, the units of which are combined in β-glucosidic

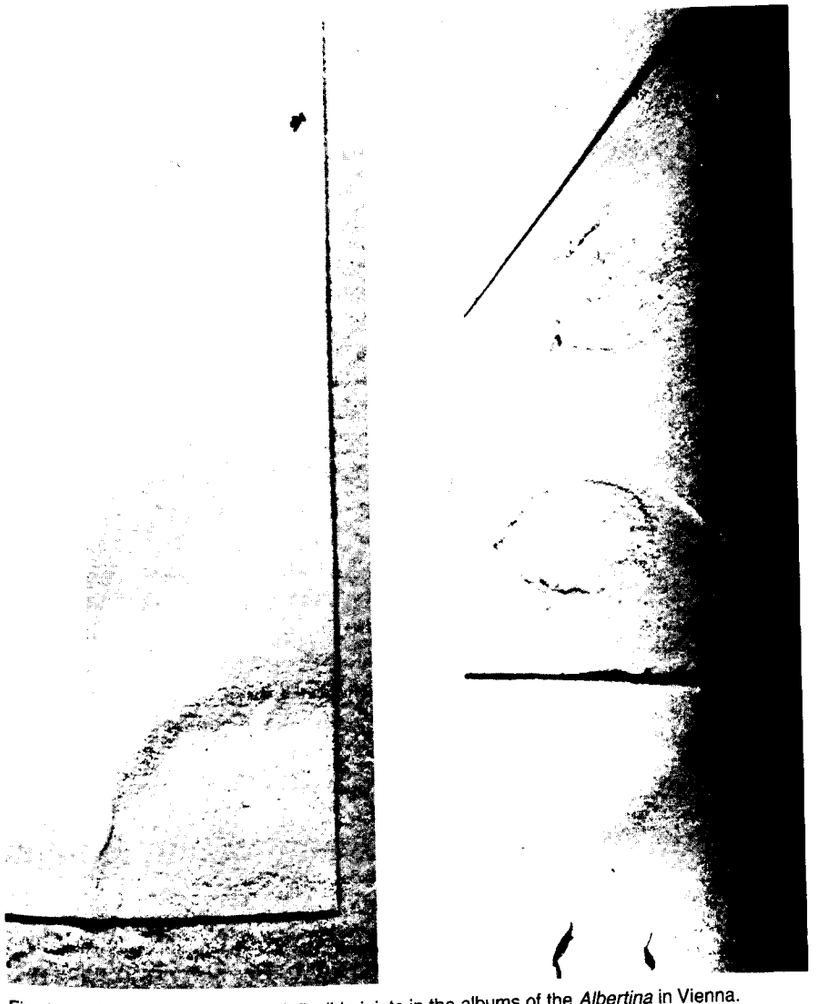

Fig. 1 and 2: Damage caused by inflexible joints in the albums of the *Albertina* in Vienna.

bonds, those of starch are exclusively α-glucosidic[7]. The formation of starch from glucose can be described by the following formula:

$$\underset{\text{glucose}}{n\ C_6H_{12}O_6} \rightarrow \underset{\text{starch}}{(C_6H_{10}O_5)n} + \underset{\text{water}}{(n-1)\ H_2O}$$

The main components of starch are amylose and amylopectin. Amylose is a linear polymer of anhydroglucose units liked together by α-1,4-glucosidic bonds.

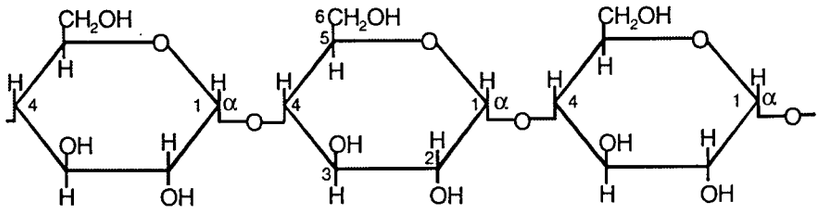

Fig. 3: Model of a chain-formed molecule of amylose.

The degree of polymerisation (DP) ranges between 250 and 1000 (average 300 to 400). The amylopectin has a branched structure with each of the branches as an amylose (with about 25 anhydroglucose units) but branching occurs through α -1,6 linkages, occasionally through α -1,3 glucosidic linkages. The average DP of amylopectin is higher than the one of amylose[8]. The proportion of these two components is variable for the different sources with consequences for the properties of different starch pastes.

The decomposition of modified, embrittled starch paste leading to liquification of the adhesive joint can be achieved by starch-digesting enzymes. Traditional techniques of humidification, e. g. the application of GORE-TEX™ humidifying poultices or hot steam failed to soften the adhesive joint to a sufficient extent. In case the adhesive joint is very hard and difficult to be penetrated by water even the application of enzymes causes problems and requires additives such as wetting agents and penetration aids.

Enzyme activity

Enzymes are proteins which act as catalysts. They are produced exclusively by living cells. Their catalytic activity is highly specialized in so far as one special enzyme is only able to transform one specific substance which is called the substrate. Any metabolic process is based on enzymatic reactions. Enzymes are produced industrially by isolation from several organisms. As catalysts they are not consumed in the course of the chemical reaction. They accelerate a specific reaction, e. g. the polymerization of a macromolecule such as starch without producing by-products. The effectivity of an enzyme towards the substrate is technically expressed in activity units[9].

Enzymes are only active as catalysts in the presence of water, that means that for any enzymatic reaction a certain amount of water is indispensable. Water has the function to undergo reactions with the functional groups of the enzyme thus

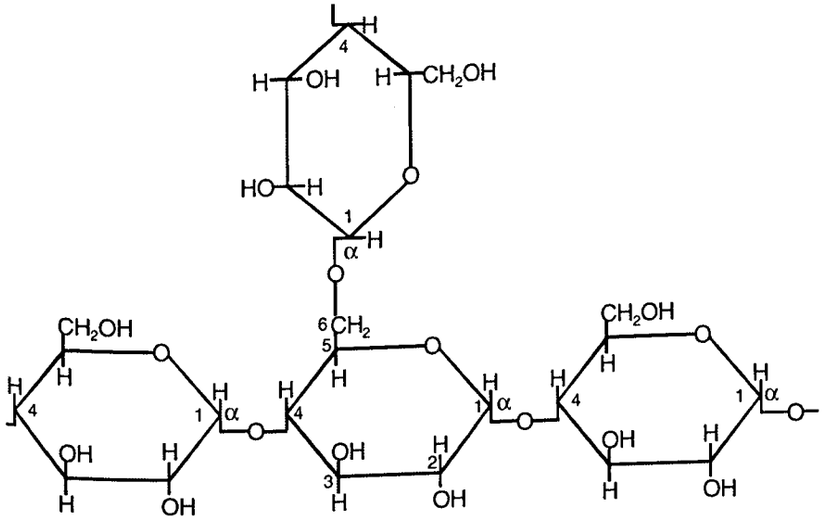

Fig. 4: Model of the molecular structure of amylopectin.

causing the development of enzymatic activity. If the enzyme catalyses the hydrolysis of the substrate, i. e. the depolymerization of starch, water is consumed in the course of the reaction. Under conditions that might be described as dry, the function of the enzyme is only possible as long as the essential layer of water within the reaction area is not removed[10].

Enzymes can only be used at moderate temperature and pH. Each enzyme has a characteristic pH and temperature optimum for the development of maximum activity. Therefore the reaction catalyzed by an enzyme is strongly dependent on these two parameters. The optimal pH range for starch-digesting amylases of animal origin ranges between 4 and 8, for amylases of microbial and plant origin it ranges between 4 and 10 with an optimum at pH 5[11]. The temperature optimum ranges from 25 to 30 °C.

Enzymes are deactivated by several water-miscible solvents like ethanol or acetone, by highly concentrated aqueous urea solution and by several detergents. Heavy shaking, so that foam is produced, can deactivate dissolved enzymes as well as extreme temperature and pH. Heavy metals (iron, copper, mercury, lead) causes an enzyme to precipitate. The deactivating process consists in disturbing or destroying the three-dimensional protein structure that is characteristic for enzymes. Some functional groups, essential for the catalytic activity, are modified, thus deactivating the enzyme[11, 12, 13].

Amylase

The key quality of enzymes is their characteristic. In a way that can be compared to the function of a key in a lock the enzyme is taken up by the substrate at specific parts of the molecule thus forming enzyme-substrate complex. The next step is splitting-off the macromolecule of the substrate to smaller units: in the case of amylases the starch molecule to oligosaccharides and maltose. The enzyme molecule is set free and can do its work at another part of the macromolecule.

Amylases are a sub-group of the glucosidases, i.e. enzymes that are able to split-off specifically the molecules of carbohydrates or glucosides. α-amylases catalyze the hydrolysis of α-1,4-glucosidic bonds in polysaccharides, and this also in the inner area of the substrate. This ability gives them their name: endo-enzymes. As a result of their activity the viscosity of a colloidal solution of starch is significantly reduced, but in the first stage of activity only little maltose is produced. In a later stage maltose in the α-form is produced, hence the name: α-amylase. β-amylases are exo-enzymes: only the monomer units at the two ends of the molecule chain are split-off as β-maltose. β-amylases liquefy the substrate, α-amylases produce sugar[11]. With α-amylase the viscosity of starch is reduced more quickly; the colour of iodine-potassium iodide solution, indicating the chain length of the starch molecules, becomes less intensive, the adhesive property of the starch is reduced within shorter time. Therefore α-amylases are preferred for application in paper restoration[14]. Cellulose is not decomposed by amylases; its β-1.4-glucosidic bonds are not accessible for the enzyme.

The optimum temperature of the α-amylase used for enzymes poultices is 60°C; the enzyme remains active up to 80°C and even higher temperature. It is a highly purified, stable microbial amylase.

Developing the Enzyme Poultice

As in the case of the *Albertina* albums, all traditional and mechanical methods to liquefy or remove the starch did not work satisfactorily, we concentrated on enzymes. Their main advantage is that no other by-products than the decomposition substances of starch are formed. The amount of water, essential for any catalytic reaction with enzymes, can be reduced to a minimum. The procedure, always done according to a specific pattern, has been described by Blüher et al.[3] and Fürst[4]. The gel has been applied onto an interleaf paper positioned directly on the objects mounted together. Thus only the enzyme (and the additives enhancing its activity) can penetrate to the place where they are needed; the gel-forming substance is retained.

This gel-forming substance is a cellulose ether. It contains the enzyme and a little amount of additives stabilizing the mixture and enhancing the activity of the enzyme. Theoretically, any restorer could prepare that gel for himself. Practically this is not an economic way because of the short shelf life thus prepared. This led to the idea of developing a ready-to-use enzyme-containing poultice which can be stored for a longer time. In principle such a type of poultice consists of a synthetic non-woven which has been infiltrated with the enzyme-containing gel and dried. Under dry and cool conditions these materials can be stored without losing enzymatic activity. Activation of the enzymatic action is possible by moistening of the non-woven.

If the gel is put directly onto the interleaf paper it is not possible to locally apply weight pressure. The gel would expand beyond the area where the two papers to be separated are mounted together. If it is embedded in the non-woven, a strictly local application is possible; pressing down the poultice using a weight is always necessary; especially if the excess starch to be removed has caused distortions of the paper in the area of the adhesive joint.

Experimental Part

In order to find an application technique and to investigate the necessary time for separation of papers mounted with starch paste adhesives the following test procedures have been undertaken:

Samples of two papers (machine made deckle edge, 150 g/m²), different with regard to their water permeability were joined together in an area of 3 x 3 cm by means of starch paste which has been prepared from 50 g wheat starch in 400 ml water. 7,5 g animal glue dissolved in 50 ml water and 4 g potassium aluminium sulphate in 50 ml water have been added subsequently. In relation to the dry weight of starch the amount of the additives expressed in percent is 8% for alum and 15% for protein glue.

The samples were submitted to accelerated ageing in a climatic chamber *Heraeus Vötsch HC 0020* according to ISO Standard 5630/3 (80°C 65% RF) for seven days. Enzyme poultices as described below were put onto the joints. After 15, 30, 45, 60, 90 and 120 minutes it was tested whether the samples could be lifted off with tweezers without leaving behind any fibre. These tests were done to check effectivity at 30 min as the shortest and 120 min as the longest duration.

Application

Two sheets of paper mounted together by means of starch paste are often more or less distorted in the area of paste application. The enzyme poultice should be applied locally only onto this area in order to avoid contamination of the treated item.

The enzyme poultice consists of three layers:

- a synthetic non-woven (polypropylene impregnated with an enzyme-containing gel)
- an interleaf paper
- a water retaining material

Firstly the interleaf paper is positioned in the area of the joint. This interleaf paper is not permeable for the gel forming components thus preventing migration of the gel into the original. On top of the interleaf paper the enzyme-containing poultice is positioned. The poultice should have the size of the adhesive joint while the interleaf paper below should protrude at least 2 mm on each side of the poultice. The third layer is a water retaining material, e. g. blotting paper or capillary matting cut in the same size as the poultice. An illustration of the poultice under working conditions is given in Fig. 5. Before application all components of the enzyme poultice have to be wetted by means of a brush. The wetting of the polypropylene non-woven in a size of 4 cm^2 requires about 0,08 ml water. The equivalent size of the water retaining material requires about 0,8 ml. On top of the poultice a waterproof foil (Mylar™) is positioned in order to prevent the drying out of the poultice during the time of the treatment. The mylar foil is protruding from the poultice 4 cm on each side and the whole is weighted down by 10 to 15 g/cm^2. After 5–10 min it should be checked whether there is a direct contact between poultice and joint anywhere and whether enough moisture is penetrating from poultice to joint. The time necessary for detachment depends on the penetrated moisture, the wettability of the paper, and the condition

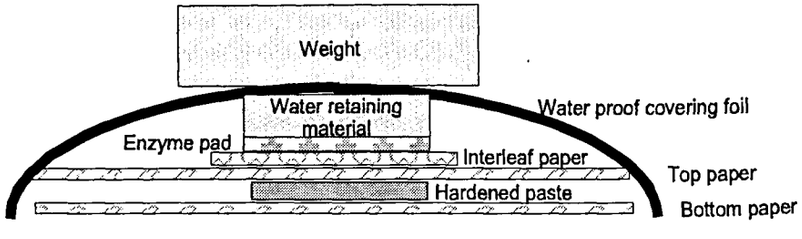

Fig. 5: Structure of the enzyme poultice.

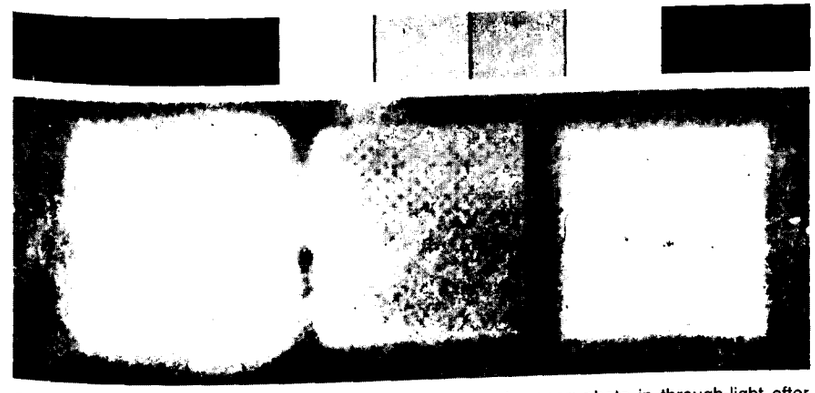

Fig. 6: Comparing different poultice materials using starch paper: photo in through-light after 20 min. Left: most even and efficient activity.

(thickness and brittleness) of the starch. Too much water will result in water stains, too little in inactivity of the enzyme.

Poultice material

In order to chose the most suitable materials for the three layers of which the poultice is composed it was necessary to evaluate the effectiveness of the enzyme action in relation to the materials used. Enzymatic activity can be evaluated by means of the starch–iodine reaction. For the test a filter paper impregnated with 0,2 % potato starch (soluble in cold water). This test paper is dipped in 0,01 % iodine-potassium iodide solution, thus causing an intensive blue staining. The application of an amylase poultice on the stained sample is resulting in loss of the blue staining as more as starch present in the test paper is decomposed (cf. Fig. 6).

Interleaf paper

The function of the interleaf paper is to prevent the gel within the polypropylene non-woven from migrating into the object under treatment. The interleaf paper must guarantee the penetration of humidity into the item in an equal and even manner, thus transporting the enzyme and the additives to the adhesive joint. It should be neutral so that the activity of the enzyme is not influenced. The most suitable material proved to be very thin cellulose tissue paper.

Choice of non-woven for enzyme impregnation

Criteria for selection:

- no swelling, not becoming unstable when wetted
- no water soluble components nor additives
- flexible, so that it adapts to uneven surfaces
- mechanically strong enough to be impregnated in a machine
- water retaining capacity just high enough for retaining an suitable amount of gel and low enough to set free the necessary amount of enzyme with a minimum of water

It was found that the higher the grammage of the synthetic non-woven (polypropylene), the lower its water retaining capacity and the higher its gel retaining capacity. It might be assumed that a higher grammage, which means a higher enzyme content within the non-woven material, would result in higher activity and shorter treatment times. Contrary to that, the results of the tests showed that a thinner material (i. e. lower grammage) with lower enzyme content works more quickly and more effectively. It can be concluded that the amount of gel within the non-woven is not the crucial criterion. Of greater importance is the ability of the non-woven to hold water and to allow even transfer of humidity to the area of application.

Water retaining material

As it may be necessary to let the enzyme work for a period of up to two hours, the enzyme poultice must be kept evenly wet for this time. This is the function of the third layer of the enzyme poultice. A highly flexible synthetic non-woven can be used for this purpose as well as a blotting cardboard of suitable thickness.

RESIDUES WITHIN THE PAPER

A criterion of high priority for the work in the *Albertina* was to keep the objects free of possibly harmful residues in a mimimal time consuming procedure. The amount of decomposed adhesive and other components resting on the objects after having them removed from their undesired support by washing and by dabbing the substance off using cotton swabs has been investigated. Cleaning by means of cotton swabs was the most efficient procedure.

Table 1: Analysis of enzyme and detergent residue of test samples dissolved using the enzyme poultice.

Sample	Cleaning procedure	Time for Enzyme Poultice Application	paper of mounted item	Enzyme residue*	Detergent residue*
1	no cleaning	105 min	top	6.1	29.7
2			bottom	3.2	10.8
3	cleaning with cotton swab	90 min	top	5,6	25
4			bottom	2,3	6,8
5	washed in demin. water 2x15 min	90 min	top	<0, 2	7,4
6			bottom	<0, 2	2,7
7**	no cleaning	105 min	top	7,6	46,7
8			bottom	4,5	13,5

* µg / 3 x 3 cm paper
** no interleaf paper

For checking the amount of enzyme residue the test samples described above were used. Additionally they were checked for possible discolouration after accelerated ageing. Three sets of test samples were made: two for checking possible residues, one for accelerated ageing.

Amylase Residue

Amylase residues have been determined through amylase activity according to the procedure described by Bernfeld[15]. The test samples after enzyme application and dabbing-off solubilized substance were blended and buffered to pH 8.0. After 30 min and suitable mixing, the paper was filtered off and a certain amount of the filtrate was checked for the capacity to decompose starch to sugar. For testing the presence of sugar the dinitro salicylic acid reaction was used. The amount of sugar formed by the filtrate is an indication for the quantity of enzyme still active; it can be correlated to the amount present in a poultice.

Generally, the amylase residues found in this way are very low. Table 1 is giving the measured results for the top paper, where the enzyme poultice has been applied, and for the bottom paper, from where the solubilized starch residues have been removed. Several checks have been done over a longer period of time[3-5]: altogether more than 80. From the very low numbers it can be concluded that it would not be necessary to inactivate the enzyme residue. Higher residue, i.e. 7,6 mg / 9 cm² application area is to be observed if the enzyme poul-

tice had been used without interleaf paper (Table 1 sample 7), what therefore should not be routinely done. Residue numbers of an application suggested for routine use, i.e. with interleaf paper and followed by removing the solubilized or softened adhesive using cotton swabs are 5,6 and 2,3 mg / 9 cm^2 application area (Table 1 test sample 3 and 4). This final cleaning seems to be effective; it is resulting in reduced residue by 8,2% or 28,1% resp. (Table 1 sample 3 and 4 vs. 1 and 2). Residues could be totally removed or, more correctly, the residual amount of enzyme is below the detection limit of the analytical procedure in cases the papers are washed after treatment. There is more residue in the paper which lies directly under the enzyme poultice. This effect was proved to be stronger with detergents being present as additives. If the enzyme poultice is applied on the reverse side of the item – that means on the support – then the residues are mostly kept within the support and the contamination of the original can thus be minimized.

Detergent Residue[*]

For analyzing possible detergent residue samples of 9 cm^2 were cut to pieces of 1–2 cm^2 and extracted for 30 min in a methanolic ultrasound bath. The extract was analyzed chromatographically. Detergent residue is significantly higher than that of enzyme – obviously, because more detergent has been used for the poultice preparation than enzyme. The highest number is 46,7 µg / 9 cm^2 application area: found if the enzyme poultice has been used without interleaf paper and without final cleaning (Table 1 sample 7). The lowest number is 6,8 µg / 9 cm^2: found in the lower paper after standard application. Washing results in minimizing, but not eliminating the detergent residue totally. Again it seems to be advisable to use interleaf paper and to apply the enzyme poultice onto the support paper instead of the art object.

Accelerated Ageing

After separation some of the samples have again been submitted to accelerated ageing. As no discoloration was found in its course the result of enzyme analysis was supported; enzyme residues would have brought about a brownish discoloration. Detergent residues cannot be proved this way. However, if the poultice

[*] The analysis for detergent residues was done by Dr. M. Schmitt, Henkel KGaA, TTA Zentrale Analytik, Düsseldorf.

is used without interleaf paper, the adhesive residues have not been removed or if the area of enzyme application has not been cleaned, then discoloration appears. Therefore such a cleaning is highly advisable. It can be done effectively using cotton swabs.

If the enzyme poultice is applied correctly, the amount of moisture brought into the object is so low that formation of water stains or reactions at the wet/dry interface as described by Dupont[16] is highly unprobable. The addition of 5 % alcohol to the water used for wetting the enzyme poultice even minimizes this danger.

Checking DP[**]

The average degree of polymerization was checked in order to find out whether either the enzyme or the detergent would contain substances that can depolymerize cellulose. Filter paper (Whatmann # 1) was impregnated with a defined amount of amylase, respectively detergent, and subsequently artificially aged using a dynamic ageing technique at 90 °C with changing humidity between 80 % to 35 % every three hours. The artificial ageing had a duration of 6 or 12 days. For reference the paper has only been impregnated with demineralized water.

The DP of the test paper before ageing was 1804; after 6 days of artificial ageing the DP was reduced to 85,5 % of the original value and after 12 days of ageing it was further reduced to 63 %. The data measured at papers impregnated with amylase or detergent showed no significant difference. It therefore can be concluded that neither the enzyme nor residual detergents cause depolymerization of the cellulose.

Treatment of Works of Graphic Art & Autographs

In the Vienna Graphic Collection *Albertina* the collection of 19th century prints, mainly engravings and lithographs is stored in so called *Klebebände* (albums) – bound volumes consisting of ca. 200 leaves onto which the prints are mounted by 6–12 droplike spots of starch paste.

The same technique for mounting and storage of works of graphic art has been used at the Dresden Graphic Collection (*Staatliche Kunstsammlungen Dresden,*

[**] The analysis of DP was done at the Institut für Makromolekulare Chemie der Technischen Universität Darmstadt according to EWNN method: Zellcheming Merkblatt IV/50/69.

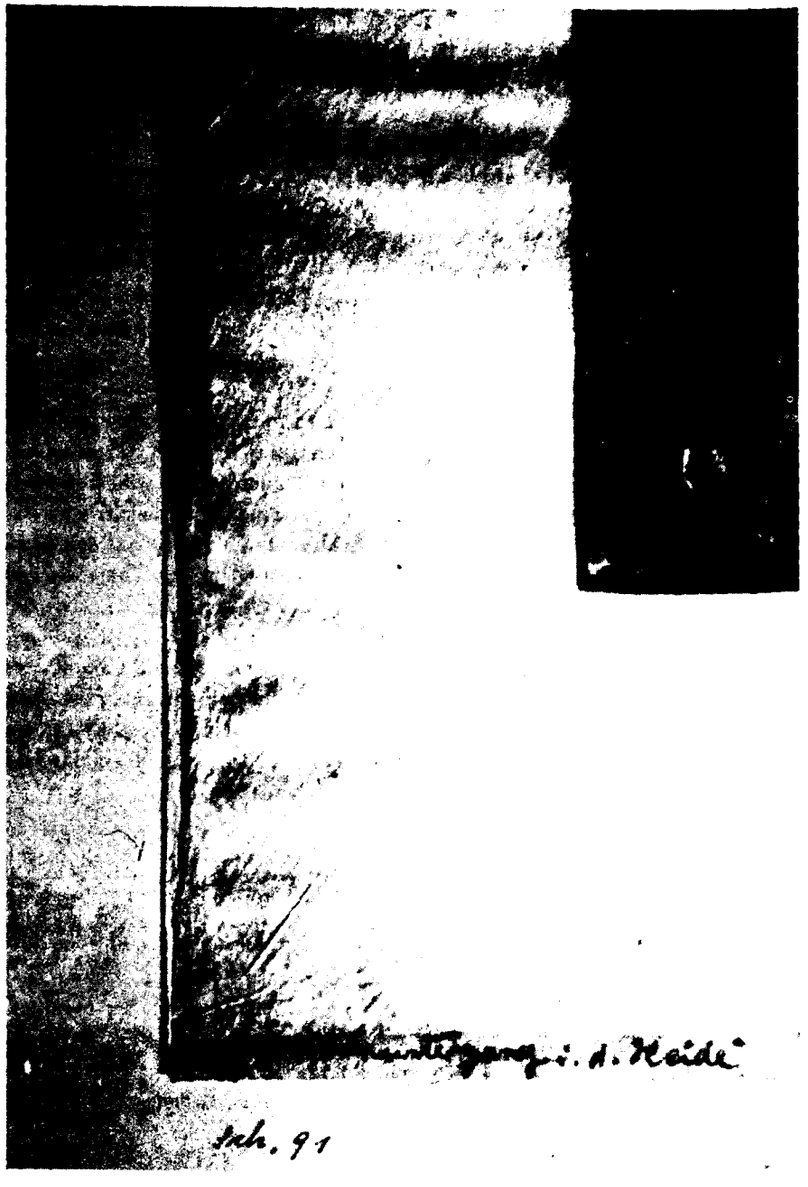

Fig. 7: Detail of a work of graphic art mounted on cardboard which shows heavy distortions as result of the mounting technique.

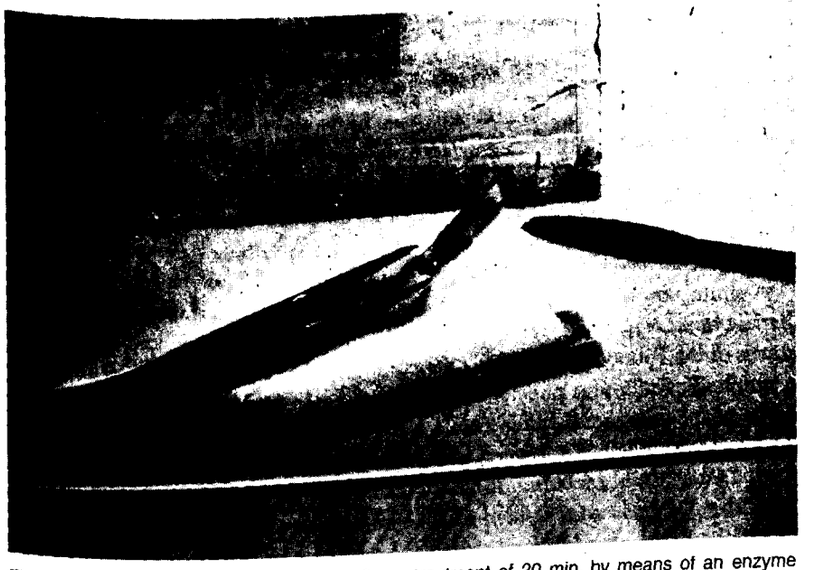

Fig. 8: Detachment of a mounting strip after a treatment of 20 min. by means of an enzyme poultice.

Kupferstichkabinett). In both collections a modified starch paste with alum and protein glue as additives as additives has been applied as mounting adhesive. The additives originally had the function to improve the shelf life of the prepared paste and its adhesive power. As already mentioned, such a modified starch paste becomes brittle and inflexible towards changes in the relative humidity. These properties of the adhesive cause tensions in the mounted originals. A large number of them shows distortion, strong folds and even creases are often the result. Hundreds of thousands of items in both collections are damaged or endangered in that way to a different extent. The enzyme poultice described in this contribution has been originally developed in order to allow an efficient dismounting of the endangered objects from their support. In view of the enormous amount of items to be treated it was necessary to develop a fast and economic technique demanding only restricted manpower.

In the *Kupferstichkabinett* of the Hamburg *Kunsthalle* works of graphic art are mounted in passepartouts and stored in boxes. The original mounting was done with strips of Chinese paper tissue glued with paste containing some alum or along the four edges of the sheet: a method suggested in 1916 by H. W. Singer[17]. Today the sheets have become very cockled (Fig. 7) because of the changed ca-

pability to swell or to extend according to the surrounding humidity in the areas where the paste has been applied. Because the wavy distorted objects, coming in contact with the other adjacent items, suffer from abrasion on the surface greatly damaging printing inks, it is necessary to remove the original mounting. This allows the intervention of flattening the endangered items. In this case the problem of dismounting the item becomes even more severe because of the sensitivity of the very thin original papers. Although the paste is principally swellable by humidity the residual viscosity of the softened paste makes detachment of the original without fibre losses impossible.

A similar problem is presented by the collection of autographs of the author *Karl Benedikt Hase* (1780–1864) which are owned by the Goethe and Schiller Archives of the Foundation *Weimarer Klassik* in Weimar. These autographs consist of a number of different papers. The text is written with iron gallotannate ink. Some of the autographs suffer from ink decay. The autographs have been folded and mounted together at several points by means of a starch paste thus forming sections that could be bound to a book. The binding technique, the stitching of the formed quires and the glueing of the book spine with protein glue caused severe destruction of the autographs if the book is leafed through. It was therefore necessary to separate them to single sheets again.

Different kinds of paper and paste had been used in these cases regarding thickness, wettability and state of ageing etc. The dismounting of these items by means of enzyme poultices could be successfully carried out. The treatment time differed strongly according to the brittleness and wettability of the paste and the capability of the paper to absorb humidity.

The detachment of works of graphic art from the albums in the Graphic Collection *Albertina* was carried out within treatment times ranging between 60 and 120 min. In this case a localized treatment within the book on the adhesion points was necessary. A treatment time of only 20 min. was necessary to remove the mounting strips from works of art on Chinese paper at the *Kunsthalle Hamburg*. In this case the enzyme poultices have been cut in the dimension of the adhesive layer along the edges of the object and had been positioned on the mounting strip (i. e. the reverse side of the original). With very low moisture in the poultice it was possible to localize humidification, swelling and enzymatic action to the adhesive layer. The original, although printed on highly wettable and sensitive paper remained nearly dry and could be separated without any losses.

The autographs of Karl Benedikt Hase in the Goethe and Schiller Archives of the Foundation *Weimarer Klassik* have been treated with very low humidity in order to prevent any negative influence of moisture to iron gallotannate inks being present. Therefore the detachment could only be realized after a three hour treatment time. It should be mentioned that in the areas of ink writing, even in

cases where the ink had already decomposed the paper, no changes such as e. g. migration of ink components, bleeding or creases in the ink strokes could be observed.

To enable wider application of the enzyme poultice, e. g. for the detachment of paper relinings of textiles or photographs additional experimental work is necessary in the future. The treatment of photographs with •-amylases in order to remove relinings presents a special problem since it has been observed by Preiss[18] that, especially immersion treatments can affect the gelatine layer. The application of ready-for-use amylase poultices which need only small amounts of humidity may be a suitable solution for this problem.

Conclusion

The ready for use amylase poultice has proved to work successfully, i.e. to remove hardened starch paste and backings with a minimum of moisture, in different collections, for different objects, including large formats. Its main advantage is that it remains usable for at least a year, that it can be used without further equipment in any workshop and that its application can be controlled. In contrast to the older technique, i.e. putting the gel-containing enzyme onto an interleaf paper positioned on the object, very little residues remain in the objects. From the analytical results reported above it can be concluded that washing the objects after treatment may be advisable, but not indispensable. Of high importance for the application of the enzyme poultice is the use of interleaf paper in order to prevent the migration of the gel from the poultice to the original. Of further importance is the removal of the softened of liquefied residues of the adhesive combined with a local cleaning procedure of the treatment area. Denaturation of enzyme residues within the original item by means of hot water, alcohol or other techniques is not necessary due to their negligible amounts[19].

Application of the amylase poultice is recommendable in all cases where embrittled starch paste adhesives cause severe problems during the separation of original mountings. In addition, the method is advantageous for the detachments of very soft papers because of the liquification of the paste which allows gentle detachment without fibre losses. The low manpower necessary for the application of the technique allows economic treatment of large amounts of items. A further advantage is the fact that no after treatment such as washing and flattening is necessary.

The ready-for-use enzyme poultice is patented and is obtainable by suppliers of conservation materials.

ACKNOWLEDGEMENTS

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SUMMARIES

The Development of a Ready-For-Use Poultice For Local Removal of Starch Paste by Enzymatic Action

An enzyme poultice for local removing brittle and hardened starch locally with a minimum of moisture has been developed. The recipe for the gel containing enzyme and the way of application aims at reproducible results to be obtained in a short time. The enzyme poultice is available ready for use and can be activated by adding water. It enables the dismounting of large batches of mounted sheets without further treatment. It is essential to use the poultice in the way described together with an interleaf paper. Contamination of originals due to the treatment can be minimized in this way.

Mise au point d'une compresse aux enzymes destinée à dissoudre localement les amas d'amidon

Une compresse aux enzymes a été mise au point afin de pouvoir dissoudre localement avec un minimum d'humidité les amas cassants et durçis d'amidon. La recette du gel contenant des enzymes ainsi que la technique d'application ont été mises au point dans l'objectif de permettre d'obtenir des résultats rapides. La compresse aux enzymes est livrée prête à l'emploi, pour l'activer il suffit de la tremper dans l'eau juste avant de s'en servir. Ceci permet de détacher aisément de grandes quantités de feuilles collées les unes aux autres sans autre traitement supplémentaire. Il est important de respecter le mode d'emploi indiqué, c'est-à-dire d'utiliser une feuille intercalaire. Ainsi il est possible de réduire les résidus au minimum.

Die Entwicklung einer gebrauchsfertigen Enzymkompresse zum lokalen Lösen von Stärkeverklebungen

Eine speziell entwickelte Enzymkompresse erlaubt die lokale feuchtigkeitsarme Ablösung von versprödeten Stärkeverklebungen. Die Rezeptur des Enzymgels sowie die Anwendungstechnik wurde mit dem Ziel entwickelt, reproduzierbare Ablöseergebnisse in zeitökonomischer Arbeitsweise zu ermöglichen. Die Enzymkompresse liegt als Fertigkompresse vor und wird vor Gebrauch durch Wasser aktiviert. Die Arbeitstechnik erlaubt auch die Bearbeitung größerer Bestände ohne aufwendige Nacharbeiten. Voraussetzung dafür ist die Verwendung der Kompresse nach dem vorgeschlagenen Kompressenaufbau unter Verwendung eines Zwischenlagepapiers. Damit können die Rückstände auf ein Minimum beschränkt werden.

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An Irish Gospel From the Eighth Century
Investigation and Conservation

by SVETLANA DOBRUSINA, DENIS TSYPKIN, NADEZHDA KULIKOVA & TATYANA VELIKOVA

Introduction

In 1997 the parchment manuscript F.v.I.8 from the collection of the Manuscript Department of the National Library of Russia (NLR), called *Irish Gospel*, created in England in the eighth century, came to the Document Conservation Department of the library. *Irish Gospel* is a unique literary monument.

The manuscript[1] contains 215 sheets of parchment of 34.5x24.5 cm with the text written in two columns on both sides of a sheet with iron-gall ink. The sections of the manuscript consist of 4–5 sheets lined with a sharpened tool. The pin-holes for line marking are seen on many sheets. It contains the Four Gospels (Matthew, Mark, Luke and John) with the *Prologue* St. Jerome. It is richly illuminated with twelve multicoloured arcades framing canon tables and has four title pages (one at the beginning of each Gospel), one large multicoloured initial at the beginning of the *Prologue* and many small coloured initials, some of them with ornament (cf. Fig. 1–2).

Regarding the origin of the manuscript the experts have no uniform opinion. Many of them consider that it was created in Northumbria. The manuscripts themselves are the main source of information about the existence and activity of European scriptoria. It is very difficult to point out the similar features of manuscripts and to prove their origin from a certain scriptorium. There are many uncertainties in the history of the *Irish Gospel*. It is not ascertained exactly when the manuscript has come to France, but it is known that it was stored at Parisian cell of Saint-Maurus, for some time. In 1716 the abbey of Saint-Germain-des-Près took possession of the codex, then it has come to the collection of P.P. Doubrovsky, and finally to the Imperial Public Library in St.-Petersburg, the ancestor of the National Library of Russia.

Fig. 1. An arcade framing canon tables.

CONDITION OF THE MANUSCRIPT

In the course of time the sheets of *Gospel* have been fairly roughly cut off and rebound. The top part of miniatures has been cut off on many sheets. The scratched record of Runic character surrounded with four crosses was found on one of the last sheets. It represents eight lines which are vertical and inclined at an angle. Decoding of this record is still pending, awaiting the study by experts.

The storage of the manuscript in various conditions for centuries has affected the condition of the parchment sheets. Conservators and restorers know quite well that parchment extremely sharply responds to the slightest variations of relative humidity and atmospheric temperature.

Gospel has come to the Document Conservation Department with wavy deformation, frequently with rigid breaks in parchment of all 215 sheets. The threads of binding are broken off in the middle of the back. Some sheets have loosened out of the block, many of them have ruptures and missing parts. The warp of sheets was enhanced by the thick layer of animal glue staying on the back of the manuscript after binding (Cf. Fig. 3, 4). It was necessary to develop a conservation technique that would not destroy available codicological information and would not affect the condition of paint layer and ink.

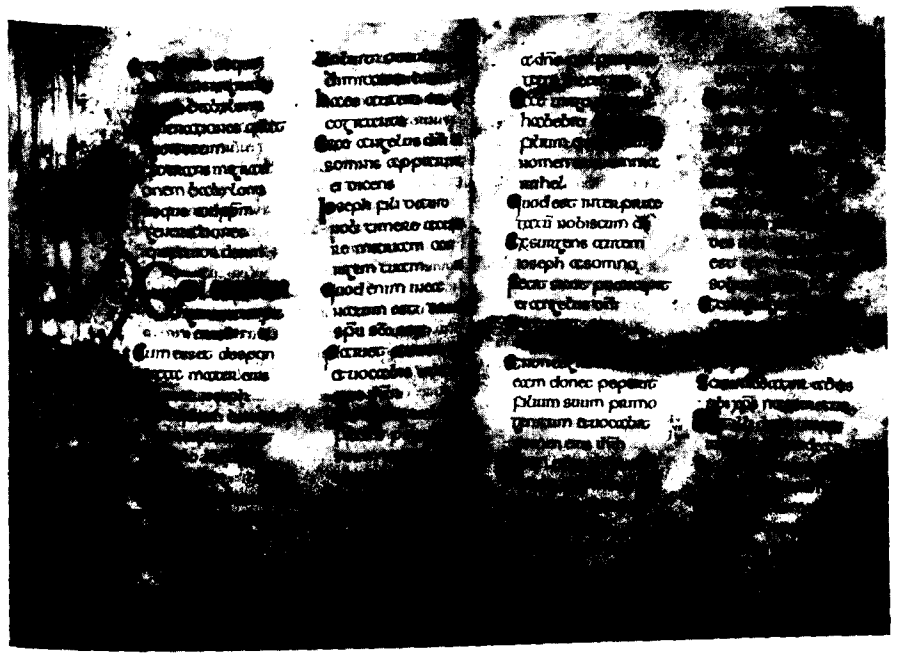


Fig. 2. Pages of the manuscript with large and small coloured initials

For this purpose we have undertaken the codicological examination of the manuscript in cooperation with the Laboratory of Document Codicological Research and Scientific Examination in the Manuscript Department of the NLR. Since the practice of examination of this kind with a view to conserve documents is rather non-standard, it seems to be useful to describe briefly general principles of the examination specifically with *Gospel*.

Fig. 3, 4. Appearance of Gospel before conservation.

PRINCIPALS OF EXAMINATION

We can designate three directions of expert examination.

The first direction includes maximum complete revealing the codicological information contained in the manuscript. For this purpose the detailed analysis with the complex description of the codicological structure of the codex is carried out. It consists in revealing the traces hidden in the document, faded and partially removed texts and images. Consequently, volume and character of codicological information are determined and decision is made what should be conserved and to what extent it should be conserved.

The second direction includes the estimation of how much codicological information can be kept untouched in the process of conservation. It should be noted that any one written document contains not only text information but inherent properties of the document. The latter is extremely important for the study of manuscript creation history, of its dating and localization, for the research of historical know how of papermaking and parchment manufacture, etc. The loss of information contained in the inherent characteristics of the document can turn out to be as significant as the loss of the text itself and bring on serious detriment to the information value of the document as a whole. Visual examination of the document itself is not sufficient to have a more general information on its inherent characteristics. Special analysis is required for it.

The third direction includes obtaining data about changes in the codicological characteristics of the document arising as a result of conservation. It is necessary to take into account these data for the comparative research of the manuscripts that have undergone conservation procedures.

MATERIALS AND METHODS

The study of codicological characteristics in the process of conservation was carried out in a few stages. In the first stage the experiments with two groups of samples were carried out. The parchment of modern manufacture (Israel) with the visible line ruling has been used as samples of the first group. The second group included the sheet fragments of three parchment manuscripts of the $16^{th}/17^{th}$ centuries with text written with iron-gall ink. Each group has been subjected to three kinds of treatment:

- with distilled water,
- with ethyl alcohol,
- with 10% urea solution in the mix of ethyl alcohol and water (1: 1).

Treatment procedure

Distilled water. A parchment sample was placed between two filter paper sheets previously humidified by distilled water under the light press of organic glass for 5 min. The parchment humidified in this way was placed between two dry filter paper and two cardboard sheets and maintained for 1 min in the typographical press. Then the filter paper was replaced and the parchment was again placed in the press for 10 min. Repeatedly, the filter paper was replaced after 2, 3, and 12 hours. This was carried out in three days.

Ethyl alcohol. A sample was treated conforming to the orientation of fibers with cotton wool wad moistened in ethyl alcohol and strongly wrung out. In this way deformed areas were manually straightened. Samples were dried in the typographical press with the essential replacement of the filter paper in a sequence as already specified.

Urea solution. A sample was treated conforming to the orientation of fibers with cotton wool wad moistened in urea solution and strongly wrung out. Deformed areas were simultaneously manually straightened. The sample was dried in the typographical press with the replacement of filter paper in a sequence as already specified.

Optical Inspection

The basic parameters analyzed during examination were the relief and linear dimensions of codicological objects of the manuscript and their details, colour and spectral characteristics of paint layer. In all cases the control of parameters was carried out before treating, five days and five months after treatment.

The analysis of object relief has been carried out using a TV-camera from a complete set of television spectral system TSS-1 (Russia) with 10–50 fold increase in visible and near IR-spectral regions (KS-19 and IKS-1 light filters). The lighting was oblique, polarized and non-polarized. The light angle of incidence was from 5 to 15 degrees. The linear dimensions of codicological objects have been determined using a MBS-2 stereoscopic microscope (Russia) with a measuring eyepiece. The accuracy of measurements, was 0. 1 mm. Colour and spectral characteristics of a paint layer have been determined with the photometric measurements. The spectra of reflection in a visible region (400–700 nm) have been obtained using a MSFU-EVM microscope-spectrophotometer (Russia). A photometry field was 0.21 min, sampling step was 10 nm.

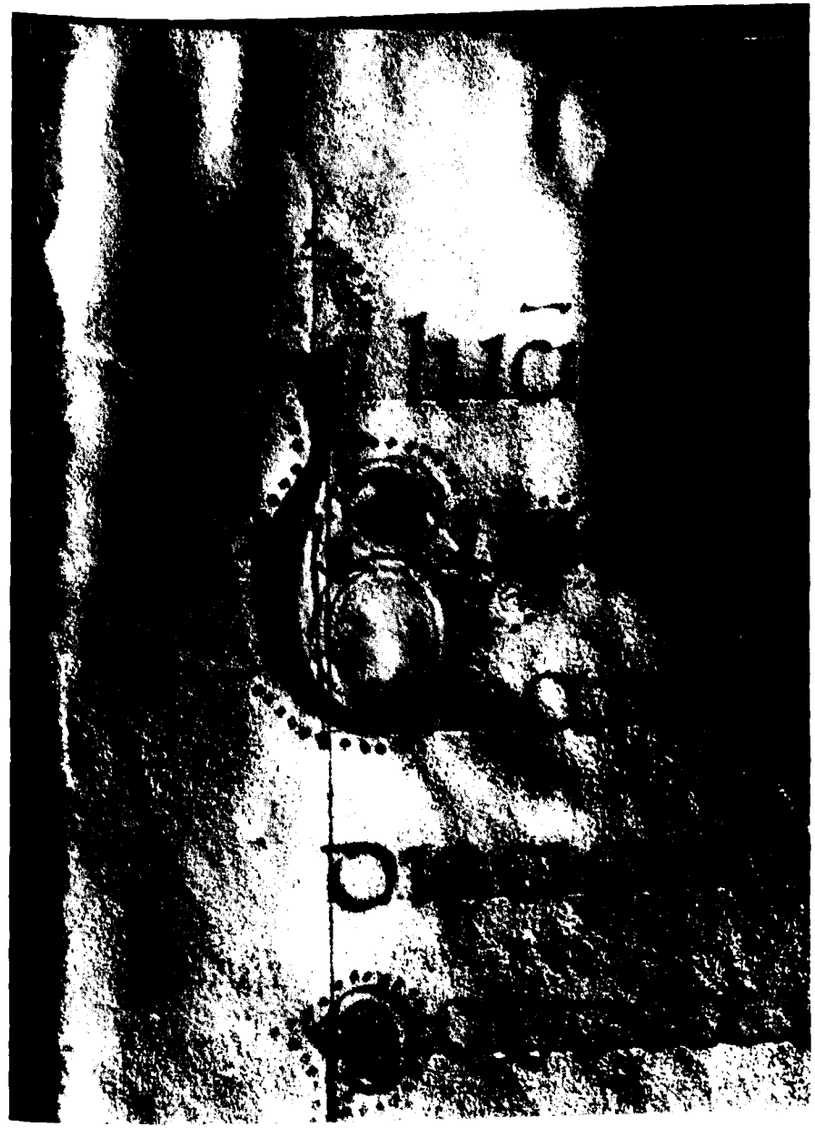


Fig. 5. Relief of the ruling lines.

RESULTS AND DISCUSSION

There is a large variety of surface relief in the parchment of the manuscript, both regarding depth and configuration of a line contour left behind by the instrument of trace formation: an awl or an implement of writing. Lining pin-holes and some traces of a pressed preparative drawing in the canon tables are the deepest in relief. Medium depth have the ruling lines (Cf. Fig. 5) and the preparative drawing of the canon tables. The depth of letter strokes in the text is an example of microrelief (cf. Fig. 6).

Fig. 6. Relief of the letter strokes.

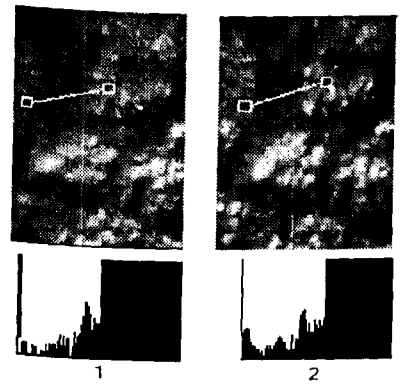


Fig. 7: Microrelief and optical density of the trace: 1: before conservation; 2: after.

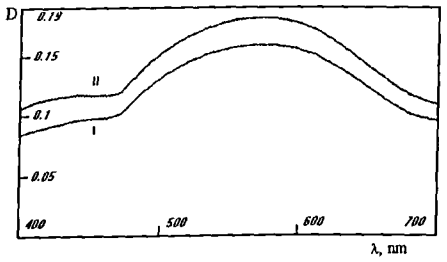


Fig. 8: Reflection spectrum of the blue paint layer; I: before conservation, II: after. D = optical density; λ = wave length

Comparison of the three methods of parchment treatment has shown that the effect of urea solution promoted a significant worsening relief clarity, of depth the lines and of letter strokes. The use of water yielded the best result. That very treatment that allows keeping any object relief safe in the process of conservation meets the modern requirements of a codicological research (cf. Fig. 7).

The effect of the chosen treatment on microrelief should be noted separately. The improvement of relief perceptibility in the writing strokes and in the strokes themselves in relation to thetfel parchment relief is noticed after conservation procedures. Comparison of vertical and horizontal linear dimensions of the text letters and their elements before and after processing allows to maintain that in all cases the linear dimensions change by tenths of a millimetre. Apparently, such an effect is a consequence of the parchment straightening during treatment (cf. Table 1).

Colour analysis

The analysis of reflection spectra of a paint layer before and after treatment has shown that the spectral characteristics remain stable irrespective of the kind of treatment (Fig. 8). The comparison of colour and chromaticity coordinates calculated on the basis of photometry data has also given positive result. As one would expect, the dye luminance insignificantly changes (increases) after treatment (cf. Table 2).

Table 1: Examples of changes in the letter linear dimensions (sheet 115).

Letters	Linear dimensions	Before conservation (mm)	After conservation (mm)
A	height	9.8	9.9
	width	12.6	12.3
M	height	9.0	9.0
	width	12.3	12.5
N	height	8.0	8.5
	width	7.6	7.5

Table 2: Colour and chromaticity co-ordinates of the blue paint layer.

		Before conservation	After conservation
Colour co-ordinates	X	15,196	17.455
	Y	14.895	17.096
	Z	4.146	4.855
Chromaticity co-ordinates	x	0.443	0.442
	y	0.435	0.443
	z	0.121	0.123

Such an approach to the choice of the parchment treatment method has demonstrated that the best possible method in this case is with the use of water. However, another question remained: what will be the reaction of the multicoloured paint layer to prolonged indirect moistening of parchment. The X-ray and microchemical analyses of the paint layer have been carried out at the Division of Technological Examination of the State Hermitage to answer this question. These analyses have shown that rather limited range of pigments in a pure state were used for *Gospel* illumination. Auripigmentum, ruddle, red lead oxide and two organic dyes of vegetable origin used together with chalk and a brown-black colour which is a complex composition on the basis of iron in combination with tannin, in addition containing flavonoids, could be identified. The paint is similar to iron-gall ink. Its colour intensity depends only on a layer thickness.

The structure of a layer is simple. The paints are put on the parchment directly, without ground. Only the light-blue paint lies on the ground of white colour consisting of chalk. There is a strengthening coating of gelatine on the surface of the whole paint layer; its thickness is comparable to that of the paint layer itself. Only in areas with yellow and orange paint it is several times thicker. On the orange paint surface it has is caused a glitter.

The obtained data on the paint layer composition and structure proves that this chosen treatment is possible.

Microbiological analysis

The mycological research of manuscript sheets also has been carried out prior to the conservation procedures.

The manuscript was stored at the NLR under standard conditions; it has not been exposed to prolonged exhibition and frequent use. Even if there were no significant damages caused by fungi or bacteria, it seemed to be of interest to study the microorganisms inhabiting the document. Seeds taken with sterile cotton wool from parchment sheets have been inoculated on the surface of agarized nutrient medium. The same was done with binding thread samples.

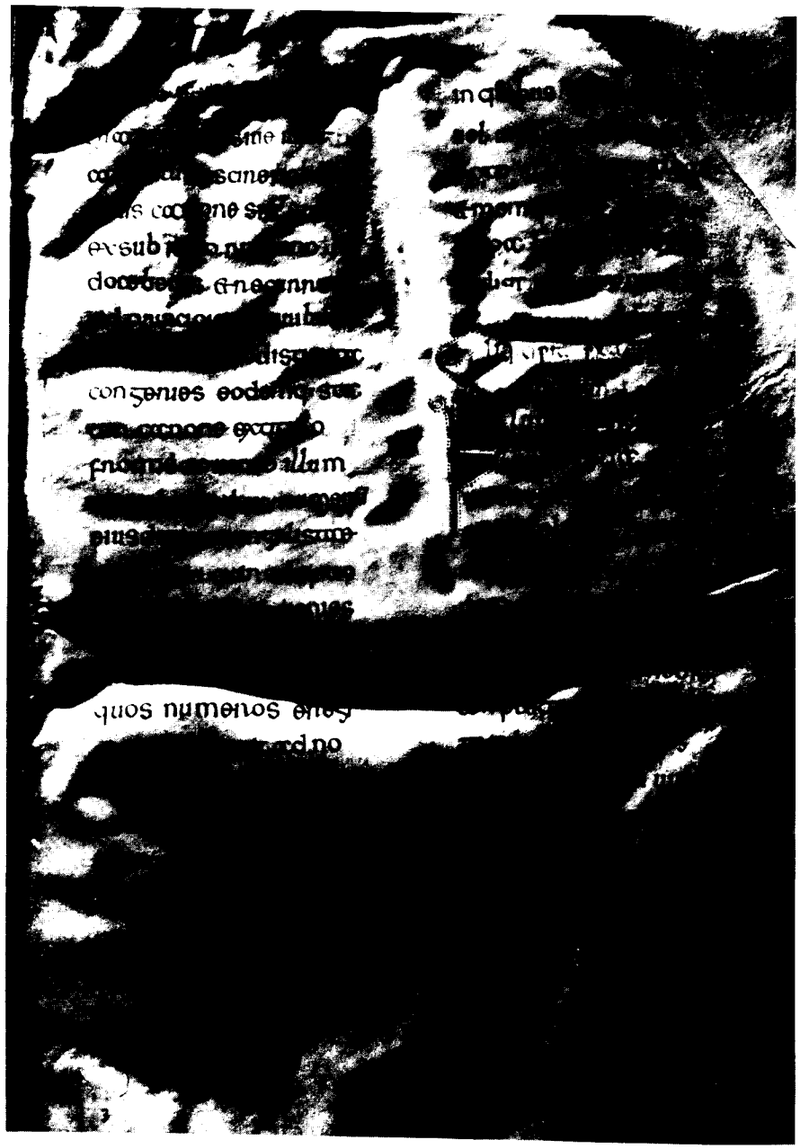
Twenty five sections of the manuscript have been analyzed in total. The content of viable microorganisms per page ranged from 3 to 94 CFU (colony forming units). Insignificant microbiological contamination (up to 10 CFU per page) was found in 40% of selected samples and more than 80 CFU per page in 36%. It has been found out that the threads are affected by bacteria.

Microflora found on the parchment was of very specific character. 21 cultures of *Micromycetes* have been found, constituting 23% of total amount of microorganisms. Only 4 cultures referred to such widespread genera as *Penicillium* and *Aspergillus*; 8 referred to the genus *Mucor* and 9 to the class *Demacetaceae.* Yeast are represented with 16 species: 18% of the total. Two of them referred to *Black yeast.* The basic amount of microorganisms, i.e. 59% of the total, is represented by bacteria, many of which being sporulating bacilli and two kinds of *Anaerobes.* It is well known that *Black yeast* is quite stable under dry conditions and that it can occur in various materials including animal tissues, among them skin, i.e. parchment. *Micromycetes,* which are more competitive in comparison with bacteria, usually constitute up to 80% of the total number of microorganisms found on parchment. All parchment destroying bacteria found on the parchment of *Gospel* are pertaining to the class *Eubactera,* families *Bacillaceae, Pseudomonadoceae* (non-sporulating bacilli *Pseudomonas*) and *Micrococcus.*

The results of the microbiological analysis prove the obvious predominance (80%) of bacteria in the manuscript parchment. The specific structure is the same as usually found in historic parchment.

TREATING THE PARCHMENT

The tests reported above with modern parchment and with fragments of the $16^{th}/17^{th}$ century provided some useful information on the impact of wet treatment on the structure of that material. But undoubtedly a work with test samples and models always differs from a work with an original, especially with such one



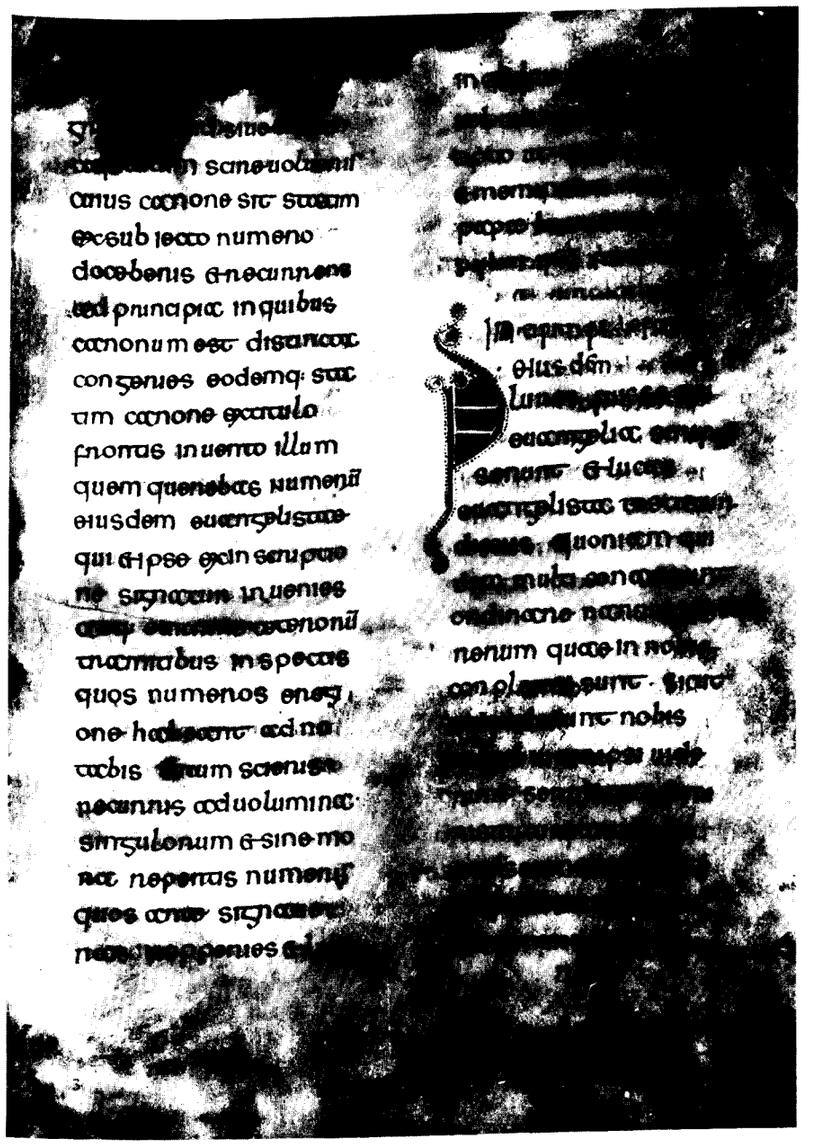


Fig. 9 and 10: Sheets of Gospel after conservation.

as the parchment manuscript dated from the eighth century. Therefore it is worth-while to describe the technology used for the original.

Since all manuscript sheets have got increased rigidity in the areas of folds, first of all it was necessary to make internal margins flexible. For this purpose a strip of dry filter paper was put on the area of the internal margins of the sheets; a strip of damp filter paper was put over the dry one, and paraffined paper was put over the damp one. A manuscript sheet with such a compress was placed between two sheets of dry filter paper, covered with a glass and left for 3 min. This manner of humidifying gave the parchment the necessary elasticity that enabled us to begin careful manual straightening. It promoted the reduction of deformation to some extent. Further smoothing has been obtained by slightly humidifying of the whole sheet surface: After straightening the folds as described a sheet was placed between a dry and a slightly humidified filter paper sheet on both sides. This stack of five sheets – moist filter paper, dry filter paper, parchment, dry filter paper, moist filter paper – was covered with a glass plate and maintained for 3–5 min. On the location of the book paintings dry paper was put in two layers. This procedure enabled us to begin careful straightening crumples, folds, and cracks. Similar operations were performed in the same sequence after turning the sheet verso up. Then the parchment was placed between two sheets of dry filter paper and two sheets of board and maintained in the hand press for an hour. The operation was repeated several times a day up to complete parchment drying. Straightened and dried parchment between dry filter paper was placed in the press for a few days. The duration of pressing depended on the parchment thickness.

To summarize the work done we can state that the over-all scientific examination provided us with ample opportunity to choose proper conservation methods, to inspect conservation treatment in certain stages, to estimate whether the codicological characteristics of the manuscript should be retained during the process of conservation and, accordingly, to receive the data on their changes. There is no doubt that, preparing conservation treatment of very valuable literary monuments, research of this kind is important.

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Summaries

An Irish Gospel From the Eighth Century

The codicological examination of a manuscript before and after conservation, i.e. "Irish Gospel" from 8th century, was undertaken in the conservation practice of the National Library of Russia for the first time. It was done in order to evaluate the codicological information, paint layer and ink stability in the process of conservation. The basic parameters analyzed were the relief and linear dimensions of the codicological objects, colour and spectral characteristics of the paint layer. The parchment microbiota of the present ecological niche was also investigated.

Preliminary experiments with parchment samples permitted to suggest a conservation method with the use of indirect moistening. The X-ray-fluorescent and microchemical analyses of the paint layer confirmed the correctness of the chosen method.

The complex evaluation of the codicological information contained in the manuscript had a considerable influence on the choice of the conservation strategy. It becomes evident that investigation of this kind is necessary to prepare for the conservation of manuscripts of particular value.

Un évangéliaire irlandais datant du huitième Siècle

C'est à la Bibliothèque Nationale de Russie que l'on a procédé pour la première fois à l'examen codicologique d'un manuscrit avant et après la restauration; il s'agit d'un "évangéliaire irlandais" datant du 8ème Siècle. Cet examen avait pour objectif d'évaluer les facteurs codicologiques, la structure des couches colorées et la stabilité de l'encre en vue d'une conservation appropriée. Les paramètres de base qui ont fait l'objet de l'analyse sont la structure de la surface, c.-à-d le relief et les dimensions linéaires du parchemin et les caractéristiques spectrales de la couleur des différentes couches. On a également étudié la microflore du biotope présent dans le parchemin.

Des expériences antérieures réalisées sur des échantillons de parchemin permettent de supposer qu'un traitement utilisant l'humidification indirecte serait une méthode de conservation adaptée. L'analyse fluoroscopique aux rayons X et l'analyse microchimique des couches de couleur ont confirmé que la méthode choisie était la bonne.

L'étude et l'évaluation complexe des informations codicologiques contenues dans le manuscrit ont fortement influencé le choix de la stratégie de conservation. Il s'est avéré nécessaire de pratiquer de telles analyses afin de préparer la restauration de manuscrits précieux.

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An Irish Gospel From the Eighth Century

Ein irisches Evangeliar aus dem 8.Jahrhundert

Zum ersten Mal wurde in der Russischen Nationalbibliothek vor und nach der Restaurierung eine codicologische Untersuchung durchgeführt; sie galt einem Evangeliar in insularer Schrift aus dem 8. Jh., genannt „Irisches Evangeliar" Ihr Ziel war die Einschätzung der codicologischen Gegebenheiten, des Aufbaus der Farbschichten und der Haltbarkeit der Tinte. Die ermittelten Faktoren waren die Oberflächenstruktur, d.h. das „Relief" des Pergaments, die Blindlinien und die Spektralwerte der Farben. Auch die Mikroflora in dem Biotop, den die Handschrift darstellt, wurde untersucht.

Voruntersuchungen anhand von Pergamentproben ließen die Behandlungsmethode des indirekten Feuchtens als geeignet erscheinen. Roentgen-Fluoreszenz und microchemische Analysen der Farbschicht bestätigten die Richtigkeit dieser Wahl.

Die Untersuchung der codicologischen Gegebenheiten der Handschrift beeinflußte in starkem Maße die Wahl der Behandlungsstrategie. Es zeigte sich die Notwendigkeit, derartige Untersuchungen zur Vorbereitung der Restaurierung von herausragenden Handschriften durchzuführen.

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1. *Codices Latini Antiquiores.* ed. E.A. Lowe. Part 9 (Oxford 1966): no. 1605.

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