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Durability of Paper and Writing

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1. Introduction

Networking of communities of researchers, infrastructure owners and users is one of the important instruments the European Commission DG Research is offering in order to establish co-operation and co-ordination between existing facilities, researchers, end-users, industrialists, manufacturers and designers. A European Thematic Network aims therefore to create an optimum use of infrastructures, to avoid unnecessary duplication, and to offer access to a broader community of researchers.

One of the causes of paper deterioration is due to the applied corrosive ink. The corrosion effect can be generalised as the effects of transition metals in paper. Other related deterioration processes take place in the presence of metal clips and other metal items. It is obvious that all these different items related to Metals In Paper, with acronym MIP, is being investigated for many years, at conservation workshops, research institutes, universities and suppliers. Research is carried out to gain a better understanding and to prevent out heritage against deterioration.

Since 2003 a European Thematic Network has been established (contract number EVK4-2002-20010).

2. Organization of MIP

Four theme groups have been formulated in our thematic network now in order to improve the communication between researchers, end-users and suppliers. Furthermore the network aims to define knowledge gaps and to foster the bilateral co-operation in order to avoid duplicate of research on European level. Dissemination of the work will be performed by symposia and the website www.miponline.org.

In the Theme group 1 (TG-1), fundamental scientific aspects of paper degradation are discussed, focussing primarily on diagnostics and analytical techniques, studies of degradation processes (including endogenous and exogenous factors), and methodologies for paper stability evaluation. The chair for TG-1 is Dr Matija Strlic from Slovenia (e-mail: matija.strlic@uni-lj.si). It was not accidentally that Dr Strlic is chairing this group as he is also co-ordinator of the EU research project Papylum, aiming to study chemiluminescent phenomena during paper degradation. Chemiluminescent effect is often observed in one of the stages of degradation of paper by transition metals. The input of Papylum’s knowledge to MIP benefits therefore the community of conservation science.

Within the applied research and applications we have three theme groups.

In our network we see the conservation of objects divided in two parts. Active and Preventive conservation, while active conservation is split in the chemical and physical aspects.

Theme Group 2 (TG-2) deals with the chemical aspects of Active Conservation. Items as conventional methods, inhibitors and deacidification are discussed here (TG-2). The co-ordinator of TG-2 is Dr Jana Kolar from Slovenia (e-mail: jana.kolar@nuk.uni-lj.si). Dr Kolar coordinates also a very important EU research project Inkcor. This research will have an impact on our current knowledge and the prevention of the degradation of objects affected with so called metal-tannin ink corrosion. It is gaining new knowledge about oxidative degradation of cellulose and stabilisation of deteriorated objects by a combination of improved non-aqueous deacidification and antioxidants.

The Physical Aspects of Active Conservation is the item being discussed in Theme Group 3. TG-3 discussion items include paper splitting, strengthening, leaf-casting and cleaning. This TG is chaired by Dr Manfred Anders from Germany (e-mail: anders@zfb.de). Dr Anders is scientific manager of a company ZFB, ZENTRUM FÜR BUCHERHALTUNG GmbH, which was established as a private company in the beginning of 1998 after having served as the Centre for Book Conservation of the German Library in Leipzig for nearly 35 years. The company has experiences with numerous conservation technique, for example the mechanical splitting of paper materials.

Conservation alone will not always prevent materials for further deterioration. Theme Group 4, deals with Preventive Conservation issues. Environmental storage conditions, boxing, and other issues are the principal items belonging to TG-4, which is chaired by Dr John Havermans from The Netherlands (e-mail: j.havermans@bouw.tno.nl). Dr Havermans coordinated previously a EU research project on the effects of air pollutants on de degradation of paper and carried out many studies related to deacidification and storage conditions.

3. MIP members

The MIP thematic network has officially 21 members. They are listed below.

Besides official MIP members, there are numerous associated members. For example, a good relation has
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been established between MIP and the French Research Group on Iron Gall Ink Corrosion and the Polish research group where for example kinetics of the acid catalysed hydrolyses of cellulose is being studied.

Other output will be a memorandum of understanding where figures are being presented on the need of conservation actions and conservation research. Based on the input of the members and members personal network, information is collected and summarized. Besides contributing to policy, research community will benefit from the memorandum.

As a result of the MIP thematic network, three new 6th framework projects were submitted to a recent call published by EC within its 6th framework programme. Proposals with draft acronyms Papertreat and SurveNIR were favourably evaluated by the evaluators and entered the negotiation phase.

5. Time goes fast

A 36-month running thematic network sounds long, however officially ends in February 2006. Nevertheless we will put our effort in organizing a joint international event again, to end our network in May 2006. Information on the organization and location will be presented at our website www.miponline.org.

This network is not just a network. MIP is created for our future. It gains contacts, new ideas and future co-operation and will define gaps in knowledge and research.

6. Acknowledgement

The author and members of MIP gratefully acknowledge the support of the European Community, 5th Framework Energy, Environment and Sustainable Development Programme, contract no. EVK4-CT-2002-20010 (MIP). This paper is the sole responsibility of the author and does not represent the opinion of the Community. The Community is not responsible for any use that might be made of the data appearing herein.

4. MIP output

So far, different symposia we organized in order to exchange knowledge. For example we organized a symposium in Capellades (Spain) in February 2004 and in La Rochelle (France) in July 2004. Also joint events are organized to obtain input and output for our network. For example Healthy Indoor Environment in September 2004 (The Hague, The Netherlands) where the MIP preventive conservation group is combined with other symposia and in November 2004, where Papyplum, Inkcor and MIP organize a joint international event in Ljubljana, Slovenia.

Table 1: Based on EU policy, we do welcome all new interest members, especially active ones.

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7. References

1. MIP website: www.miponline.org
2. Papyplum website: www.papyplum.uni-lj.si
3. Inkcor website: www.infosrvr.nuk.uni-lj.si/jana/Inkcor/index.htm
6. Community Research & Development Information Service: www.cordis.lu
1. Introduction

Iron gall ink is probably the most important ink in Western history, widely used from the middle ages to 20th century. Due to the inks’ corrosive properties, the damage caused so far is extensive, with 60–70% of priceless Leonardo da Vinci oeuvre showing signs of degradation and Bach’s hand-written music virtually falling apart.

Due to the alarming data concerning deterioration caused by the corrosive ink, several European partners joined forces within a fifth framework project InkCor – Stabilisation of iron gall ink containing paper. The main objectives of InkCor project are to significantly improve the present know-how of the phenomenon of ink corrosion and to establish best non-aqueous conservation practices for iron gall ink containing documents, enabling their preservation and undisturbed access.

Consortium consists of eight partners: National and University Library, Slovenia; University of Ljubljana, Faculty for Chemistry and Chemical Technology, Slovenia; Institut “Jožef Stefan”, Microanalytical Centre, Slovenia; The Netherlands Institute for Cultural Heritage; Nationaal Archief, The Netherlands; Teylers Museum, The Netherlands, ZFB – Zentrum fuer Bucherhaltung, Germany; and Musée du Louvre, France. Partner structure is interdisciplinary, consisting of art historians preservation officers a panel of conservators representing museums, archives and libraries, conservation and analytical chemists and a physicists, as well as a SME performing mass deacidification, all specializing on a certain aspect of iron gall ink corrosion.

2. Results

Excellent co-operation between European partners with different expertise resulted in a range achievements:

- Numerous iron gall ink recipes from the collected historical sources were evaluated and entered into the ICN Art Technological Sources database.
- Ink corrosion database, a tool for visual assessment of numerous historical artefacts was created and will aid conservators in describing and documenting the documents.
- Model rag papers were produced and their properties, such as pH, ageing stability, brightness stability during thermal ageing, metal content, etc, determined. They were used for evaluation of paper stabilisation treatments throughout the project.
- Another study aimed at the evaluation of those factors, which result in the variable conditions of historical documents containing iron gall ink. Namely, while some are completely destroyed, others may be in excellent condition even centuries after their creation. In order to establish the main properties, common to severely degraded documents, the effects of the type and quantity of transition metals in ink, as determined by in-air PIXE method, pH of the ink containing paper, grammage of paper, its absorptivity and the width of ink lines were evaluated against the degree of corrosion. Using multiple linear regression analysis, a correlation has been obtained between the width of the applied ink lines, pH, grammage of paper and the extent of ink corrosion. From these properties, which can be non-destructively obtained from most historical documents, it is therefore possible to predict the stability of historical iron gall ink containing paper.
- Simple identification test for iron, developed by ICN, was evaluated and a novel one, aimed at identification of copper ions was developed, enabling conservators to identify the corrosive inks.
- In-air PIXE method was used to determine the content of transition metals in 99 documents. Iron content in ink containing paper reached values as high as 1656 mmol g⁻¹, while it did not exceed 38 mmol g⁻¹ in areas, which did not contain iron gall ink. The results furthermore demonstrate that inks, containing substantial amounts of copper were used throughout the time span covered by our study. Molar ratio of copper to iron surpassed 10% in 32 manuscripts, while it was higher than 60% in 6 documents. Molar ratios of other potential catalysts were lower, not exceeding 5% for chromium, 6% for manganese and 10% for cobalt.
- It was demonstrated that, under alkaline conditions, copper ions are much better catalysts of peroxide decomposition than iron ions. They may be the
main source of damage exerted to numerous iron gall ink containing documents, once deacidification had been performed. Efficient antioxidants should therefore not focus on stabilisation of iron ions alone.

– Evaluation of non-aqueous deacidification systems demonstrated that a solution deacidification is preferred over a suspension system. Research within InkCor project led to several improvements of the existing commercial process for mass deacidification of books, which have been already implemented by the SME partner, Zentrum fuer Bucherhaltung (ZIB). The quality of deacidification agent magnesium titanium ethoxide was improved, resulting in diminished yellowing of treated papers. Conditioning room was built to allow for faster conversion of deacidification agent into the corresponding carbonates.

– In order to develop a non-aqueous method for stabilisation of iron gall ink containing paper, a number of antioxidants was evaluated. The most promising turn out to be a group of peroxide decomposers, which are able to inhibit oxidative decay irrespectively of the type of transition metal which catalyses it.

Results demonstrate that while deacidification using magnesium ethoxide in ethanol (0.05 mol L\(^{-1}\)) decreased degradation of iron gall ink containing paper by 50 ± 10%, treatment with a non-aqueous InkCor process resulted in 80 ± 10% slower degradation (Figure 1), as compared to the untreated paper. In addition to stabilising paper containing iron gall inks, new process inhibits degradation of the paper itself (without iron gall ink) in alkaline environment,\(^8\) thus offering additional benefits of the proposed potential stabilisation method. As a result of the research undertaken within the project ZfB, National and University Library of Slovenia and University of Ljubljana, Slovenia jointly submitted a patent for a new non-aqueous paper stabilisation method containing antioxidants.

After three years of research, the project will draw to a close in February 2005. Until then, the novel treatment for papers containing corrosive iron gall inks will be extensively evaluated by the researchers and end-users in the project, in order to determine whether it can be safely used for stabilisation of historical artefacts.

3. Acknowledgement

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4. References


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Figure 2: Rates of degradation of untreated (O), deacidified with magnesium ethoxide (Mg(OEt)\(_2\)) and stabilised with InkCor process during ageing at 80 °C and 65% RH. The rates were calculated using the Eckenstam model.\(^{13}\)
1. Introduction

Deacidification of paper is one of the most often performed active conservation procedures. The need for optimal deacidification is well justified considering the vast quantities of acidic paper in Western libraries and archives, e.g. in Poland.¹ Due to the production process, papers produced in the period ca. 1850–1990 are acidic, and the rate of their degradation is such that it is quite possible that in the next century or two, most of the artistic, written and printed documentation on paper from the period will irreversibly fall into pieces (Figure 1) if no action is taken.

However, optimisation of deacidification is a complex task, not only due to the variety of paper materials used, but also due to the fact that the degradation processes, i.e. oxidation, taking place in moderately alkaline paper, were relatively rarely studied² and not well understood. Since cellulose oxidation is a slow process, the need for extremely sensitive analytical techniques was also evident. For these reasons, the consortium of five partners: University of Ljubljana, Faculty for Chemistry and Chemical Technology, Slovenia; National and University Library, Slovenia; Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia; The Netherlands Institute for Cultural Heritage, Amsterdam, The Netherlands; and Centre National d’Evaluation de Photoprotection, Aubiere, France, gathered with the goal to construct a new instrument exploiting a rarely studied phenomenon observed during oxidation of paper, i.e. chemiluminescence, the weak light emitted by molecules as a result of a chemical reaction. This innovative approach, combined with comprehensive studies of thermooxidative and photooxidative degradation of cellulose and paper led to optimisation of aqueous deacidification techniques and new guidelines regarding evaluation of paper stability, thus increasing the accessibility of cultural heritage on paper.

2. Results

The consortium, driven by expertise of five research laboratories, two of them in end-user institutions, and one in an institute involved in instrument production for the scientific market, ensured a highly focussed approach leading to the following results:

- Construction of a state-of-the art chemiluminometric instrument, the first of its kind. The measurement procedure is straightforward: a sample (even a complete object) is simply inserted into the instrument and the emitted light can readily be measured – degradation of paper at room temperature can virtually be seen. The instrument allows the use of humid atmosphere, which is known to affect degradation of cellulose and paper, and it also allows the observation of samples without destructive sampling. The instrument is a valuable addition to the conservation scientist’s laboratory, and is already commercially available.³ Its use extends well beyond conservation research, as it may be used for degradation studies of a variety of organic materials, including e.g. food.
process were elucidated, such as the influence of carbonyl groups.\textsuperscript{4, 5} It is thus recommendable to wash any degradation products out of paper and to perform a reduction pre-treatment of paper to be deacidified, if possible.

- Application of advanced kinetic calculations to chemiluminometric data lead to development of degradation software with which we can predict rates of degradation at room temperature.\textsuperscript{6, 7} These data are of extreme importance for the collection manager, as accelerated degradation experiments performed in ageing chambers are of little significance for ageing during storage conditions. In future applications, such prediction methods may allow the conservation scientist to evaluate a conservation treatment on an original, as only a micro-sample is needed.\textsuperscript{8}

- By comparison of natural light-ageing with three different experimental techniques, it was shown that the content of peroxides during oxidation of cellulose is extremely low\textsuperscript{9} – this led to the conclusion that antioxidants with the role of radical scavengers might not be very effective for stabilisation of paper.

- Relative humidity was shown to have an extremely important role during degradation of moderately alkaline paper – by correctly adjusting the relative humidity level, an up to 10-times decreased rate of degradation was observed at the conditions of study.\textsuperscript{10} This research indicates an important future line of study, which should lead to better guidelines for long-term storage conditions.

- A comprehensive set of experiments was performed at four temperatures of accelerated ageing, allowing us to extrapolate the ageing behaviour of a variety of treated models and real historic papers to room temperature. Thus, we obtained the data on stability of differently treated papers (containing CaCO\textsubscript{3}, MgCO\textsubscript{3}, selected antioxidants) at the conditions of use.

- By comparison of natural light-ageing with three different experimental techniques of artificial light-ageing, we produced guidelines for the conservation researcher on how to conduct studies on photo-stability of paper. Our studies have shown an extreme sensitivity of photo-aged papers towards later oxidative ageing in darkness.\textsuperscript{11} This leads to the conclusion that for exhibited objects, the deacidification also has to be carefully selected: MgCO\textsubscript{3} and halides showed a stabilizing effect.

- Manual deacidification of paper using aqueous solutions of Ca(HCO\textsubscript{3})\textsubscript{2}, Mg(HCO\textsubscript{3})\textsubscript{2}, and Ca(OH)\textsubscript{2} were carefully optimised regarding concentration of the alkali, time of immersion, the resulting pH and alkaline reserve.

- At the project completion, members of the project, in cooperation with other renowned scientists from the field, have set to write a book on paper degradation, summing up the recent advances.

- The Papyrus webpage became an important resource of information and literature data on paper degradation. The database will continue to be developed in the future: http://papylum.uni-lj.si

Research within the Papyrus project thus lead to construction of a new valuable tool for the conservation researcher, the most important result. Using the tool, and a variety of other optimised and even newly developed methods, a profound understanding of cellulose oxidation was gained. The extensive experimental plan using altogether more than 150 different paper samples lead to data on rates of degradation at storage conditions and during irradiation with daylight during exhibitions – on the basis of such information, the collection manager is able to choose the optimal treatment.

The chemiluminometric approach has already led to first useful implementations outside the Papyrus project, e.g. studies of laser-treated paper\textsuperscript{12, 13} and of cotton textiles.\textsuperscript{14} This demonstrates the validity of our research directions.

The project also points to topics important for future research. On one hand, guidelines and risk assessment for storage conditions should be evaluated, especially regarding recommendations on relative humidity. On the other hand, lignin (not an object of our study) was shown to exhibit strong chemiluminescence during oxidation – the newly developed methodology could thus help solving other acute problems in conservation and preservation of paper-based cultural heritage for the future. The developed chemiluminometric technique deserves to be explored further in the area of cultural heritage materials of organic origin, e.g. textiles, varnishes, synthetic polymers, etc.

3. Acknowledgement

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4. References


1. Introduction

The MASTER project is researching the application of novel organic polymers as early warning sensors for environmental deterioration of Europe’s organic objects in museums, galleries, historic houses, archives and libraries. The intention is to develop a sensor that can indicate the rate of chemical change, or damage, that objects are likely to suffer in a particular storage or display environment. The main processes of chemical deterioration for organic objects will involve either oxidation or acidic processes, or possibly a combination of both. These processes may result from inherent vice, but, as is well known, are to a large degree caused by environmental factors such as moisture, pollutants, light and UV radiation. Chemical deterioration is usually accelerated by increased temperature and relative humidity and many material deterioration processes are the result of these parameters acting synergistically. The MASTER project is researching novel sensors that can capture these synergies to give a more direct early warning of the potential for damage to organic collections, than is possible from parameter (i.e. pollutant concentration, temperature, relative humidity, light, etc) monitoring alone.

2. Sensor research and development

At present three different early warning systems are being investigated.

A novel polymer is being researched as a potential ‘generic sensor’, i.e. a sensor that will respond to the range of environmental parameters implicated in the chemical deterioration of organic materials, as listed above. Certain polymer films are known to deteriorate chemically and photochemically due to environmental stress and light. They do so at a rate that is appropriate to a sensor: measurable deterioration appears after a few weeks’ exposure in typical environments. This is also sufficiently long to give a good estimate of the quality of the long-term environment objects are exposed to. The chemical deterioration of certain polymers has been shown to be detectable by simple techniques such as UV-visible spectrometry. The generic sensor prototype is manufactured by spin coating the polymer onto a glass substrate. Its response to different environmental factors is being calibrated in the laboratory at Norwegian Institute for Air Research in controlled exposure experiments, under different regimes of pollutant concentrations, humidity and light. On exposure the generic sensor will give a single number response that can be used as an early warning measure of the quality of an environment.

Two other sensors that can give more specific information about the quality of a storage or display environment are also being researched. These are designed to respond selectively to oxidation and acidic deterioration processes. Under development at the Albert-Ludwigs Universität, Freiburg, these ‘quantitative oxidising/acidity’ (QOA) sensors are also polymer based, but gain their specificity through the use of dye systems that can respond to either oxidation or acidic processes. The dyes and polymer are dissolved in a solvent and spin coated onto a glass substrate. The speed of the sensor response is controlled by the dye system and also the polymer used in the coating. Polymers with high gas permeability give a faster response than those with low permeability. In this way a sensor technology originally developed for occupational hygiene processes can be adapted to give a response within one month’s exposure in a typical indoor cultural heritage environment. An oxidising dye system, based on the use of indigo and other pollutant-sensitive dyes is being tested in the laboratory and its response is being calibrated. Measurement is by a simple UV-visible spectrometer method, as for the generic sensor. Work is still under way to find a suitable, stable acidic dye system.

3. End-use involvement with the research

A key aspect of the MASTER project has been the involvement of an End User Group, made up of representatives of European cultural heritage organisations, who have a wide experience of caring for
cultural heritage collections, both at the strategic and practical levels. They have given their input to the project through two workshops where the proposed research was presented to them and they were required, collectively, to present a response from a practical perspective, on what was needed to make a sensor that they would find useful in their own work in collections care. Whilst remaining within the original research plan, the research has responded to the end user requests. One of these requests was for a visible change sensor and research is under way to find suitable oxidation and acidity systems that undergo visible colour changes. So far only laboratory studies have been conducted, but promising dye and pH indicator systems have been identified and are being tested.

4. Field test programme

Twelve month field tests of the generic and QOA sensors are under way at ten cultural heritage institutions across Europe. At each test site there are exposures in the outdoor environment, indoor environment and an enclosed environment, such as a display case or storage cupboard. In parallel, diffusion tube measurements are being made of the concentrations of sulphur dioxide, nitrogen dioxide, ozone and organic acids; light, temperature and relative humidity are also being measured. These data will be used to interpret and correlate the sensor response at the conclusion of the twelve-month field test programme. Also, samples of standard paper and silk are being exposed at the indoor and enclosed sites for the full twelve months of the field test in order to assess their deterioration in comparison with the sensor response and environmental conditions. The silk will be analysed for polymer molecular weight distribution by size exclusion chromatography, a method developed by Historic Royal Palaces; whilst degree of polymerisation (DP) of cellulose in the exposed paper samples will be determined by viscometry at the University of Ljubljana.

5. Integration of the sensor into preventive conservation strategy

As well as the technical research of the project, in order to support the application and interpretation of the sensors, research is under way to determine how the sensor application can be incorporated into preventive conservation strategy as an early warning device. This strategy approach will link to existing work on for instance the development of European conservation standards, published studies of environmental deterioration of organic materials and current thinking on risk assessment and value. The approach will be pragmatic, and will take into consideration the different priorities, resourcing and buildings of the diverse institutions that care for organic objects in Europe. It will give information on how to interpret sensor responses and the steps that should be followed in using the sensor and the subsequent actions that may need to be taken.
1. Background

Exposure to artificial or natural light may damage valuable heritage objects, by causing discoloration, fading, or brittleness of the historic material. Rather than limiting the time of exposure for each object, it is advisable to monitor the lighting conditions, e.g. by using a data logger. However, a continuous monitoring program would be rather expensive and applicable only for selected examples. An obvious attempt to avoid complicated measurements is to use a sacrificial simulation material on which the effect of light can be studied. For this purpose, the only system available on the market has been the Blue Wood Standard (BWS), developed for the industrial sector. Its application in museums was limited because of the low sensitivity to museum lighting conditions.

2. Objectives of the LiDo-project

The LiDo project (EVK4-CT2000-00016) was conceived in response to the need for a more sensitive and standardised dosimeter, which should be easy to handle, environmentally robust, inexpensive, cumulative and designed for wide use in the heritage sector. The first step in the work program was concerned with the investigation of different combinations of dyes/matrices/substrates and their response to different light levels by laboratory experiments. The field exposure was carried out in selected museums in London, Paris, Berlin, Florence and Prague. The final step of the project was dedicated to the development of a standardised preparation method and quality control for light dosimeters, which will be marketed under the name “LightCheck®”.

3. Achievements

As a final result of the project two types of light dosimeters are available, based on the same principle: a light sensitive coating on a substrate changes colour during exposure to light. A calibration has been established between the colour and the luminous exposure. The luminous exposure given in the colour reference scale corresponds to the potential damage of the lighting conditions on site. Both types of dosimeters are more sensitive than BWS, covering a complementary range of application: LightCheck™ Ultra “LCU” is designed to monitor the exhibition of very light sensitive objects (and short exposure times), whereas LightCheck™ Sensitive “LCS” is applicable for the more durable objects (and longer exposure times).

LightCheck™ is introduced as a new early warning system for preventive conservation, which permits to evaluate the quantity of light received by an artefact during exhibition. This will allow a better control of environmental conditions and will provide a new tool for the survey of guidelines and standards in conservation.

The goal set up for the project has been reached: new light dosimeters have been developed, tested in the laboratory under controlled conditions and in field exposures. At the end of the project a marketing strategy will ensure a commercial distribution of the product and thus the transfer to market.

The achievements of the project were presented to a broad audience during a public workshop in Florence (27/28 Nov. 2003). The web page for the LiDo project at www.lido.fhg.de provides links to actual publications and on how to order LightCheck™ (see also: www.lightcheck.co.uk). The research within LiDo was awarded with the “Pan-European Grand Prix for Innovation” in Monaco, on 6th December 2003.

4. References

1. Introduction

Non-destructive optical techniques have always belonged to the most important investigation methods applied in paper and writing durability research. Visual inspection of a document is a fast and inexpensive way of detecting critical areas, where e.g. ink corrosion occurs in an advanced state, or where discoloration or staining jeopardizes the legibility. From visual inspection alone, the experienced researcher can get a qualitative impression of the general condition of the inspected material.

However, for comparing the state of conservation of documents with each other without actually having to view them simultaneously, quantitative analytical methods are required. Besides a number of other sophisticated spectroscopic techniques, optical reflectance spectroscopy and colour measurement, has been used successfully for analysing local material properties in relation e.g. to paper degradation.

Unfortunately, practically all of the quantitative optical techniques are per se non-imaging, i.e. that each measurement represents the average properties only around a single point on the document. Due to the limited measuring speed, scanning the document to obtain an adequate spatial resolution is usually totally impractical, so that these quantitative methods involve some major problems inherent to non-imaging techniques. For example, identifying representative document areas with a sufficiently homogenous response in the first place, and re-addressing exactly the same small area reliably in subsequent measurements is often a huge challenge.

An advanced multi-spectral digital imaging system, such as the ARTIST camera\(^1\), gathers optical information from a significant document area with a high spatial resolution, and can thus overcome the problems typical for single-point techniques. However, at present such imaging systems are almost exclusively used in a non-quantitative way, and even when used quantitatively, their comparatively small number of wavelength bands (about 5–10) is totally insufficient for analytical reflectance spectroscopy.

We are currently developing an instrument for truly non-destructive paper and writing durability research, which combines the high spatial resolution of a digital camera with the large number of wavelength bands required for high-resolution spectral reflectance and accurate colour measurements. The instrument is to be used for application studies aiming at a reliable identification of different types of ink, early-detection of ink corrosion, and an objective quantification of the resulting degree of document degradation.

In this contribution, we discuss the operating principle of this so-called hyperspectral imaging system and we present initial experimental results obtained with a laboratory setup, which already indicate the huge potential of this novel technique.

2. The operation principle of hyperspectral imaging

The term hyperspectral imaging (HSI) refers to the acquisition of a series of digital images at a large number (50–100) of different, well-defined optical wavelengths in the ultra-violet, visible and near-infrared. HSI results in the simultaneous, precise determination of the reflectance spectra from all areas of a document with a high spatial resolution. The reflectance spectra often show significant differences for different types of ink (or other substances), which may look identical in direct viewing or conventional RGB imaging. Using dedicated software, the spectral properties can be exploited for distinguishing inks or areas exhibiting different degrees of paper degradation, as well as for automatic mapping of their distribution, e.g. in form of false-colour images.

Figure 1: Schematic setup of a hyperspectral imaging system to be used for paper and writing durability studies.
Among several possible concepts for realizing a hyperspectral imaging system, we have chosen the setup shown schematically in Fig. 1. The document under investigation is placed in a light-proof cabinet and illuminated from two sides under an angle of 45° with two identical light sources emitting monochromatic light (spectral bandwidth 10–20 nm). The center wavelength emitted by these light sources can be tuned in steps of 10 to 20 nm over the entire wavelength range from 380 to 1100 nm. The advantage of this instrument configuration is that the stress to the document is absolutely minimal, as the light intensity is much lower than in conventional setups and contains no harmful UV and heat radiation.

A high-resolution monochrome CCD camera takes at each wavelength an image of the document. The tuning of the light sources and the image acquisition of the CCD camera is controlled and synchronized by a computer. Dedicated software converts the raw image data into calibrated reflectance images, resulting in a complete spectral reflectance curve for each image pixel, corresponding to a resolution of 300 dpi and more. The spectral data in the visible range can be used e.g. for calculating CIE colour values.

In the planned research, the calibrated reflectance images will then be analysed for spectral signatures, which can be related e.g. to different types of inks, ink corrosion, or other types of paper degradation.

3. Initial experimental investigations

For initial experiments, we built a laboratory hyperspectral imaging setup, where a document area of about A8 size was illuminated with a wavelength tunable light source (bandwidth <15 nm). A modified version of our ARTIST camera was used to image the document area at each wavelength.

In order to investigate differences in the spectral reflectance curves of different types of inks, we overlapped two manuscripts in the field-of-view of the camera and imaged them at 57 different wavelengths in the range of 540 to 1100 nm (step width 10 nm).

From the calibrated reflectance images shown in Fig. 2, it can be seen that the writings in both documents have a high contrast at 570 nm, however, at longer wavelength the contrast in the lower document is considerably reduced while the writing in the upper document virtually disappears at 1000 nm.

For a quantitative spectral analysis, we extracted from the hyperspectral image series the spectral reflectance curves at 4 small ink areas (size ~0.3 mm²) in each document.

As shown in Fig. 3, the spectral reflectance curves of these 8 regions of interest (ROI) clearly fall into two groups. ROIs 1–4 in the upper document exhibit very low reflectance values at short wavelengths, and a steep increase at >700 nm. As compared to this ROIs 5–8 from the lower document feature somewhat higher reflectance values at short wavelength, and a more gradual increase towards longer wavelengths.

These spectral signatures of the two writings were exploited for mapping their distributions in the false colour image shown in Fig. 2. This was generated by calculating for each pixel the ratio of the spectral reflectance values at 840 and 570 nm, and choosing blue colour to indicate ratio values >4, red for ratio values <4 but >1, and gray tones for ratio values <1. By applying this very simple algorithm, the resulting false-colour image shows the writing in the upper document mainly as blue pixels, and in the lower document only as red pixels.

4. Summary and conclusion

In summary, we discussed the design of a hyperspectral imaging instrument dedicated to research in paper and writing durability. Initial experimental results obtained
with a laboratory setup show that such an instrument can be used successfully for distinguishing between different types of inks.

In conclusion, our investigations indicate that the hyperspectral imaging instrument has a huge potential to become a standard research tool for a fast, non-destructive, spatially resolved analysis of historic documents, e.g. for assessing their condition or enhancing their legibility.

5. References

The primary methods of paper-making have ensured that paper is a material composed primarily of the fibrous polysaccharide cellulose. Native crystalline cellulose is comprised of chains arranged in parallel with a two-fold screw symmetry along the chains due to the β-[1,4] linkage of the D-glucose subunits. Two phases coexist within native cellulose type I, Iα and Iβ.

The degradation of cellulose in paper may be a function of processes such as acid hydrolysis, or of a free-radical mediated oxidative process. In both cases, scission of the cellulose polymers is evident. Factors such as the presence of inks, temperature, pH, humidity and the application of cleaning techniques may be implicated in accelerating cellulose degradation.

The precise method of historical degradation of cellulose is unclear. Recent studies have indicated that amorphous regions of cellulose may be more susceptible to damage than crystalline regions.

X-ray diffraction is a tool that can be used non-destructively, i.e. without the requirement for drilling or cutting samples in to small sections for analysis. In this manner, valuable documents may be assessed and returned to their collections without apparent damage. A number of features of the cellulose within paper can be analysed by X-ray diffraction, including the degree of crystallinity, crystal size and orientation. Presented here is preliminary analysis of X-ray diffraction profiles (fig. 1) from historical papers (circa. 19th century), which is compared with modern paper and celery, which is rich in type I cellulose from the cell walls.

X-ray diffraction analysis was conducted at beamline 14.1 at the Daresbury Synchrotron Radiation Source, England, UK. Samples were exposed to the synchrotron beam for 10 seconds per image. The X-ray wavelength was 0.1488 nm, and the sample-to-detector distance was 30 mm. This allowed for clear observation of the main diffraction peaks from paper.

2-dimensional X-ray diffraction images were converted to 1-dimensional linear intensity profiles using in-house software. Figure 2 shows a linear profile from one of the historical papers.

Crystallinity in samples is difficult to determine as an absolute value as assumptions need to be made regarding the shape of an amorphous contribution to the diffraction profile. However, a relative crystallinity value ($X_c$) to compare samples can be made from:

$$X_c = \frac{I_{200}}{I_{\text{TOT}}}$$

where $I_{200}$ is the integrated intensity derived from a Lorentzian peak fit of the (200) reflection, and $I_{\text{TOT}}$ is the total intensity at that position; i.e. the sum of the peak intensity and amorphous background. Peak fitting was carried out using the program Xfit (Collaborative Computing Project 13 (CCP13)). Such $X_c$ values allow for a rapid qualitative comparison of different samples.

Table 1 displays $X_c$ values for historical papers and reference samples. Paper 1 showed an area clearly damaged by the ingress of water; X-ray diffraction images were taken from both intact and damaged areas of that sample. Paper 2 is a historical newspaper with
ink writing on the surface; diffraction images were taken from the inked and non-inked regions for comparison.

**Table 1**: Crystallinity values ($X_c$) of historical paper and reference samples. Mean values are presented, ± 0.04.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Historical Paper 1</td>
<td>0.513</td>
</tr>
<tr>
<td>Historical Paper 1 – Damaged area</td>
<td>0.383</td>
</tr>
<tr>
<td>Historical Paper 2</td>
<td>0.412</td>
</tr>
<tr>
<td>Historical Paper 2 Inked region</td>
<td>0.443</td>
</tr>
<tr>
<td>Historical Paper 3</td>
<td>0.322</td>
</tr>
<tr>
<td>Historical Paper 4</td>
<td>0.394</td>
</tr>
<tr>
<td>Modern Paper</td>
<td>0.518</td>
</tr>
<tr>
<td>Celery (Cell Wall)</td>
<td>0.401</td>
</tr>
</tbody>
</table>

Of the historical samples presented here, papers 1 and 2 have relatively high $X_c$ values compared to papers 3 and 4. Historical paper 1 displays an $X_c$ value similar to that of modern paper. Of interest here is the effect of water damage and ink on the cellulose crystallinity. The water damaged paper displays a much lower crystallinity value than the undamaged area of the same sample, indicating that the crystalline regions have undergone damage. The sample with ink on the surface, however, displays a slight increase in $X_c$ values, indicating that the presence of ink has the effect of increasing the relative crystallinity of the sample, possibly by degrading the amorphous regions of cellulose preferentially. This indicates that the method of cellulose degradation is varies with differing external effects. Further examination of this phenomenon may provide a clearer understanding of the mechanisms of cellulose degradation in paper.

This analysis provides an indication of the potential for the use of X-ray diffraction to analyse historical paper documents. This technique may be expanded, as microfocus X-rays, with beam sizes as small as 2µm, can allow for surface-to-surface scans of paper documents to analyse the effects of surface treatments and ink on the structure of cellulose throughout paper cross-sections.

**Acknowledgements**

Thanks to the staff at beamline 14.1 at Daresbury, for technical assistance and advice. We are grateful to Hildegard Homburger, Berlin, for providing the paper samples.

**References**

ESTIMATION OF THE PROGRESS OF OXIDATIVE DEGRADATION OF PAPER USING CHEMILUMINOMETRY AND STANDARD DOUBLE-FOLD TEST

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Degradation of cellulose and loss of its use properties is caused by two main processes, particularly by acid-catalyzed hydrolysis and oxidation. The first reaction is direct cleavage of 1,4 β-glycosidic bond which takes place after its interaction with hydrogen ions and leads to semiacetal chain-end groups. On the other hand, oxidation by oxygen is much more complex process occurring via oxidation of hydroxyl groups on glucopyranosyl structural units into carbonyl and carboxyl groups. The latter facilitates scission of the cellulose backbone as well. Both, production of chain-end semiacetal groups and oxidation of hydroxyl groups are accompanied by weak light emission (chemiluminescence). The light emission may be released from several reaction steps involving peroxyl free radicals recombination. Peroxyl radicals are formed in the decomposition of hydroperoxides and the process of their termination is usually accompanied by the main chain scissions. Somewhat complicating factor is chemiluminescence from hydrogen peroxide in alkaline medium where singlet oxygen is the product of self-termination of two hydrogen peroxyl radicals. It appears, therefore, that chemiluminescence may be related to the process of chain scissions and the chemiluminometric method may serve as an important complementary method in studies of cellulose degradation. Such a case was shown for degradation of pure cellulose (Whatman filter paper)1, however, more complex real paper systems containing different additives including lignin, still remain the subject of further studies.

In the present paper we describe chemiluminometric experiments in isothermal conditions (at constant temperature) and in dynamic conditions (using various temperature gradients), for several papers: newsprint, bank and writing paper with and without deacidification treatment, and additionally aged from 0 to 24 days at 105 °C. The rate constants estimated from dynamic chemiluminometric experiments for 105°C are compared with a series of standard tests on remaining use properties of the aged paper samples.

Using the example of a bank paper (Figures 1a and 1b) we see a correlation between the number of double folds and relative polymerization degree obtained from transformation of chemiluminescence intensity $I$ vs. temperature $T$ experimental curves in oxygen atmosphere, using the equation:

$$I = \Phi_W = \Phi \frac{dDP}{dT} \frac{dT}{dt} = \Phi \frac{dDP}{dT} \beta,$$

where $\Phi$ is proportionality constant, $\beta$ is the rate of heating, $DP$ is the degree of polymerization and $t$ is time. The experimental runs for original (a) and deacidified (b) bank papers were attempted. The proportionality constants $\Phi\beta$ were calculated from non-isothermal analysis of the chemiluminescence intensity vs. temperature experimental curves, i.e. from the total surface below the determined curve1. For the determination of the relative degree of polymerization, the temperature 90 °C was chosen arbitrarily but any other temperature below 120 °C gives the similar shape of plot. The correlation also exists between the rate constant of sample degradation found e.g. for 105 °C and the number of double folds in machine direction. The observed correlations are promising and might lead to a more intensive use of the chemiluminometric technique for estimation of paper stability.

Correlation between the number of double folds for the sample of bank paper and its relative degree of polymerization determined from the surface below the chemiluminescence intensity – temperature runs in oxygen atmosphere at 90 °C and the rate constant of sample degradation at 105 °C are presented in Figures 1 and 2. The samples of original acidic (a) and deacidified (b) bank paper were artificially aged in air by dry heat at 105 °C according to ISO 5630/1 for periods of 3, 6, 12 and 24 days. The numbers in the plots denote days of accelerated ageing.

Acknowledgments

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Figure 1: Number of double folds (machine direction) for bank paper vs relative degree of polymerization determined from the surface below the chemiluminescence intensity – temperature runs in oxygen atmosphere at 90 °C.

Figure 2: Number of double folds (machine direction) for bank paper vs. rate constant of the sample degradation at 105 °C.

References
1. Motivations

Millions of books worldwide are menaced by paper disintegration due to malignant and inevitable degradation of cellulose chains caused by acid catalysed hydrolysis of glycosidic bonds. In order to prevent this process mass deacidification programmes have been launched. These now go hand in hand with research which should deepen our understanding of the observed phenomena.

According to the most recent findings, cellulose degradation should be regarded in terms of oxidative and hydrolytic mechanisms1-3 where the two reaction paths are autocatalytically accelerated by active oxygen species and protons, respectively. Notwithstanding, paper degradation kinetics is still based on formal rate laws4,5 which are with better or worse results, used to generate kinetic curves representing accelerated ageing of cellulose.

Typically, paper degradation progress is traced by mechanical or physical properties of paper such as tensile strength, fold endurance1,6, dynamic modulus or mechanical loss tangent7. However, these properties provide only macroscopic information. Another implemented parameter has been the degree of polymerisation representing an average polymerisation state of cellulose chains. Even though of paramount and practical importance, these parameters do not give a real insight into molecular behaviour during the degradation process. By contrast, highly sensitive to structural changes in materials, vibrational spectroscopy seems still to have an unexploited potential in modelling of kinetics of cellulose degradation, in spite of copious amount of published material.

The goal of this work is a verification of oxidative and hydrolytic paths in cellulose degradation mechanism to finally combine them in a formalism of mixed-controlled kinetic model7. In particular, it concentrates upon refining an in situ FTIR transmission technique to study accelerated ageing of paper materials. The most essential advantage it has over other IR techniques is that the technique provides information from the same sample area and allows us to observe real time chemical changes in material under controlled conditions. Due to the spectral complexity our focus in this work has been the 1400-1800 cm⁻¹ region where CO groups of different degrees of freedom occur. However, there are controversies in the literature concerning band assignment even in such a limited range.

1. Experimental

For the kinetic studies, we used model paper (P1) samples: bleached sulphite softwood cellulose paper with 99.5 wt % cellulose content (grammage: 78 g/m², BET: 1.21 m²/g) obtained from the Netherlands8. In order to collect transmission spectra thin paper plates were prepared from P1.

The spectra were recorded by a FTIR spectrometer (Bruker Equinox 55) with a MCT detector at an optical resolution of 2 cm⁻¹ and 2 level zero-filling. For the accelerated ageing tests the quartz reaction chamber with ZnSe optic windows was placed in the sample compartment of the spectrometer. The chamber was equipped with an electric furnace enabling heating in the broad temperature range (to 900°C) and with a gas supplying and evacuating system.

3. Results

Benefiting from the above mentioned advantages offered by the in situ experimental setup we have proposed methods of paper spectra standardisation:

1. Spectra normalisation using an internal standard defined as an integral absorbance of the CH 1900 cm⁻¹ band in the range 3000-2800 cm⁻¹, and denoted as standard absorbance;
2. Removal of water molecular vibrations from carbonyl vibration region by preliminary desorption of H₂O from samples and by recording the spectra at elevated temperatures;
3. Introduction of the oxidation index, defined as a ratio of integrals of bands at 1730 cm⁻¹ to that at 1620 cm⁻¹.
Complementarily, to remove water vibrations from the CO spectrum region, isotope exchange was applied and optimised. The applicability of this method for ageing experiments is, however, limited, because the properties of D-exchanged samples are different from original protonated samples.

The boundary conditions of experiments selected by us proved to be able to discriminate between hydrolysis of glycosidic bond and oxidation of carbon atoms in glycopyranose anomers. Accordingly, under the conditions of various gas mixtures (dry air, water vapour, humid air) two types of experiments were performed: (i) short ageing tests at three selected temperatures (100, 150, 250 °C) and (ii) longer isothermal tests. Following the changes in spectra in the carbonyl range as they increased with oxidation time (an example in Figure 1), various intermediates of cellulose oxidation were distinguished starting from the least oxidised monocarbonyl groups, through diketones to aldehydes and carboxyles.

The band assignment was supported by the spectra fitting by mixed Lorentzian-Gaussian function optimization and literature data. The changes in band intensities during paper oxidation were found to correspond to a parallel-consecutive mechanism. In the first approach a simple model taking into account both band positions, and presumed reaction mechanism, is proposed and is schematically presented in Figure 2.

The assumptions were verified by independent experiments. The position of -COOH stretching mode at 1730 cm\(^{-1}\) was confirmed by the experiment utilizing the acidic groups neutralization with a dilute KOH solution (Figure 3). As a result of the reaction with KOH, the intensity of vibrations at 1730 cm\(^{-1}\) weakened (curve b). At the same time the sub-bands coming from other intermediate products of cellulose oxidation revealed.

**Figure 2:** Consecutive-parallel mechanism of partial oxidation of cellulose, where intermediate products are represented by functional groups included in monomers and associated with frequencies of their vibrations.

**Figure 3:** Model paper (P1) sample: a) aged for 110 h in dry air at 150 °C, b) then neutralised with 5×10\(^{-2}\) mol/dm\(^3\) KOH solution and washed with distilled water.

4. References

DETERMINATION OF pH OF PAPER

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1. Introduction

Of all paper properties, acidity/alkalinity is probably the crucial parameter for stability of its most important structural element, cellulose. Considering the role of this parameter also in permanent paper standards, its proper determination is of primary importance. Several procedures for determination of paper pH have been evaluated, ranging from standard extraction procedures, surface pH, “micro” pH determination, and use of coloured acid/base indicators, on 55 different samples. This work is published as a full paper elsewhere.

2. Materials and methods

Paper samples

Papers and pulps of various origins were used and the type of fibres was determined according to SCAN-G3:90 and SCAN-G4:90 standards. From books, only paper parts without print were used. Deacidified samples were prepared by immersion in solutions of 0.04 mol L⁻¹ Mg(HCO₃)₂ or 0.01 mol L⁻¹ Ca(HCO₃)₂. All samples were equilibrated at room conditions prior to use.

Determination of pH

The following procedures were used:

- Tappi 509 om-02 (cold extraction, 1 g of sample per 70 mL of water, 1 h);
- Tappi 529 om-88 (pH of paper surface using a flat combined glass electrode);
- Determination of pH using colour acid/base indicators-containing pen (pHydrion, Talas, New York, USA);
- Determination of equilibrium pH: to 1.00 ± 0.01 g sample, 70 mL MilliQ water was added. The sample was stirred at 250 r.p.m. and pH was followed continuously until an equilibrium (up to three days) was achieved.
- New method: to 0.070 ± 0.005 g sample in a reaction tube, 5 mL MilliQ water is added, previously aerated for 30 min in order to obtain a CO₂-saturated solution (for samples with pH > 7). Samples are defibrillated in a reaction tube using a precision hand drill with a stand at 25,000 r.p.m. for 15 min.
- “Micro” determination of pH: samples are cut out with a sharpened surgical needle of inner diameter 0.8 mm. The average weight of such samples depended on the grammage of a particular paper, but was approximately 10 µg. Aerated water was added (2 µL) and the pH was determined once the reading stabilised (after max. 5 min) using the MI-415-2cm micro combined glass electrode (Microelectrodes Inc., Bedford, USA).

3. Results and discussion

Water in paper, if present in sufficient quantities, may contain dissolved matter, some of which in ionic state. While, at present, the concentration of H₃O⁺ ions in this matrix cannot be measured, the compounds can be extracted and the pH of extract determined. It is evident, though, that pH in paper will be affected by its water content.

Determination of pH is relatively straightforward if paper samples are acidic. For such samples, all extraction procedures will give data in good agreement with the standard cold extraction procedure. Irrespective of the fact that the true pH in cellulosic fibres is difficult to determine, it seems that CO₂ should be taken into account when determining pH of alkaline paper, since the material is usually in equilibrium with the atmosphere in which it is stored and this regularly contains CO₂. None of the present standard procedures take this into account.

A comparison between the equilibrium values and the values obtained with the standard extraction method (Fig. 1) shows that the standard method gives values up to 1 pH unit too low for gelatine surface sized samples and values up to 2 pH units too high for samples containing MgCO₃. The agreement between the two methods is excellent only for acidic samples.

![Figure 1: A comparison of the determinations of equilibrium pH values with those obtained with the standard procedure. Only acidic samples are included in the correlation.](image-url)
With the new procedure, a remarkable correlation with the determinations using the method of determination of equilibrium pH is evident (Fig. 2), in which dispersions of paper samples are given ample time to equilibrate with the atmosphere. In the correlation, all samples included, even the surface-sized, although these samples are not homogeneous.

If samples are alkaline, the following can be concluded:

- If the duration of extraction is short or if the mixing is inadequate, the slow dissolution of alkali-earth metal carbonates and the slow absorption of atmospheric CO₂ will not allow for proper equilibrium to be achieved. Determinations of pH of such alkaline extracts using the standard extraction methods will lead to pH values which may be up to 1.5 pH units too high. The repeatability is nevertheless below 0.15 pH units, yet sample consumption is high: 1 g is needed.

- With the surface method, the repeatability is lower, up to 0.30 pH units, yet this may also reflect sample inhomogeneity. The time of dissolution and the amount of water are sufficient for rapid dissolution of an equilibrium amount of CaCO₃, meaning that the pH of such samples determined by the surface method will not correlate with the measurements obtained by the standard cold extraction procedure. Determination of surface pH cannot be considered as a non-destructive method, due to marks left at the edge of the wetted part of paper, along which paper degradation proceeds faster. Gelatine used as surface sizing leads to lower surface pH of papers than the bulk pH by up to a few units. This may be problematic if the decision on whether to deacidify or not is based on such information.

- If using the standard cold extraction procedure, the time to achieve equilibrium is excessively long especially in the case of MgCO₃-containing papers yet it can be shortened to 15 min if intensive mixing is used. Having optimised the type of mixing and the sample to water ratio, we propose a new procedure. Using this new procedure, pH of CaCO₃-containing pulps was determined to be approx. 8.5, and the pH of MgCO₃-containing pulps approx. 9.5. In paper, the type and amount of additives may influence these values considerably. Repeatability of determinations using the proposed procedure is lower than 0.12 pH units, the amount of sample needed is 0.07 g. A rapid equilibration (15 min) with atmospheric CO₂ can be achieved, which makes this method suitable for routine determination of paper pH.

- Miniaturisation of the procedure using micro-combined pH electrodes leads to a satisfactory correlation with the proposed method, yet with lower repeatability: values of 1.0 pH unit are acceptable. The amount of sample needed for such determination is low (circular cut of diameter <1 mm), yet several samples are needed to obtain a satisfactory average value.

- Determination of pH using pH pens may provide rough estimations, with errors up to several pH units. Caution should be taken especially if degraded, intensively yellow papers are under observation, as colour evaluation is then difficult. This may be problematic if the decision on whether to deacidify or not is based on such information.

- Due to the slow dissolution of alkali-earth metal carbonates, changes in relative atmospheric humidity and the resulting changes of water content in paper lead to fluctuations in local pH in paper. This should be taken into account in paper stability studies, if experiments with dynamic humidity (humidity cycling accelerated ageing) are performed.

4. Acknowledgements

Ministry of Education, Science and Sports of the Republic of Slovenia is gratefully acknowledged for supporting this research (Programme P1-0153, project L1-5237).

5. Reference


Conservation and preservation decisions take into account some general strategic guidelines and are based on condition of the collection in question. The condition can generally be defined by physical, (micro)biological and chemical state of paper preservation. Since chemical damage is usually not visually detectable, it thus represents an especially difficult and critical parameter contributing to well-informed collection management. Since most classical and widely available methods of analysis are either too expensive, too time-consuming, require extensive sample preparation, are destructive, or even require a large amount of sample, their application to originals, even for microanalysis, is hardly conceivable. For these reasons, an NIR (near infrared) spectroscopic analytical technique was developed potentially enabling us to evaluate whole collections within a reasonable timeframe. The technique does not require any sample preparation; collection and evaluation of a spectrum is a straightforward procedure, and it is non-destructive. Using an additionally developed software tool NIR-PR (NIR Paper Rating), safe evaluation of the condition of an artefact or even a collection is possible. The use of NIR spectroscopy for characterization of paper is well-known and has already been used in paper degradation studies.

The NIR-PR tool makes use of standardized measurement categories (parameters) which are used to describe the state of degradation. Among these, mechanical properties, degree of polymerization (DP), lignin content and pH are undoubtedly the most important, although other parameters such as carbonyl group content can also be determined. The basis for any quantitative NIR method development is a good set of reference data. These must be obtained from a large and well representative set of sample papers of historical origin.

The data of chemical; and predominantly mechanical characterization were subsequently correlated with NIR spectra using advanced chemometric (statistical and mathematical) methods, e.g. multivariate statistics. From the obtained correlations, the state of degradation of a certain sample can be evaluated.

In this contribution, we will shortly review the state of the art of the methodology and explore some future needs and prospects.

### 1. Method development

As a result of a considerable number of analyses, a classification model has been developed and implemented in the NIR-PR tool.

The classification according to the NIR-PR tool is done in the following way. After spectroscopic characterization of a sample, evaluation of the state of degradation according to the determined physical and chemical parameters is performed on the basis of preset criteria. These criteria are independent of the general strategic preservation plan, and are selected in order to mirror the decision-making system on the basis of which a sample is considered more or less stable. An inclusion of a proposal of a treatment strategy in the NIR-PR is optional. The recommendation regarding the applicability of mass deacidification can also be included (Fig. 1).

<table>
<thead>
<tr>
<th>Group 1</th>
<th>State 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good condition</td>
<td>Group 2</td>
</tr>
<tr>
<td>State 3</td>
<td>Group 3</td>
</tr>
<tr>
<td>Group 4</td>
<td>Bad condition</td>
</tr>
<tr>
<td>State 5</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1:** Classification model for the rating of paper condition.

On the basis of such a model three ratings are given: States 1, 3 and 5. With an increased set of data in future investigations a finer division and better definition of the thresholds 1–3 and 3–5 is planned.

In order to obtain a satisfactory set of workable data, more than 100 different wood pulp and cellulose papers produced between 1886 and 1993 were analyzed in a destructive way. The real historical samples were obtained from a variety of sources in Germany – in the phase of method development, we have not attempted to obtain a sample set representative for a variety of paper sources and geographical origins. Among the more important parameters, tensile strength (F_{max}) in the machine direction and intrinsic viscosity were determined. The definition of limits of the Groups and States in Figure 1 was done according to the obtained
Durability of paper and writing data. After the limits were defined, the data obtained from NIR spectra by chemometric evaluation were grouped accordingly.

Additionally, as the individual properties are not all equally significant for the definition of paper condition, statistical weights had to be associated with each property.

In order to minimise the error associated with NIR-PR, separate methods were developed for the two sets of samples: wood pulp and bleached cellulose/cotton. This was necessary due to the widely different spectral characteristics. Besides, the intervals of measured chemical and mechanical parameters depended on the paper variety very much. E.g., lower tensile strength $F_{\text{max}}$ was determined in wood pulp papers than in cellulosics as a rule.

In order to enable this division into two categories, the lignin content of papers was characterized during spectroscopic evaluation first: if lignin content was found to be lower than 10%, the sample was characterised as bleached cellulose/cotton paper.

2. Experimental

NIR is the spectral area between visible and mean infrared light (12,000–4,000 cm$^{-1}$, i.e. 850–2,500 nm). Absorption of light in this interval of wavelengths corresponds to a great variety of combination and overtones, which increases the information content of the spectrum. Its exact analytical interpretation is therefore hardly possible. However, using the chemometric approach, the complex interrelated information within a spectrum is reduced to a few specific basic patterns (absorption bands), the parameters of which can then be correlated with known properties of the measured system, i.e. paper. Such treatment of NIR spectra allows for easy, fast and chemical-free quantitative analyses.

The spectra are obtained on the basis of trans-flection (transmission and reflection): the sample is irradiated with non-destructive NIR light from an integrated source and the reflected spectrum is recorded using an array detector. High reproducibility can be achieved if good resolution and thermal stability can be assured.

The NIR system developed by our group consists of a portable dispersive NIR spectrometer with a specially constructed external “sampling head” for solid materials, which is connected to the spectrometer by means of an optical fibre and is equipped with a sample carrier and a plate to gently press the sample down on the sampling head during a measurement. A computer, which is an integral part of the instrument, allows for immediate display of the results (Figure 2).

The paper to be characterized is placed on the outlet of the external light source. In order to assure high precision, at least three consecutive measurements are carried out per evaluation in three or more different parts of the sample (measurement spots). The spots should be selected in a statistical manner in order to take into account possible sample inhomogeneities. The recorded spectra are automatically averaged, followed by an instant display of the rating according to the NIR-PR tool. The required time of analysis per object depends on the required sample handling: for the actual recording of spectra and calculating the results, milliseconds are needed.

Due to the large penetration depth of NIR light, measurements have to be carried out on several layers of paper or with a ceramic background such as the one used for calibration. Text on the paper does not interfere with measurements; however, sections with high colour saturation (e.g. illustrations with a high percentage of black pigments) are to be avoided. While only minimal pressure against the sampling head is sufficient for a book, a metal plate should be used for loose sheets in order to obtain higher reproducibility.

3. Software tool

The elaborated method was integrated into a Microsoft-Windows-based software application with an appropriate user interface. The combination of the spectrometer and application software enables the operator to start evaluation with a mouse click. After having chosen a specific file and entering an appropriate sample description, internal calibration of the system and measurement is started by the software, automatically. The evaluation progress is displayed on the monitor. As a result, the paper condition is displayed, described by the state (Figure 1).

For the evaluation of large collections, the results are compiled in a table. The number of characterized samples is not limited. In addition to sample description, a commentary, as well as the date and time are optional parameters. Certainly, the results of all individual measurement categories are also compiled in the file, which can be easily converted into a Microsoft Excel file or other similar application.
4. Outlook

Wood pulp and bleached cellulose containing acidic papers account for a greater part of endangered paper collections in libraries, museums and archives. NIR-PR enables us to survey the condition of such collections on a scientific basis in a repeatable manner. It is also useful to monitor the ageing behaviour of collections by performing repeated evaluations. The non-destructive NIR-PR evaluation represents a powerful tool which enables the collection manager to plan efficient preservation strategies.

In the EC 6th Framework research project SurveNIR we will considerably expand the sample sets with regard to the geographical and material characteristics (date and type of production) thus extending the possibilities of the NIR-PR for surveying extremely large and variable collections.
During its production and processing, cellulose is modified both chemically (oxidation and hydrolysis) and structurally (type and degree of crystallinity). The purposes of these modifications are to change cellulose fibre reactivity (number and location of functional groups) and to inhibit or at least minimise possible degradation. The processing of cellulose has an influence on the fibrillar structure, i.e. crystallinity of cellulose decreases, resulting in swelling of the polymer as well as increased accessibility of active groups on the fibre surface. Chemical degradation can be expected to occur primarily on amorphous cellulose and on the surface of crystallites. The borderline between accessible and not accessible cellulose is not well defined. Other changes may also take place, e.g. reorganization of cellulose chains. Previous research has, however, mainly focused on analysis of the fine structure of cellulotic fibres. Much less attention has been given to the reactivity of cellulose fibre surfaces, which is a consequence of reactions on fibre surface and correlates with charge.

The charge of cotton fibres, due to dissociation of acidic groups in neutral or alkaline conditions, may originate from the original chemical composition of the fibre wall but also from changes during the different process steps. Some pre-treatment processes lead to a decreased number of acidic groups; while during others new acidic groups may be generated. The variation of dissociable acidic groups and, consequently, of charge has an influence on the adsorption capacity and, therefore, on fibre reactivity.

In this work cotton fibres were oxidized with the aim to change the total charge (content of accessible acidic groups) and surface charge (content of acidic groups on the fibre surface). Oxidation of fibres was done selectively with potassium periodate(VII) followed by sodium chlorite(III). It has been shown that oxidation in this way may cause carboxyl groups to be introduced mainly at the C₂ and C₃ positions. The purpose of this study was to evaluate how selective oxidation affects surface properties of fibres. Another very important objective was to compare different methods and evaluate whether they are applicable and sensitive enough to observe the changes in nature, content and accessibility of acidic groups in the fibres, with special emphasis on the X-ray Photoelectron Spectroscopy (XPS).

X-ray Photoelectron Spectroscopy has recently gained much attention in the analysis of organic materials. Due to an analysis depth of only a few nanometers and easy elemental quantification, the technique has been used for surface characterization of inorganic materials for decades. In the case of organic fibres, the surface sensitivity and enhanced energy resolution of modern instrumentation, which enables quantitative determination of differently bonded carbon atoms, have made this technique a valuable research tool. XPS has been mostly used to analyze pulp and exopolysaccharides. When characterizing lignocellulosic materials, two alternative methods can be used. The first is based on quantitative elemental analysis of the surface, where the O/C ratio, which is different for cellulose, lignin, and extractive, is used. In the second method, differently bonded carbon atoms and, consequently, different functional groups on the surface are determined quantitatively from high-resolution spectra by means of deconvolution. In this case, the component at 285 eV, which is due to carbons without oxygen bonds, can be used to determine surface coverage of lignin and extractives.

In this work, surface chemistry of oxidised cotton fibres is analyzed with XPS. In addition to this method, polyelectrolyte titration was used to obtain information about charge location and accessibility of charged groups. The results from XPS were combined with those obtained by polyelectrolyte titration in order to obtain a consistent picture of the location of dissociable groups on the fibre surface.

The combination of XPS with titration confirms the presence of two processes during oxidation: low molecular fraction elimination and new acidic group formation in the cellulose chains. Domination of both processes is dependent on oxidation time, but the first one is more effective. The XPS method confirms that the surface concentration of acidic groups is considerably lower than the bulk concentration. This suggests that during oxidation the content of carboxyl groups on the surface decreases, while in amorphous regions it increases. The first is the consequence of “cleaning” effect; the second is the consequence of formation of new acidic groups. During the oxidation, the small periodate ion might be able to enter the cellulose fiber interior and the glucose unit may be oxidized at C₂ and C₃ so that new – CHO are formed.
inside of fibres. In the second oxidation step these groups inside of fibers are oxidized to carboxyl groups.

The use of XPS analysis in combination with titration method seems to be very promising for the future observation of the influence of chemical modification, e.g. oxidation, on the fibre surfaces for textile as well as for paper use. Therefore, these methods could be useful as a control tool for determination the degree of degradation, until fibres still keep suitable practical characteristics.

References
Accelerated ageing tests are at the heart of key preservation management decisions, for it is through these tests that we learn how materials age and how we can control the environment, or provide a chemical treatment such as deacidification, or avoid exposure to harmful chemicals, and thus extend the useful life of our treasured collections. Therefore, it can be frustrating if accelerated ageing tests, which make up the very foundation for our preservation actions, are themselves built on questionable assumptions. While we have had no option but to continue the use of such tests for the lack of a better option, the literature is replete with nagging doubts and questions about their reliability.\(^1\)\(^-\)\(^5\) In the formulation of standards for permanent paper, while accelerated aging tests are often specified as options, they have rarely been required. Instead, we have learned to place our faith on compositional requirements such as a minimum level of alkaline reserve and the near-absence of lignin to define permanent paper, even though this approach does not always make good sense. For example, cotton papers, which have already been proven to be one of the most permanent papers, would not meet the requirements of most present-day standards for permanent paper since they would fail the alkaline reserve and pH requirements. Even worse, overly recycled papers of poor quality with minimal strength but with the right compositional content can potentially pass muster as permanent papers.

In order to move from composition-based standards towards performance-based standards, we need to develop an accelerated ageing test in which we can have a high enough degree of confidence so that we can let go of the protection that a composition-based standard can provide us. To achieve this reality, research at the Library of Congress was focused throughout the nineteen nineties on the development of an accelerated test that would simulate the ageing of paper in real life, and settle forever the debate about the value of accelerated ageing tests that has raged at least since George Richter recognized in 1934 that “…there will probably continue to be two schools of thought on the relative merits of (accelerated ageing tests) – those who believe in them and those who do not.”\(^6\) With the research we present here we hope to be able to move towards a single school of true believers. Instead of following the oft-trodden path of expounding the linearity of Arrhenius plots through a limited range of elevated temperature and relative humidity conditions, we focused on a comparison of the chemical products which result from the ageing of paper. In particular, we analyzed papers aged naturally as well as by accelerated ageing for carbohydrate species using ion chromatography and aliphatic acids such as formic and acetic, which we discovered form in surprisingly abundant concentrations, by capillary electrophoresis. Test papers were selected with a view to extend the study to the greatest variety of papers, and included acidic as well as alkaline papers made from cotton, bleached northern softwood kraft and groundwood pulps. These six papers were aged as loose sheets (which has been the norm for most accelerated ageing tests), as book-like stacks and inside air-tight glass tubes. The choice of these three ageing configurations was based on our earlier work, which had shown us that acidic degradation products tend to accumulate inside polyester encapsulations and other enclosures, and thereby hasten the ageing of paper.\(^7\)\(^,\)\(^8\) The similarity of the nature of degradation products formed under natural ageing and under accelerated ageing within glass tubes was most striking as demonstrated by the chemical analysis for the carbohydrate and acid species formed in the ageing process. These data provided unequivocal proof of the great similarity between reaction mechanisms underlying the natural and accelerated ageing processes. On the other hand, lower rates of degradation were observed for experiments carried out with loose sheets. It was also clear that in these experiments the volatile acids were not being retained within the paper matrix. This work resulted in the development of an accelerated ageing test in which paper samples conditioned under a standard environment are aged inside airtight glass tubes at 100 °C for 5 days to gauge the retention of their original strength properties. The lowest strength loss, preferably no more than 20 percent, qualifies the paper to be of the highest permanence quality regardless of its chemical composition. Since this test does not require the use of expensive ageing chambers that can simultaneously control relative humidity and temperature, it can be used by many more facilities where only simple ovens, which can only control temperature, may be available. Besides the economy that it offers, this test is also much faster since it requires only 5 days as compared to conventional ageing tests, which generally require 30 days, and even more importantly, do not simulate the natural ageing process. This test has now been adopted as an ASTM standard, and efforts for its adoption as an ISO standard are in progress to the best of our knowledge.

In the process of development of this test, we also acquired a new understanding and appreciation of the chemical mechanisms by which paper ages. Thus far,
we had blamed acidic alum-rosin sizing and environmental pollutants for the inexorable embrittlement of our ageing book and manuscript collections. While these factors do contribute to the ageing process in paper, their contribution is not as significant as that of the acids that form as a result of the degradation of cellulose and hemicelluloses as they interact with oxygen and moisture over time. The formation of these acids leads to a self-promoting hydrolytic degradation chain reaction, or auto-catalysis, in which the acid concentration continually builds upon itself, leading to a constantly escalating acidic environment that promotes an ever-increasing rate of cleavage of the cellulose molecules. These findings belie the school of thought that the ageing process somehow reaches a state of equilibrium leading to an asymptotic condition under which the rate of ageing ultimately slows down almost to a stop.

The practical implications of this new understanding of the mechanism responsible for the ageing of paper are hugely significant as well. The hitherto overlooked role of these naturally generated acids in catalyzing the hydrolysis of the cellulose molecule is also the fundamental reason for the non-correspondence of other accelerated ageing tests with the natural ageing process since these accelerated ageing tests allow the acids which cause the most damage to escape freely, and thereby paint a less than accurate picture of the real rate of ageing. Because of reliance on such faulty tests, we have grossly underestimated the benefit that can be derived from deacidification. Likewise, we have underestimated the harm that can be done by high relative humidity conditions since exposure of loose ageing sheets to higher humidity conditions, at which the abundance of water molecules as well as the elevated temperature levels force the acid molecules formed in the ageing process to escape into the environment. In real life, hydrogen bonding enables retention of newly formed acid molecules within the paper matrix. The efficiency of acid retention is even higher when the paper is prevented from interaction with air as when it is situated within the body of a book, or a picture frame, or a polyester capsule.

Therefore, the threats from humid environments and developing acidic conditions in paper are appreciably higher in real life that estimates from conventional accelerated aging tests would have us believe. The new accelerated aging test presented here overcomes these drawbacks.

References
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1. Genesis

Accelerating ageing, its importance and necessity of analyzing the data thus obtained, have been already emphasized by Porck\(^1\). He pointed out that “the small number of research projects that have tried to verify the predictive value of artificial aging analysis strongly contrasts with the widespread use of this analysis in practice”.

The analysis is based on the use of Arrhenius equation for extrapolation of kinetic data. Hence application of the equation to the description of complex phenomena of cellulose degradation, being the problem typical of preservation science, will be discussed below.

2. Fundamentals

Fundamentals of the chemical kinetics should be recalled here. If one wants to use Arrhenius equation for the description of temperature dependence of rate constants, then one must be sure that the considered kinetic equation is in agreement with the results of isothermal experiments in the whole range of temperatures studied. When the kinetic equation is simple (an elementary step or rate determining step (\(r_d\)) of a complex reaction are the examples) the application of Arrhenius relation is straightforward. However, in the more general case, when \(r_d\) is absent, kinetic equation is more complicated, and it contains two or more rate constants. This implies the use of two or more Arrhenius plots for the interpolation or extrapolation of kinetic data within a temperature range.

Taking into account another fundamental premise – a reaction mechanism cannot be proven by kinetic data; it can be, however, easily excluded – let us consider the following example.

3. Hydrolytic and oxidative pathways of mixed-control mechanism of cellulose degradation

The rate of acid hydrolysis is described by the Ekenstam equation. If, under certain conditions, this equation does not hold, then acid hydrolysis cannot be the only pathway of cellulose degradation. The results of the kinetic studies dealing with applicability of Ekenstam equation\(^2\) have been summarised in Fig. 1.

Model paper samples containing cellulose only, pure and impregnated with aluminium sulphate, have been aged for 2–21 days within the temperature range 40–100 °C. Every kinetic curve, characterized by temperature (°C) and Al content (% by weight) has been indicated by a single point in Fig. 1. On the abscissa, the deviation of the curves from Ekenstam equation has been shown.

It was indicated in publication\(^2\) that within the shaded area of Fig. 1 a single degradation route (this being acid hydrolysis) dominates, whereas outside the area (i.e. at higher temperature and higher Al content) oxidation of cellulose should also be taken into account. Thus Arrhenius equation can be safely applied to the rate constant of Ekenstam equation inside the shaded area only.

Figure 1: Residual standard deviations (expressed as \(DP\) values), obtained for paper samples impregnated with various amounts of Al, as a function of temperature. Taken from ref. 2 – however, in the description of the original drawing, time (days) has been indicated erroneously instead of temperature (deg).

Two degradation routes exist outside the area – acid hydrolysis and oxidation – and, therefore, the Ekenstam equation does not hold. Another, at this time unknown, equation (let’s call it a mixed-control equation) will properly describe the kinetic data. The postulated equation will contain two rate constants – \(k_h\) and \(k_o\) – for acid hydrolysis and oxidation respectively. There will be two Arrhenius plots: \(\ln(k_h)\) versus \(1/T\) and \(\ln(k_o)\) versus \(1/T\), and, consequently, two activation energies can be calculated. It seems obvious that continuity behaviour should be observed in such a case. One can expect that the mixed-control equation, when extended to the low-temperature region (inside the region encircled by the borderline in Fig. 1), will yield Ekenstam equation as the limiting case. Therefore the Arrhenius plot for \(k_h\) should be valid (i.e. no sharp direction changes observed) in the whole range of experimental conditions – outside and inside the Fig. 1 borderline. On the other hand, as assumed, the kinetic
data providing \( k_{o} \) values are restricted only to the temperatures outside the borderline. This is why the extrapolation of \( k_{o} \) value to the temperatures below the borderline should be avoided.

4. The concept of Arney and Novak revisited

The ideas outlined just above can be emphasized by taking into account the publication by Arney and Novak\(^3\) entitled informatively “Accelerated Ageing of Paper. The Influence of Acidity on the relative Contribution of Oxygen-Dependent and Oxygen-Independent Processes”. Arney concludes that the rate of paper degradation is a sum of four terms, depending on (i) oxygen pressure, (ii) pH value, (iii) both oxygen pressure and pH, and (iv) neither oxygen nor pH. Hence, there are four rate constants, and, consequently, four Arrhenius plots could be drawn. In fact, a complex mixed-control mechanism is taken into account in the publication in question.

5. The case of metallurgy

There is nothing new in the concept of mixed-control mechanisms. The idea can be directly linked to the fundamentals of chemical kinetics. If no rate-determining step can be postulated, then one should suggest a kinetic equation considering two or more elementary steps occurring with similar rates and contributing to the overall reaction rate in a similar way. This idea, initially introduced in solid-state chemistry in mid-twentieth century, has been successfully extended in the research on solid-gas reactions, being of primary importance in metallurgical processes. An extremely simplified example would help the reader to understand the concept in question.

Let us consider the reduction of iron ore grains by hydrogen. The shape of grains is considered as being approximately spherical. The reduction temperature and the grain radius are variables equally important as the temperature and pH of paper in the process of cellulose degradation. The reaction of oxide reduction on the grain surface and diffusion of water vapour and hydrogen within the porous structure of the grain are partial processes of the overall reduction of ore; similarly acid hydrolysis and oxidation are partial processes of the overall process of cellulose degradation.

Fig. 2 has been redrawn after the already classical drawing published in the monograph of Szekely\(^4\). Three zones can be observed in this Figure: that of chemical control, diffusion control and mixed control:

– in the region of chemical control the chemical reaction is a rate-determining step, and a kinetic equation has one term containing only one parameter: reaction rate constant;
– in the diffusion control region the gas (H\(_2\), H\(_2\)O) diffusion in the pores of solid is a rate-determining step, and the kinetic equation has only one term containing only one parameter characterizing the diffusion phenomena in solid – e.g. effective diffusivity;
– in the mixed-control region there is no rate-determining step, and the kinetic equation consists of two terms – called reaction term and diffusion term – containing two parameters: reaction rate constant and effective diffusivity, respectively.

One can easily notice that the kinetic equations valid in the regions of chemical control and diffusion control are boundary cases of the more general equation describing the overall reduction process in the mixed-control region. Examples of mixed-control equations can be found in the textbooks by Levenspiel\(^5\).\(^6\).

6. Conclusions

The success of extrapolation procedure during the analysis of accelerated ageing experiments depends on getting the proper mixed-control description of degradation phenomena within the high-temperature range. Not enough primary kinetic data, enabling characterization of simultaneous hydrolytic and oxidative degradation of cellulose, can be found in literature. The advance of both processes should be independently determined by properly planned experiments. It is obvious that model samples of paper should be studied first.

7. References

1. Introduction

Papers made of mechanical pulps as well as aged cellulosic materials contain lignin or other phenolic components. When exposed to daylight, they may exhibit pronounced yellowing that decreases their readability and possibly mechanical strength. During the past decades, much research was devoted towards understanding the main reaction pathways and structures of coloured compounds.\(^1\)\(^-\)\(^3\) It was shown that photo-irradiation induces cleavage of lignin ether bonds to produce phenoxy or phenoxyalkyl radicals which in turn react with oxygen. The result is the formation of benzoquinone derivatives that absorb light in the violet and visible region.

In order to inhibit the photo-induced processes, a great number of different compounds, their combinations as well as the effect of chemical modification of pulps were studied.\(^4\)\(^-\)\(^6\)

Combined applications of UV screens and radical scavengers were the most successful. It was observed that in this way a synergistic effect can be obtained leading to a decreasing demand for stabilizers.\(^7\)\(^-\)\(^9\) The inhibiting compounds are usually sprayed or poured over the paper surface. This can be an obstacle for their use in industrial papermaking due to the lack of an appropriate technology. In addition, radical scavengers have the most pronounced effect if they are close to the sites of radical formation, i.e. where lignin is localized. On the other hand, UV absorbers have the optimum effect on the paper surface. Therefore the application techniques have to be different for these two types of inhibitors.

2. Experimental

In the present study, a stabilising effect of hydroxyphenyl benzotriazol-type UV absorbers combined with novel radical scavengers based on sulphur-containing amino acids was investigated in applications on surface-sized or surface coated systems. For the investigations, model papers made of a mixture of an ECF-bleached sulphate pulp and a bleached mechanical pulp with an increasing fraction of the mechanical pulp were used. The irradiation was carried out in a Xenotest 150S unit at 20 °C and 50% relative humidity. Optical properties of the papers were characterized by their ISO brightness or CIE L*a*b* colour data.

3. Results and discussion

In the first experiment, paper samples were sized with an aqueous solution of polyvinyl alcohol (3 g m\(^{-2}\)) containing different amounts of the radical scavenger acetyl cysteine. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>Content of stabilizer</th>
<th>Brightness after irradiation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>10 h</td>
</tr>
<tr>
<td>No sizing</td>
<td>83.8</td>
</tr>
<tr>
<td>Sizing without stabilizer</td>
<td>81.4</td>
</tr>
<tr>
<td>Sizing with 0.5% stabilizer</td>
<td>84.8</td>
</tr>
<tr>
<td>Sizing with 1.0% stabilizer</td>
<td>85.6</td>
</tr>
</tbody>
</table>

These results demonstrate that a single application of the radical scavenger has only a minor stabilising effect. To cover the paper surface, a thin coating of polystyrene-polylbutadiene coating with calcium carbonate and china clay pigments was used. The addition of a UV screen (Ciba Tinuvin 328) led to further stabilization (Table 2).

<table>
<thead>
<tr>
<th>Content of UVA in coating colour (%)</th>
<th>Brightness after irradiation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>83.2</td>
</tr>
<tr>
<td>0.5</td>
<td>81.0</td>
</tr>
<tr>
<td>1.0</td>
<td>81.1</td>
</tr>
<tr>
<td>2.0</td>
<td>81.9</td>
</tr>
<tr>
<td>3.5</td>
<td>83.3</td>
</tr>
</tbody>
</table>

In comparison with the uncoated sample, the coating itself has a remarkable effect on brightness stability. When 3.5% of the UV screen is applied, brightness after 20 h irradiation increased by another 10%.

When both types of inhibiting systems where applied onto paper surface, their mutual impact exceeded that of the sum of the single components. With 1% of acetyl cysteine in the surface sizing and 2% of the UV screen in the coating colour, brightness of 70.3% was obtained after 20 h of irradiation.

4. Conclusions

These results led to the conclusion that a combination of stabilisers may be interesting also from the point of view of conservation, since especially the paper manufactured during the 19th and the beginning of the 20th century contain considerable amounts of lignin or...
may incorporate low molecular phenolic compounds due to ageing processes. These papers will undergo light-induced discolouration. Coating these materials with very thin layers of combinations of stabilizers presented in this study could help to preserve their optical properties as well as mechanical strength for a long period.

5. References

DEGRADATION OF CELLULOSE HANDSHEETS AS STUDIED BY BEGIN AND KAMINSKA METHOD

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The method of accelerated aging developed by Canadian Conservation Institute (CCI) and Library of Congress, and recently accepted by ASTM as a new standard (ASTM D 6819-02), intends to mimic the mechanical and chemical changes occurring in paper under natural conditions in a new way. A wide array of existing methods and standards (see: 2) does not take into account the factor evident to every reader opening an old book – its odour. In an aging experiment with free-hanging separate sheets of paper, the degradation products can be easily desorbed from the sheets, thus not affecting paper degradation any further – in contrast to real situation, where closed books or archive materials are tightly packed on shelves.

1. Reproducibility of the proposed test method

A series of samples used in the ASTM/ISR study was aged according to the ASTM D 6819-02 method and tested for the retention of their folding endurance, zero-span tensile strength and tear index. Results of measurements were compared with those published in the CCI report. Tests have been performed at both recommended temperatures: at 90 °C for 14 days and at 100 °C for 5 days. Obtained results are consistent with the published data. The values of double fold and tear index measured for samples aged at 100 °C are compared in Fig 1 and Fig. 2.

Noticed discrepancies can be attributed to the considerable measurement error, typical of mechanical properties of paper. Additionally, sealing of the used glass tubes is an important factor for the lab-to-lab repeatability.

2. Sealing of tubes

It has been found that recommended glass tubes do not allow to obtain a perfect seal at the aging conditions (Lab-line No. 308-9 and Kontes No. K736500-3515). Silicone rubber O-rings and Teflon resin gaskets used in the available hybridization tubes, although mechanically and chemically stable well above 100 °C, are considerably gas-permeable at the aging temperatures. The water loss from the tubes was observed by measuring the moisture content of the paper during aging (IR through-the-glass moisture-meter, Fibro). It was additionally confirmed by weighing the tubes after the prolonged times of aging. Flat, 2 mm thick disk, made of Viton fluoroelastomer (Du Pont Dow) were found to have satisfying sealing qualities. Additionally, to ensure tight sealing, the standard polypropylene screw caps were replaced with caps made of glass-fibre reinforced PPS (polyphenylsiloxan) (Bola H993-45, Germany) which were tightened on a tube with a dynamometric wrench at 18 Nm.

3. RH inside the tube

An attempt was made to verify the actual aging conditions inside the tube, i.e the RH of air and the sample moisture content.

Since opening the sealed tube containing the tested sample will invariably lead to a sudden change of its moisture content, the only way to determine this content is by an in-situ measurement. Such a measurement could be carried out either with the use of a moisture sensor placed inside the tube during the aging test or by a moisture meter located outside the tube and capable of measuring the moisture content through the glass. The latter method has been applied (Fibro MCA 1410 Moisture Content Analyzer), and the RH of air inside the tube during aging at 90 °C was
established as 59% for a sample of the model paper P1.4 This result shows that the conditions of aging in sealed tubes differ significantly from those established in the ASTM/ISR research program.3 Moisture content of paper P1 at various RH was measured in the climatic chamber at 90 °C. Using the obtained relation (shown in Figure 3) for the same temperature, the relative humidity in the glass tube with P1 paper was calculated from the IR moisture measurement for the sample. Additionally, under such conditions the total gas pressure inside the tube was determined not to exceed 2 atm.

4. Degradation rate

The P1 paper samples used for the studies of degradation rate were aged in sealed tubes at 90 °C. For each aging time, the degree of polymerization was measured (viscometrically) for samples from at least two different tubes. The kinetic curve (in the linearized coordination system) obtained for the samples aged with the new technique is presented in Figure 4. The rate constant of paper degradation was calculated according to the Ekenstam equation. The found value of the rate constant \( k = 2.3 \times 10^{-5} \) correlates well with the results of our previous study, where P1 paper samples were aged in closed vessels containing saturated solutions of salts.5 Using the relation between \( k \) and RH presented in the referred work, the rate constant for the conditions inside sealed tube with P1 paper could be estimated as \( 2.9 \times 10^{-5} \).

In this work the discussed kinetic curve have been also related to other kinetic curves obtained for P1 paper aged under similar conditions (T, RH) but as free hung sheets in a climatic chamber.

5. References

ENCAPSULATION AND AGEING OF PAPER

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1. Introduction
One of the preventive conservation measures to be undertaken is to avoid contact with the polluted air with the paper stored in, for example, an archive. This can be done by applying an air-purification system or by storing paper in a closed environment. There are advantages to be mentioned when paper is being encapsulated. For example, it can reduce the storage volume and encapsulated records are easier to transport. However, wrapping of paper by means of a polymer is under discussion for many years. Especially wrapping using a light vacuum using a synthetic polymer (encapsulation). Depending of the material used for wrapping, papers ageing due to acid contaminants from the ambient will be reduced as the polymer will act as a barrier. Besides protecting paper against its deteriorable environment, the microclimate in the bundle of paper will have its own behaviour and may have a contribution to the ageing of the wrapped paper. In 1980 the Library of Congress reported in their work that polyethylene encapsulation of paper would not enhance the ageing, especially if alkaline (deacidified) paper sealed. This conclusion was contradicted by other researchers. Passaglia concluded that the microclimate established within a closed environment could be a danger for the encapsulated paper as degradation products coming from the paper remain trapped and therefore could affect the stored paper. Pauk and Pork showed by their research, that after subjecting paper sealed in different polymer films to accelerated ageing (alternating climate), the deterioration was enhanced.

Using a light vacuum during encapsulation will result in low oxygen environment. As shown by several researchers, a reduced oxygen environment will reduce the deterioration of paper, however for acid paper, the deterioration by acid catalysed hydrolyses may continue.

Looking at research undertaken with encapsulated paper, one critical point has to be considered. The way of ageing applied differs very much. During ageing the climate in the polymer bag or pouch have to be considered and none of the researchers who investigated paper encapsulation have taken this phenomenon into account. Sealed or encapsulated paper will create its own environment as there always is an equilibrium of the water in the (micro)environment and the paper. The water activity in the pouch is therefore seldom comparable to the water activity of the ageing environment. Therefore results obtained of paper wrapped in a pouch and artificially aged can not be compared with paper hanging free in climate oven during artificial ageing. The aim of our work is to find a comparable way of the ageing of paper wrapped and unwrapped by investigating the moist behaviour of the paper and its environment during ageing.

Besides, we had the opportunity to store special papers for about 10 years in a pouch at the National Archives of The Netherlands. This paper presents the first result of the effects of encapsulation of paper related to long-term storage.

2. Experimental

2.1 Materials
Two different papers were used. These papers were received in 1994 from a European Research Project on the effects of air pollution on the accelerated ageing of paper (STEP): Paper-1, a bleached softwood cellulose paper (pH cold water extract 6.3) and Paper-3, an acid mechanical pulp paper (pH cold water extract 5.3). The pouches applied were Archipress Archival Pouches from Minigrip (Putten, The Netherlands). It is based on laminated uncoated polyester. Bundles of 50 sheets were encapsulated according to the Archipress specifications using the Archipress H 1000 machine (vacuum 2–3 mbar, reached within 25 seconds).

Water sorption and desorption of paper was done with a climate chamber and an external balance connected to a data logger. The temperature and relative humidity measurements were performed using PT100 and humidicap sensors.

2.2 Modelling the ageing
Usually the ageing conditions are given in international standards, e.g., 90 °C and 50% relative humidity. However it is obvious clear, that due to the paper content and the way of sealing the in-pouch climate will differ from the out-pouch climate. Therefore water sorption and desorption behaviour of the papers used and the in-pouch and out-pouch water activity were measured in a climate chamber for which firstly the climate varied from 20 to 90 °C at a constant relative humidity of 50% followed by changing of the relative humidity from 50 to 80% using an interval of 5% at constant equilibrium temperature.

The equilibrium, where the water activity of the paper in the pouch was comparable to that of paper in the ageing chamber was 70 °C and 55–57% RH. Therefore it was decided to apply an ageing climate of (70.0±0.5) °C and (55±2)% RH.
Chemical deterioration depends on the temperature applied and time of ageing. Therefore we decided to apply an ageing time of 24 days at the conditions as described previously. After the ageing period, chemical, physical and mechanical paper properties were evaluated, i.e., pH of the cold water extract of the paper according to ISO 6588, the copper number according to ASTM D 919, the brightness according to ISO 2470, folding number according to ISO 5626 and tensile strength according to ISO 1924.

2.3 Natural ageing

Ten pouches were filled with 50 sheets of Paper-1 and Paper-3 respectively, according to the Archipress procedure (see above). The pouches were stored at the National Archives in The Hague at the storage room located at the ground floor. This storage room was kept at Archival Storage conditions, i.e., (17±1) °C and (52±3)% relative humidity and was also used for our research on the effects of air purification on the stability of archival records which will be published soon. Light at the storage room was only activated on moments we were working in the storage room, while the levels of pollutants (SOx, NOx, O3) were continuously recorded. The papers were stored on July 1995 and 2 pouches per paper grade have been opened on July 2004. So the actual storage time was 9 years.

3. Discussion

3.1 Accelerated ageing

Looking at the acidity of the encapsulated papers used, it was found that for both used papers the pH decreases after ageing (ΔpH for Paper-1 and Paper 3 was 0.5 and 1.0, respectively), especially for the encapsulated acid mechanical paper. The acidity of the unwrapped acid mechanical paper, however, was not significantly affected. From the results, it may be concluded that acidification will continue more extensively for the encapsulated papers, than for the non-encapsulated one, due to the microclimate. Comparable results were found in previous research on the effects of an inert gas on the ageing of papers.

The copper number represents the reducing aldehydes and reactive keto groups and is therefore a good indication for the degradation of the paper. In case of Paper-1, the difference between encapsulated and non-encapsulated paper was not detectable. For Paper-3 the acidic paper from mechanical pulp, however, the copper number increased for both ageing conditions, but was more severe for the encapsulated paper. According to the manufacturer, no oxygen should be able to enter the sealed pouch. Therefore we suggest that the micro climate in the pouch, contains enough oxygen to enable more extensive thermal oxidation within the closed environment than in the open one for the lignin rich Paper-3.

Looking at the ISO Brightness of the papers used, we notice that it decreased during ageing, however no differences were found due to the way of ageing, i.e., encapsulated on open. For the mechanical properties of the paper, i.e., tensile strength and fold number, we found also no significant differences for encapsulated or free papers.

3.2 Natural ageing

When opening the pouches after 9 years of storage at ambient conditions, a strong smell was observed. The smell was stronger for Paper-3 then for Paper-1. Later air analyses using tenax tubes and GC/MS showed that among the volatile compounds was acetic acid, which can be produced by acid hydrolyses of wood components such as lignin and polysoses. More results of the air in the pouch will be published separately.

The pH of the cold water extract, measured immediately after opening the pouch, was for Paper-1 and Paper-3 5.4 and 5.3 respectively. Looking at the initial values (6.4 and 5.8 respectively), we see that for both papers the acidity increased due to the encapsulated storage (pH 1.0 and 0.5 respectively. So, for both papers the acidity increased due to the encapsulated storage. Paper-3 also became more yellow compared to the original papers, and to similar paper, stored at the archives in e.g. boxes. For the mechanical properties, again no significant differences were found between the original value and the value after 9 year of storage.

4. Conclusions

Based on the results of accelerated ageing at 70 °C and 55% RH, the conclusion can be drawn that encapsulation of paper using a laminated uncoated polyester pouch and a slight vacuum, will neither influence the mechanical paper properties in a positive or negative way.

However, based on our modelling studies, paper deterioration will continue and acidification will even be enhanced by paper encapsulation using a slight vacuum.

These results were confirmed by our studies where papers were stored encapsulated for 9 years.

Based on our work, encapsulation of paper using a slight vacuum is not recommended.

Finally we recommend to carry out studies of the effects of encapsulation on alkaline and deacidified papers.

5. References


GRAFTING POLYMERIZATION: AN INNOVATIVE TECHNOLOGY FOR PAPER CONSERVATION

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1. Introduction

New specific polymeric materials suitable for the conservation treatment of paper have been synthesized and tested on model paper samples obtained by accelerated ageing.

An innovative technology based on a grafting reaction of acrylic monomers onto cellulose was invented and optimized, with the aim to improve mechanical properties of degraded paper.

The effectiveness of the technology was evaluated by characterizing the grafted samples.

Significant paper objects of historical, artistic and archaeological value will be conserved using this methodology.

This study is part of “Papertech. Innovative materials and technologies for the conservation of paper of historical, artistic and archaeological value”, a research project, supported by the European Commission under the 6th Framework Program, with the aim to develop innovative diagnostic techniques and protocols to evaluate the deterioration of paper and to study innovative materials and technologies for its conservation.

2. Experimental Part

2.1 Materials

The cellulose substrate was Whatman paper.

Reagents were commercial products supplied by Aldrich. Monomers (MMA, methyl methacrylate and EA, ethyl acrylate) contained an inhibitor (hydroquinone monomethyl ether), which was removed by passing each through an Aldrich Inhibitor Removers column; the purified monomers were subsequently stored at low temperature (4°C) and in the dark.

Sodium iodate(VII) (NaIO4), acetone and methanol were laboratory grade products from Aldrich and were used without further purification. Deionized water was used throughout the work.

2.2 Methods

With the intent to create photosensitive groups onto cellulose, allowing the formation of radical sites for the UV photoinduced grafting process, oxidation of paper with iodate(VII)1 was carried. The reaction is specific in that the C2-C3 bond of the glucosidic ring is cleaved and the 2- and 3-hydroxyl groups are converted in two aldehyde groups, without significant side reactions.2,3 The oxidized samples become “models” enabling us to investigate the different levels of degradation in real materials.

Therefore, the samples were treated with different solutions of iodate(VII) and for different times. The ratio sample/solution was kept at 1g/100 ml in all experiments. At the end of oxidation, samples were washed with deionized water up to neutral pH and dried.

The photo-initiated grafting reaction was carried out on artificially aged paper. Cellulose samples, after oven drying, were swollen in deionized water for 5 min; this was done to open up the fibrous structure of cellulose and encourage homogeneous uptake of monomers during grafting.4 The wet samples were placed in a quartz reaction vessel (V = 10 L), it was kept at low pressure for a short time, so that the fabrics were still damp; then the liquid mixture of monomers was loaded, vaporized, and diffused into the reactor. Subsequently, at room temperature, the whole unit was exposed to UV radiation from a mercury vapor lamp (400 W, with complete spectrum emission from 180 nm to visible light), placed at 60 cm from the reactor, so that no cooling system was required. The polymerization was stopped by pressurizing the reactor up to room conditions. The unreacted monomer was removed by washing the fibers with a mixture methanol-water (V/V 30/70), a good solvent for acrylic monomers, but not for the polymers. After this procedure the sample, containing grafted cellulose and homopolymer, was filtered and brought up to constant weight. The drawback of the graft polymerization is the simultaneous and inevitable formation of homopolymer; it is removed from the grafted material by extraction with acetone for 72 h at room temperature.5 The quantity of grafted monomer is evaluated as the weight increase of the sample after extraction of the homopolymer:

% Grafting Yield (GY) = [(W2 – W1) x 100]/W1,

where W1 is the initial weight of the sample and W2 is the final weight of extracted sample.

2.3 Characterization

Tensile measurements on grafted samples were performed on an Instron tester. Young’s Modulus (E) and elongation (e) at break were evaluated. Samples were
tested at 20 mm/min draw rate until breakage. An average of 15 tests for type specimens was used to calculate the tensile properties.

Thermal stability was evaluated by DSC analysis. DSC Mettler Toledo 821 was used with oxygen flow (120 cm³ min⁻¹); the analysis was performed between room temperature and 650 °C at heating rate of 5 °C min⁻¹, on 5–10 mg samples in an aluminum holder.

3. Results and Discussion

Grafting polymerization was carried out by varying some reaction parameters: the sample oxidation conditions, the duration of polymerization, and the monomer/cellulose ratio. In Tables 1 and 2 the grafting yields with MMA and EA are reported, respectively. In MMA grafting, the ratio monomer/cellulose was fixed, whereas the oxidation conditions and the polymerization time were varied. When grafting EA, all parameters were varied. From the data reported in the Tables, it is evident that PEA (poly ethyl acrylate) leads to a higher yield than PMMA (poly methyl methacrylate) and that higher grafting yields are obtained at higher ratios of monomer/cellulose and longer reaction times. After about 10 h an almost complete conversion of the monomer is obtained and the reaction can be considered to be complete. Grafting does not modify the visual aspect of the material, which is important for objects of historical interest.

Table 1: Grafting yields for MMA on paper oxidized with NaIO₄ 0.1 M for 2 h. Ratio MMA/cellulose 1.5 mmol/100 g.

<table>
<thead>
<tr>
<th>Polymerization time (h)</th>
<th>Grafting Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>86</td>
</tr>
<tr>
<td>10</td>
<td>89</td>
</tr>
</tbody>
</table>

Table 2: Grafting yields with EA on paper oxidized with NaIO₄ 0.1 M for 2 h. Polymerization time: 4 h.

<table>
<thead>
<tr>
<th>EA/cellulose ratio (mmol/100g)</th>
<th>Grafting Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>104</td>
</tr>
<tr>
<td>2</td>
<td>176</td>
</tr>
</tbody>
</table>

The stress-strain behavior of original, oxidized and grafted paper was measured by tensile deformation; all samples were tested to break. Young’s Modulus and elongation at break are reported in Table 3; grafting with MMA and EA has been performed on Whatman paper oxidized in 0.1 M iodate(VII) for 2 h, in the same reaction conditions; polymerization time 4 h, monomer/cellulose ratio 1.5. These results indicate that in the presence of grafted PEA the mechanical behavior of paper changes considerably; particularly the flexibility of cellulose increases. This fact is due to the low glass transition temperature of PEA (−24 °C).

Table 3: Results of tensile testing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated paper</td>
<td>1100</td>
<td>1.6</td>
</tr>
<tr>
<td>Oxidized 0.1 M 2 h</td>
<td>1000</td>
<td>1.4</td>
</tr>
<tr>
<td>Grafted PMMA</td>
<td>1100</td>
<td>1.3</td>
</tr>
<tr>
<td>Grafted PEA</td>
<td>222</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Thermal degradation of cellulose and modified cellulose has been extensively studied by DSC, it involves a set of concurrent and consecutive reactions. A strong exothermal peak at about 300–340 °C is attributed to cellulose depolymerization and to charring and oxidation of the decomposition products. A second peak observed above 400 °C is likely due to oxidation of the char. DSC curves of the oxidized samples show changes in respect to the original Whatman paper. After each oxidation the first peak shifts to lower temperature, because the oxidized cellulose is already degraded with a large fraction of oligomers and therefore less energy is necessary for their thermal decomposition. In the grafted paper, two degradation steps concerning cellulose and acrylic polymer, are observed and the key peak splits in two. Regarding cellulose decomposition, the peak shifts to higher temperature than the untreated paper. The shift can be explained assuming that the grafted cellulose has a better thermal stability due to the presence of acrylic polymer.

4. Conclusions

The studies reported here give an insight in understanding the structural changes occurring when cellulose-based materials are oxidized and grafted with acrylic polymers. Methyl methacrylate and ethyl acrylate were grafted onto Whatman paper, previously oxidized by sodium iodate(VII), with the intent to reproduce natural oxidative ageing. Moreover, by properly choosing the type of monomer to be grafted, the properties of the resulting copolymer can be modulated, especially mechanical and thermal behavior. From the point of view of the mechanical behavior, the results indicate that PEA can be successfully employed in grafting. Due to the high glass transition of the poly(methyl methacrylate) chains (105 °C), the treated samples were brittle and stiff.

The level of degradation and the effectiveness of grafting were evaluated using thermal analysis.

Synthesis of graft copolymers represents an interesting way to obtain composites with specific properties that might be also applied in the preservation of cultural heritage items of cellulosic nature. This method does not alter the main features of the materials and no surface coatings are formed on the grafted samples, as demanded by appropriate restoration practice.
5. References

THE EFFECT OF ARTIFICIAL AGING AND SIZING ON DISCOLORATION OF PAPER STUDIED BY UV-VIS-NIR SPECTROSCOPY IN COMPARISON TO ANCIENT PAPER

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1. Introduction
The preservation of paper artefacts poses a serious problem for libraries, archives and museums worldwide. In order to develop appropriate conservation methods, an advanced knowledge of the degradation processes which affect them is essential. Besides different paper degradation effects, discoloration and foxing are the most obvious to the naked eye. Notwithstanding this fact, as yet no attention has been paid to the characterisation of ancient paper degradation by means of optical spectroscopy although the application of this technique provides information on paper status in a non-destructive way. However, an improved comprehension of the relation between paper structure and its optical properties, is required. In fact paper sheets are complex materials consisting in a felt of cellulose fibres (in ancient times deriving from linen) in addition to other substances depending on the production technique employed, such as gelatine, which has been used to size paper in the Western world since the beginning of paper making history1,2. The process of paper degradation may be seen as a combination of acid hydrolysis, which deteriorates the mechanical properties of sheets, shortening the cellulose polymeric chains, and the so-called “slow-fire” caused by the oxidation of materials with subsequent development of carbonyl and carboxyl ligands, mechanical weakening, and discoloration of the remaining substratum3,4. On the whole, it appears that while the overall process of paper degradation is quite clear, it is its effect on the optical properties of discoloration and foxing that requires further investigation.

Recently we have carried out an optical reflectance spectroscopy study of ancient paper with different kinds of degradation, with either widespread discoloration or foxing5. Paper optical response was measured in the wavelength range of 250–1100 nm. Even if the specimens under study were of different manufacture, geographical origins, and ages, displaying a broad range of widespread discoloration, they all show an extremely similar spectral form. A similar spectrum was also observed by measuring foxing spots of several intensities on a single foxed sheet. In all these samples, increasing paper degradation implies a reduction of the reflectivity in the higher energy side of the spectrum. This behaviour seems to suggest the existence of a main cause common to all samples, driving their optical response and leaving aside other paper specimen differences.

In this contribution, in order to gain a better understanding of these results, we describe our results on the optical characterization of sized and non-sized modern paper samples artificially aged, and their comparison to the ancient paper specimens. Moreover, the independent role of cellulose and sizing materials on the paper discoloration phenomena has been investigated by measuring separately the modification of their optical properties following artificial aging.

2. Experimental

Whatman No. 1 paper samples, made of pure cellulose, were manually sized using a brush. The samples were obtained from paper sheets acquired approximately six years ago and then stored at 23 °C and 50 % relative humidity (RH). The gelatine used in sizing was prepared following a traditional recipe for parchment glue, as reported in the medieval manuscript entitled “De arte illuminandi”7. Modern parchment used for this purpose was handmade by the small industry laboratory of Otello Scaricacciottoli, Paglieta, Chieti (Italy). An aqueous solution of gelatine at a concentration of approximately 3% in weight were obtained, which achieved a dry weight uptake in the paper of approximately 10%, as measured before and after the sizing process. Samples for gelatine transmission measurements were prepared by using sizing material prepared in the same way as described above. Flat surface solid gelatine film of approximately 80 µm thickness with negligible optical scattering were produced on a quartz substrate. Several accelerated aging processes were performed in a climatic chamber at constant temperature and relative humidity. Three aging procedures were used: I) 21 days at 80 °C and 65 % RH; II) 21 days at 90 °C and 80 % RH; and III) 40 days at 90 °C and 80 % RH. The experimental setup used for optical reflectance is described in ref.6. Transmittance spectra of gelatine films on quartz substrates were measured by a Jasco V-570 spectrophotometer by using 2 nm resolution.

3. Results and discussion

In the upper part of Fig. 1, reflectance spectra of ancient paper samples, presenting various kinds of widespread discoloration and foxing are shown. For a description of
Durability of paper and Writing

the spectra labels see Table 1. In the lower part of the same image the reflectance spectra of artificially aged Whatman paper samples sized with gelatine are plotted. All spectra are normalized to the reflectance of Whatman paper No. 1. It is evident that ancient papers and artificially aged papers show a similar spectral behaviour. This similarity is even more manifest in Fig. 2 where the reflectance of a paper sample produced in France in 1413 (S6) and a gelatine sized aged Whatman paper (A4, aging procedure III) are directly compared showing an identical trend. This striking result makes us confident that the sample preparation protocol and the artificial aging procedure used in this work are well suited for studying the discoloration processes of ancient paper. Even though the same aging procedure has been applied to non-sized papers, none of these samples displayed in the measured range relevant reflectance modification. To bring attention to this result, the almost flat reflectance spectrum of a non-sized Whatman paper (W3) aged under procedure III is reported for comparison in Fig. 2.

The fact that the spectra of samples made by pure cellulose (Whatman paper) remain constant regardless of aging procedures, encouraged us to study the optical response of collagen alone. To achieve this, we artificially aged the gelatine films deposited on quartz substrates by using the same protocols described before. Due to the transparency of gelatine samples, the effect of aging has been observed in transmittance. Transmittance spectra of three gelatine samples are reported in Fig. 2. It is evident that, the same spectral region involved in the discoloration of ancient as well as aged paper is affected by a similar variation in aged gelatine transmittance.

Studies concerning the relation between the found changes in spectra to molecular changes are presently on going. In conclusion, the independent analysis of the aging effect on pure-cellulose and pure-gelatine samples seems to strongly support the hypothesis that the main contribution on paper discoloration is due to gelatine. In view of these results, it will now be an interesting prospect to attempt to understand the gelatine aging. Similarly, the analysis of possible cellulose-gelatine cooperative effects in discoloration of sized paper will also be necessary.

4. References


<table>
<thead>
<tr>
<th>Spectrum Label</th>
<th>Sample description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Milan, 1430, good state</td>
</tr>
<tr>
<td>S2</td>
<td>Milan, 1430, intermediate state</td>
</tr>
<tr>
<td>S3</td>
<td>Milan, 1430, bad state</td>
</tr>
<tr>
<td>S4</td>
<td>Nuremberg, XV century, very bad state</td>
</tr>
<tr>
<td>S5</td>
<td>Perpignan, 1413, good state</td>
</tr>
<tr>
<td>S6</td>
<td>Perpignan, 1413, intermediate state</td>
</tr>
<tr>
<td>F1</td>
<td>France, XVI century, area without foxing</td>
</tr>
<tr>
<td>F2</td>
<td>same paper as F1: light foxing spot</td>
</tr>
<tr>
<td>F3</td>
<td>same paper as F1: intermediate foxing spot</td>
</tr>
<tr>
<td>F4</td>
<td>same paper as F1: heavy foxing spot</td>
</tr>
<tr>
<td>A1</td>
<td>Gelatine sized Whatman paper no. 1 not aged</td>
</tr>
<tr>
<td>A2</td>
<td>Gelatine sized Whatman paper no. 1 aged procedure I</td>
</tr>
<tr>
<td>A3</td>
<td>Gelatine sized Whatman paper no. 1 aged procedure II</td>
</tr>
<tr>
<td>A4</td>
<td>Gelatine sized Whatman paper no. 1 aged procedure III</td>
</tr>
<tr>
<td>W3</td>
<td>Whatman paper no. 1 aged procedure III</td>
</tr>
<tr>
<td>G1</td>
<td>Gelatine on quartz substrate not aged</td>
</tr>
<tr>
<td>G2</td>
<td>Gelatine on quartz substrate aged procedure I</td>
</tr>
<tr>
<td>G3</td>
<td>Gelatine on quartz substrate aged procedure III</td>
</tr>
</tbody>
</table>

Figure 1: Reflectance spectra of ancient paper (upper part) compared to those of Whatman paper samples sized with gelatine (lower part). Curves labelled S are relative to widespread discoloured ancient specimens while the curves labelled F have been measured on foxing spots of increasing intensity on the same ancient sample. A detailed description of ancient paper samples is given in Table 1.

Figure 2: Reflectance spectra of S6 ancient paper sample compared to those of artificially aged Whatman paper non-sized (W3) and sized with gelatine (A4) both aged using procedure III. In the lower part are shown the transmittance spectra of gelatine samples: G1 is not-aged, G2 and G3 are aged with procedures I and III, respectively.

Table 1. Correspondence between the spectra labels and the samples measured.


IRON GALL INK CORRODED AUTOGRAPHS OF THE 18TH AND 19TH CENTURIES

CONSERVATION OF MATERIAL CHARACTERISTICS VERSUS CONSERVATION TREATMENTS

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The conservation of so-called “exterior” characteristics of documents during conservation procedures represents a challenging task. The wide range of materials and their different degradation states are illustrated by means of autographs of the 18th and 19th centuries. Taking into account the modern methods of conservation it is necessary to select optimised procedures for each single case of damage.

There are, basically, aqueous and non-aqueous conservation treatments available for stabilisation of documents. Besides the chemical and mechanical stabilisation of ink and paper, also other types of information such as the iconic and material specifics of documents (e.g. surface of paper, watermarks, color of ink, shellack and wafer seals, stamps) need to be preserved. The method used here depends on the actual state of damage and also on the historical type of material.

1. Aqueous conservation treatments

By applying aqueous methods of mechanical strengthening in combination with aqueous methods of chemical stabilisation all three central conservation aims can be achieved:

1. Removal or inactivation of ferrous ions.
2. Neutralisation or alkalinisation of sulphate ions.
3. Strengthening of the weakened paper.

We must be aware that aqueous treatments change the original composition of the inks. As a consequence, future analysis of the inks would not provide any reliable information about the historical recipes and the characteristic behaviour of the aged inks.

The following aqueous treatments are used:

– Conventional treatment:
   An extremely thin tissue of Japanese fibres, known as “Gossamer tissue” (1.7 g/m²), is suitable for mechanical strengthening of weakened paper in aqueous media. Depending on the degree of damage and the type of historical material a stronger tissue up to 5 g/m² is required for effective stabilisation of the paper. However, note that thicker application tissue may affect transparency.

– The tissue method and leafcasting machine:
   A standard conservation method, applied at the Institute of Book and Manuscript Restoration of the Bavarian State Library (IBR) Munich, involves the use of Japanese fibres for strengthening weakened paper by forming a tissue in the leafcasting machine. The tissue can be applied partially in order to keep free unaffected areas from fibres.

   – The tissue method and the use of a suction table:
     Sensitive objects can be strengthened by a tissue produced in the leafcasting machine involving the use of a suction table. The supporting tissue can be applied selectively to the weakened parts of the paper.

2. Non-aqueous conservation treatments

In the case that aqueous treatments for the stabilisation of ink corroded papers are not suitable, we rely on alternative, non-aqueous treatments. At present, non-aqueous conservation treatments do not remove or inactivate transition metals. Therefore, the chemical stabilisation is restricted to the neutralisation of acids by the application of carbonised magnesium ethylate. A tissue coated with acrylate is used for the mechanical strengthening.

3. Concerns relating to the use of aqueous treatments

Aqueous treatments may raise problems, because they may effect the ink. Similarly, they may interfere with other writing fluids, the stamping-ink, the wafer and shellack seals. Furthermore the paper itself, its surface and dimensions as well as its watermarks need to be considered. In the case of progressive damage there is the risk of worsening the degradation of the ink and the paper. Aqueous treatments may also cause changes of the historical materials. Importantly, autographs of the 18th and 19th centuries involve a wide range of writing materials. On one single document we may find different kinds of ink used by the author and the contemporary readers, and notes on envelopes in red chalk by the post office in the case of correspondence. Furthermore we may find later additional notes of scientists as the first traces of research in direct neighbourhood to stamps of the later owners of the documents. There are serious concerns that the different kinds of inks and other writing fluids, pens, pencils or crayons are not stable against “bleeding” or other reactions caused by water. Even worse, fixatives might be unstable in inappropriate chemical contexts.
The texts with microscopically fine ink endlines represent a valuable source of information about the individual writing style of a historical personality. Even tiny remains of the drying sand, used by the author immediately after writing, may provide significant insights into historical situations.

The seals, the fragile remains of wafers, the thin, flat, baked adhesive disks made from starch as well as the binders and the pigments deserve special attention. Their natural fragility could lead to the complete breakage and loss. Therefore, wafers on a document may prevent the use of aqueous treatments. Similarly, difficulties occur with shellack seals, which consist of shellack dissolved in turpentine, colophonium and red pigments. Although they appear to be stable, under the microscope they often reveal a lot of fine cracks. Moreover aqueous treatments require a thorough drying process. Seals need to be carefully protected during this treatment. Nevertheless, centrifugal folds, the “wrinkles”, and the tensions around the seals might be the side-effects of aqueous treatments.

4. Concerns relating to the use of non-aqueous treatments
Non-aqueous treatments need to be examined carefully regarding the long-term behaviour of synthetic adhesives and possible changes of the optical as well as haptic impression of the document.

5. Selection of objects
Also here, regarding the complexity of damaging factors and historical types of material on the one hand, and the different conservation treatments on the other hand, we have to choose the best method for each single object without affecting the iconic and material information. Each case of damage requires its specific conservation treatment. Among undesirable side-effects are not only such apparently things like bleeding of the ink or increased mechanical degradation in the corroded areas. Special attention deserve the more subtle characteristics of the historical materials in order to minimize the risk of affecting them during the conservation treatments.
EFFECTS OF GELATINE SIZING ON IRON GALL INK CORRODED PAPER

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1. Introduction
Many types of sizing can be used in the traditional restoration of iron gall ink manuscripts and each workshop has its own practices. Up to now, gelatine sizing is not widely used in France although recent work performed in Germany1 has shown that gelatine sizing may delay iron gall ink corrosion of paper. The mechanical tests performed on laboratory samples showed that gelatine can retard the loss of physical properties of paper containing iron gall ink during ageing. However, using this technique alone, no distinction can be made between the effect of a gelatine reticulation and the impact of gelatine on iron gall ink corrosion. For this reason, we tried to evaluate the impact of gelatine as a sizing agent on the degree of polymerization (DP) of cellulose by using a size exclusion chromatography (SEC).

2. Experimental methods

2.1 Sample preparation
The paper samples were made of cotton linters, unbleached, unfilled and unsized, 80 g/m² (provided by TNO-ref. PAPER2). The iron gall ink was composed of FeSO₄·7H₂O (Aldrich 31.007-7), gallic acid (Sigma G7384) and gum arabic (Sigma G9752), molar ratio of iron and gallic acid was 5.5:1, iron and gum arabic concentrations were respectively 23.29 g/l and 31.4 g/l. The pieces of paper (6 × 12 cm) were immersed in a freshly prepared ink for 5 minutes. To improve the homogeneity of the inked samples, each of them was placed between 2 sheets of blotting paper. The surplus ink was removed by moving a metal roller usually used to perform the Cobb test2 (20 cm wide and weighing 10.0 ± 0.5 kg) once back and once forward over the pad. By using this technique alone, no variation of iron distribution from one sample to another and from one area to another on the same sample, instead of 30% when the roller is not used.

2.2 Artificial ageing
As C. Rémazeilles has shown that a dynamic ageing technique3 has the same effect on the DP of cellulose as a static one4, all the samples were aged in a climate chamber Vötsch VC 2033 at 55 °C and 75% RH. In order to obtain pre-degraded samples, the ink containing papers were pre-aged for 7 days. Then a second ageing was carried out after conservation treatments of the pre-aged samples. After 5, 12 and 17 days, series of samples were removed from the oven for analysis.

2.3 Conservation treatments
In order to study the effect of gelatine sizing (220 Bloom) on inked paper, different methods of application were compared: 5 min. immersion in water, 5 min. immersion in a 1% gelatine solution, spraying with a 1% gelatine solution, coating with a 10% gelatine solution using a brush. The first two treatments were used to evaluate the migration of iron ions in the solution during immersion. The last two treatments were used to compare the effect of concentration of gelatine on cellulose. No significant change in the content of iron ions due to conservation treatment is expected in these two samples.

2.4 Size exclusion chromatography
The DP of ink containing paper was analysed using the SEC technique. The procedure for samples preparation and chromatographic conditions were the same as described by Heike Jerosch5, except for the columns which were three Phenogel GPC, 5 mm, mixed bed, 300 × 7.8 mm plus a Phenogel GPC, 5 mm, mixed bed, 50 × 7.8 mm.

Before the swelling step, the gelatine containing samples were soaked 2 times in hot water (70 °C) in order to remove the gelatine sizing as much as possible.

2.5 Iron content determination
The content of total iron in the laboratory samples was determined by spectrophotometry using bathophenanthrolinedisulfonic acid as a colour reagent. 36 cm² of inked paper was placed in a crucible then incinerated at 570 °C. After complete cooling, 3 ml of 6N HCl was added and heated 5 min. at 150 °C. This solution was diluted to 50 ml with deionized water then 10 ml were taken and placed in a 25 ml volumetric flask. 7.5 ml of 100% acetic acid adjusted to pH 4.7, 500 ml of a 20 g/l hydroxylamine hydrochloride solution (Acros Organics 5471-11-1), 500 ml of a 5 g/l bathophenanthrolindisulfonic acid disodium salt solution (Sigma B1375) were added in this order and the mixture was brought up to 25 mL with water. Hydroxylamine hydrochloride was used to reduce the Fe(III) in Fe(II) which forms a deep pink coloured
complex with bathophenanthroline. The total iron concentration was determined using a Perkin Elmer Lambda40 spectrophotometer settled at 156 nm. The calibration was performed by adding 1.25, 2.5, 3.75 and 5 ml of a 0.01 N Fe(SO$_4$)$_2$$\cdot$7H$_2$O solution to the 25 ml flask.

3. Results and discussion

3.1 Iron migration during immersion

Before and after treatment, each laboratory sample was incinerated for total iron quantification. Before any treatment, the quantity of iron measured in all the 15 inked samples was 12 ± 0.5 mg/cm$^2$. This quantity is equivalent to the average one measured in a previous study by C. Rémazeilles on 50 historical manuscripts (dated from 1826 to 1842) containing iron gall ink, using PIXE analysis.

After conservation treatments (3 samples were analysed per treatment), as shown on figure 1, the same quantity, about 25% of original iron content, was removed from the inked papers during immersion treatment in water or in 1% gelatine solution. As expected, no iron ions were washed out after spraying and coating treatments.

Surprisingly, it is remarkable that even when a significant quantity of iron ions is washed out after immersion (25%), the depolymerisation of the cellulose is not reduced more than 15% compared to the reference.

Figure 1: Iron content in pre-aged inked samples after conservation treatments. Error bars represent standard deviations.

3.2 Effects of conservation treatments on the DP of the cellulose

The evolution of the weight average molecular mass Mw versus artificial ageing is plotted on figure 2 for treated and non-treated samples. This graph shows that the Mw values are similar for non aged papers before and after gelatine sizing, confirming the fact that the gelatine does not disturb the SEC analysis of cellulose.

Looking at the evolution of Mw versus artificial ageing, compared to the reference, no clear long term effect of the conservation treatments is observed. It is also not possible to make a distinction between the washing effect and the effect due to the presence of gelatine. Nevertheless, we can notice that the treated samples’ molecular mass remains quite stable during the five first days of artificial ageing; so the conservation treatments could have some positive short-term effect on inked papers, although additional work is needed to confirm this observation.

Figure 2: Changes of the Mw of treated inked papers cellulose during artificial ageing at 55 °C and 75% RH. R.S.D. is 5%.

4. Conclusion

In the light of the results obtained by SEC, it appears that neither water immersion nor gelatine sizing have any significant effect on ageing stability of iron gall ink containing paper. Gelatine may however still affect the rate of diffusion of the ink or its components during aqueous treatments, as suggested by Gelsa Kolbe$^6$.

5. References

2. Tappi test method T441 om-90.
EVALUATION OF RELATIVE FE$^{2+}$ AND FE$^{3+}$ CONTENTS OF ORIGINAL MANUSCRIPT FRAGMENTS BY MEANS OF $\mu$-XANES AND MÖSSBAUER SPECTROMETRY

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1. Introduction

The corrosion of paper due to iron gall ink is generally attributed to a combination of two mechanisms: acid hydrolysis and oxidation enhanced by the presence of free Fe$^{2+}$. The presence of free Fe$^{2+}$ and free Fe$^{3+}$ in original samples can easily be detected with a spot colour test. Yet this detection remains qualitative, and little information is available on the quantity of Fe$^{2+}$ and Fe$^{3+}$ present in the original inks.

In this work, an attempt was made to estimate the Fe$^{2+}$/Fe$^{3+}$ content in a set of original manuscripts using instrumental techniques $\mu$-XANES and Mössbauer spectrometry. These manuscripts consisted of valueless documents in variable states of preservation: some were in a perfect condition, whereas others were highly damaged. Particular attention was paid to a sample featuring white crystal-like precipitates within the ink containing areas of the paper.

Microscopic X-ray absorption near-edge spectroscopy ($\mu$-XANES) measurements were performed with a lateral resolution of 30-50 µm in order to determine the local Fe$^{2+}$/Fe$^{3+}$ ratio. For comparison, an average estimation of the Fe$^{2+}$/Fe$^{3+}$ ratio was also obtained by means of Mössbauer spectrometry on two suitable samples (sample M and C) for which great quantities of dark-coloured damaged material were available.

2. Experimental

2.1 $\mu$-XANES experiment

The XANES experiments were carried out at beam-line L of HASYLAB (Hamburg, Germany). By varying the energy of the primary X-ray beam in small (typically 1 eV) steps across the K-absorption edge of Fe, the XANES profiles recorded from hand written characters in a 16th century prayer book could be well described as a linear combination of the reference profiles FeSO$_4$$\cdot$7H$_2$O and Fe$_2$(SO$_4$)$_3$$\cdot$5H$_2$O, allowing to estimate the relative abundances of Fe$^{2+}$ and Fe$^{3+}$, as was confirmed by cross-validation with Mössbauer spectroscopy. In the present work, only in a limited number of cases, this simple regression model was found to be sufficient to adequately describe the experimental XANES profiles. Since it can be expected that Fe in aged iron gall ink is present as a very complex mixture of different compounds, it is rather difficult to make a quite rigorous description of the XANES profiles. The numbers cited below, which were obtained on the simple sulphate model, can only be regarded as preliminary and semi-quantitative.

2.2 Mössbauer experiment

Mössbauer measurements were performed at room temperature using a constant acceleration HALDER type spectrometer, with a $^{57}$Co source (Rh matrix) in transmission geometry. The spectra were recorded at 293 K. It was necessary to perform the measurements on a stack of approximately 10 sheets together to enable recording of spectra in a reasonable timescale of two weeks. Moreover, for such sample preparation line broadening effects can be neglected. The velocity was calibrated using pure iron metal as reference material. The experimental data were resolved into symmetric doublets with Lorentzian lineshapes using an iterative least-squares fit program. When the refinement of the Mössbauer spectra showed an important and abnormal widening of the peaks, the spectra were fitted assuming a quadrupolar splittings distribution.

2.3 Examined documents

The historical samples examined in this study were classified according to the four-level system developed by Reissland. Seventeen samples were examined; four of these were in an advanced state of degradation (type 4) while the majority was in a better condition (types 2 and 3). Some samples, though originating from the same sheet of paper, had a totally different outlook and were classified in different categories. With the exception of two samples dating from the middle of the 18th century, all the selected samples had the same origin: they were written between 1826 and 1842, consisted of handmade paper with a similar filigree and were stored together in identical conditions during the same period of time. They show neither water nor bacteriological damage.
3. Results

For all the samples except sample M, XANES examination of the inked areas pointed out a Fe\(^{2+}\)-abundance consistently lower than 10–15\%. Unfortunately, the sensitivity of XANES technique to low Fe\(^{2+}\) content is rather poor, and further methodological development is required in order to evaluate more accurately the Fe\(^{2+}/\text{Fe}^{3+}\) ratio. However, XANES measurements performed on sample C are consistent with a Mössbauer measurement estimating the Fe\(^{2+}\) abundance to be in the 11–15\% range.

The case of sample M is quite different from the others. It has the highest iron content (2.10\(^{18}\) at/cm\(^2\) to 5.10\(^{18}\) at/cm\(^2\)). The semi-quantitative XANES measurements performed on different parts of this sample are summarized Table 1. Whereas Mössbauer spectrometry performed on dark-coloured completely damaged fragments, indicates that, on average, up to 90\% of the total iron correspond to Fe\(^{2+}\), quite variable results are obtained using \(\mu\)-XANES, depending on the area where the measurements were carried out. The white crystal-like precipitates, which can be observed on some of the inked areas (see Fig. 1a), on average show about twice as much Fe atoms per unit area than the surrounding black ink (see Fig. 1b). Although it was not possible to obtain XANES data from the precipitates separately, on average the ‘crystals’ appear to contain significantly less Fe\(^{2+}\) than the surrounding inked areas (see Fig. 1c).

<table>
<thead>
<tr>
<th>Area</th>
<th>Number of measurements</th>
<th>Fe(^{2+}/\text{Fe}^{3+}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper in good condition</td>
<td>3</td>
<td>10 to 30</td>
</tr>
<tr>
<td>Brown halo around characters</td>
<td>2</td>
<td>35 to 40</td>
</tr>
<tr>
<td>Ink</td>
<td>9</td>
<td>35 to 70</td>
</tr>
<tr>
<td>White crystals on ink</td>
<td>6</td>
<td>20 to 50</td>
</tr>
</tbody>
</table>

Micro-Raman spectrometry was used to identify sulphate (SO\(_4^{2-}\)) as the major anion present in the precipitates; however, the vibration mode signature shows similarities to but is not identical to that of either FeSO\(_4\)\(\cdot\)7H\(_2\)O or Fe\(_2\)(SO\(_4\))\(_3\)\(\cdot\)5H\(_2\)O.

4. Conclusion

This preliminary work shows that XANES and Mössbauer measurements performed on two original samples were rather consistent with each other. However, it appears rather difficult to fit some of the experimental XANES data using the simple sulphate model. This confirms that the iron present in manuscripts has various chemical environments which are more complex than a mixture of FeSO\(_4\)\(\cdot\)7H\(_2\)O and Fe\(_2\)(SO\(_4\))\(_3\)\(\cdot\)5H\(_2\)O. Thus, more attention should be paid to the selection of references in order to improve the precision of the measurements.

Great care should also be taken when choosing the area, which is relevant to the average ink composition. Indeed, the observations made on sample M, show great variations of the Fe\(^{2+}/\text{Fe}^{3+}\) ratio even in a small area ranging approximately 1 mm\(^2\). These variations were related to the presence of crystal-like aggregates on the surface of the ink.

5. References

THE IMPACT OF GUM ARABIC ON IRON GALL INK CORROSION

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1. Introduction

In the occidental world, gum arabic has been extensively used as a binder in iron gall ink preparation, but its influence on iron gall ink corrosion has not been extensively studied. In this work, we investigate the impact of gum arabic on iron gall ink corrosion using laboratory samples made of cotton linters cellulose paper with no additives. This paper was impregnated with different solutions combining the three main ingredients of iron gall ink, namely, gallic acid, ferrous sulphate and gum arabic. The paper degradation versus artificial ageing was evaluated using bursting strength determinations, FTIR spectrometry, and size exclusion chromatography (SEC). The degradation of the gum itself was evaluated using gas chromatography/mass spectrometry (GC/MS).

2. Experimental

2.1 Materials and solutions

The composition of selected paper samples was very close to that of pure cellulose: most of the samples were TNO cotton linters cellulose paper. Only for SEC, Whatman paper was used.

The ink ingredients were all laboratory grade (table 1). Only freshly prepared solutions were used. In order to evaluate the influence of gum arabic, we prepared two series of samples, the first one with a mixture of iron sulphate and gallic acid called “Fe+Ac”, and the second one with a mixture of iron sulphate, gallic acid, and gum arabic, called “Fe+Ac+Gu”. The molar iron sulphate to gallic acid ratio was chosen to be 5.5 regarding previous work performed by Han Neevel.

<table>
<thead>
<tr>
<th>Table 1: Chemicals used for preparation of the inks.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron sulphate</td>
</tr>
<tr>
<td>Reference of the product</td>
</tr>
<tr>
<td>CAS 7782-63-0</td>
</tr>
<tr>
<td>Concentration used (g/L)</td>
</tr>
</tbody>
</table>

2.2 Preparation of the samples

For mechanical measurements, inks were applied on the paper in square patterns about 1 centimetre wide using a computer guided plotter pen (Phillips Digital Plotter PM 1855), with a 0.5mm point. For the other samples, the paper was simply soaked in the respective solutions for approximately 10 s and dried in an ambient atmosphere. The iron concentration per surface unit is considered to be homogeneous within ± 25%. The quantity of iron deposited on TNO cotton linters cellulose papers was determined in the centre of the samples using atomic absorption spectroscopy (13 mg/cm² ± 5 %). The average quantity of iron deposited on Whatman papers was measured by spectrophotometry using bathophenanthroline disulfonic acid as a colour reagent (37 mg/cm² ± 5 %).

Most of the samples were artificially aged in a Vötsch 0020 oven at 90 °C and the relative humidity fluctuating every 3 hours between 80% and 35%. Only samples prepared for SEC measurements were artificially aged using a lower temperature (71 °C) and a constant relative humidity (75%).

2.3 Apparatus

The loss of mechanical properties during artificial ageing was determined using a normalized bursting tester (Adamel-Lhomargy EC 05).

FTIR measurements were performed on a Paragon 1000 PC spectrometer provided by Perkin Elmer. The artificially aged papers were grounded by hand with potassium bromide (KBr) in an agate mortar. Measurements were carried out on the resulting powder using the diffuse reflectance mode.

SEC measurements were performed at the same conditions as those described by Heike Jerosch except for the columns (three Phenogel GPC, 5 mm, mixed bed, 300 × 7.8 mm, with a Phenogel GPC, 5 mm, mixed bed, 50 × 7.8 mm).

The GC/MS measurements were carried out on a HP5890 chromatograph (Hewlett Packard) interfaced by direct coupling to an INCOS 50 quadrupole mass spectrometer (Finnigan). The experimental conditions, including preparation of samples have been depicted previously.
3. Results

3.1 Mechanical properties

Figure 1 reports the loss of mechanical properties versus artificial ageing at 90 °C. The bursting strength values measured on non-aged samples are similar to that of virgin paper. During artificial ageing, the paper becomes locally more brittle and breaks along the ink patterns. After 3 days of artificial ageing, one can observe that the “Fe+Ac+Gu” samples are more resistant than the “Fe+Ac” samples. Yet, all samples were rapidly degraded, and after 7 days of artificial ageing, no differences can be measured, mainly because of the large scatter of the results obtained by the bursting tester.

pH determinations were carried out with a flat-surface electrode on the samples which were aged at 90 °C. The two series of samples have similar pH values (3.5 ± 0.5) and, these values seem to be constant during the 42 days of artificial ageing.

Figure 1: Evolution of bursting strength versus artificial ageing (T = 90°C, RH = 35–80%) for TNO cotton linters cellulose paper impregnated with two different solutions combining iron sulphate (Fe), gallic acid (Ac) and Gum Arabic (Gu).

3.2 FTIR measurements

The sensitivity of the FTIR technique is rather poor. Also, on non-aged samples, the presence of gallic acid, and/or gum arabic on the paper induces absolutely no change in the FTIR spectra, which is quite similar to the cellulose absorption spectrum. These components are far too diluted in the cellulose to be detected. One has to go very far in the paper degradation process to observe some changes in the FTIR signal. These changes are limited to the region 1700 cm⁻¹ to 1800 cm⁻¹ which is characteristic carbonyl groups stretching vibration (see figure 2). We are inclined to think that these changes are mainly due to the paper itself, and not to the additives. Figure 2 shows that, in the presence of gum, alkene and carbonyl groups are less numerous in the degraded cellulose.

3.3 Size Exclusion Chromatography

In order to evaluate the influence of gum more accurately, we undertook a second set of experiments using lower temperature of 71 °C of artificial ageing and SEC analysis to measure the changes of Mw of cellulose. The evolution of Mw versus time of artificial ageing (figure 3), confirms clearly the positive influence of gum, which reduces the rate of degradation of cellulose.

Figure 2: FTIR absorption spectra of TNO cotton linters cellulose paper impregnated with two different solutions containing iron sulphate (Fe), gallic acid (Ac) and gum arabic (Gu), and artificially aged for 42 days at T = 90 °C and RH = 35–80%.

Figure 3: Decrease of cellulose molecular weight versus time of artificial ageing (T = 71 °C, RH = 75%) for Whatman paper impregnated with two different solutions combining iron sulphate (Fe), gallic acid (Ac) and gum arabic (Gu).

3.4 Gas Chromatography

In order to evaluate the stability of gum arabic during ageing, we mixed pure gum arabic with ferrous sulphate powder and put the mixture in the climatic chamber for artificial ageing at 90 °C with the relative humidity fluctuating every 3 hours between 80% and 35%. Within a few days, the colour of the mixture turned dark brown, whereas the colour of gum alone, artificially aged at the same conditions, was still very light. GC/MS measurements confirm this observation: no significant changes are observed on the chromatograms when gum arabic is aged alone, while drastic changes are observed when it is mixed with ferrous sulphate. The intensity of signal of arabinose,
and rhamnose decreases, and some galactonic acid appears. This proves that gum Arabic degrades very fast in the presence of iron. Its positive influence on iron gall ink corrosion is also limited in time.

4. Conclusion
Research presented demonstrates that, when gum arabic is added to the ink, the degradation of the paper is delayed. We are inclined to believe that this effect is mainly due to physical factors, as the gum coats the paper fibres, and thus limits the diffusion of oxygen or free iron. This protective effect is limited in time because the gum is itself very sensitive to iron sulphate.

5. References
3. C. Remazeilles, PhD thesis, University of La Rochelle, 2001 July 18\textsuperscript{th}.
LASER CLEANING OF PAPER - A STEP TOWARDS OPTIMISATION

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1. Introduction

In conservation, laser cleaning is becoming more and more popular. Commercial laser cleaning systems have become available during the last years and are now being increasingly used in conservation studios across Europe, where well over 20 such systems are available today.¹

Laser-based cleaning is a well controllable method for removal of soiling from the surface of a substrate.² It is furthermore highly selective, contact- and reagent-less. In many cases it gives the conservator a level of control not achievable with the traditional cleaning methods. Two general approaches to laser cleaning are used: dry and wet (water assisted) approach. While in the case of dry laser cleaning only interaction of light with soiling leads to a cleaning effect, wet laser cleaning takes advantage of interaction of laser light with water deposited on soiling. For paper, dry laser cleaning is used.

During laser cleaning, removal of soiling should in principle proceed without alterations of the underlying substrate of an artefact. This is possible only if light absorptivity of soiling is considerably higher than that of the substrate and if there is no interaction between soiling particles and the substrate. In case of sensitive organic materials, e.g. paper, parchment and textiles, this is frequently not the case and surface modification after laser cleaning may be observed, exhibited as discoulouration or yellowing.

Yellowing as a result of laser cleaning is a particularly disturbing phenomenon and it has been noticed in a variety of applications.³ Interactions between the substrate and laser light may be such that both formation of new chromophores (discolouration or yellowing) and destruction of already existing chromophores (bleaching) may occur simultaneously⁴,⁵, especially if the substrate is a complex material, e.g. lignin-containing or gelatine-sized paper. Yellowing is a common phenomenon observed when fibrous materials are cleaned using ordinary laser cleaning parameters (Nd:YAG – 1064 nm or 532 nm; 0.1-1 J/cm², repetition rate 10-50 Hz, 5-10 ns pulse duration). Formation of chromophores during dry laser cleaning of paper is not a sufficiently understood phenomenon and a higher level of knowledge could lead to better optimised cleaning parameters, thus reducing undesirable side effects. This was the scope of our work.

2. Experimental

Purified cotton linters cellulose paper (Whatman N⁰ 1 filter paper) was used as a model. To obtain an exaggerated soiled model, well defined charcoal powder (low content of impurities, uniform particle size) was used as model soiling in high surface density. It was deposited onto paper by filtering aqueous suspension through paper sheets. Viscometry according to standard procedure,⁶ using fresh cupriethylenediamine solvent was used to determine the degree of polymerisation (DP).⁷ Accelerated light ageing studies were performed in Xenotest Alpha light ageing chambers. Accelerated thermal ageing (up to 160 h, 90 °C, 65% RH) was performed in a Vötsch VC0020 climatic chamber. Chemiluminescence experiments in N₂ atmosphere were performed with Lumipol 2 instrument. Colorimetric measurements of samples were performed with a Minolta CM-3610d diffuse reflectance VIS spectrophotometer with the specular component excluded. The reflectance was measured in % relative to polymeric Minolta standard. CIE L*a*b* system⁸ was used to evaluate the colour changes.

Two Q-switched Nd-YAG lasers at fundamental (1064 nm) or doubled frequency (532 nm) were used in this study. Soiled samples used for chemiluminometric analyses and study of light ageing stability were treated with 1 J/cm² fluence and 8 mm spot diameter laser pulse. For optimisation of cleaning process other laser with lower fluences (0.05 and 0.1 J/cm²), 5 mm spot and 1 and 10 shots per second repetition rates was used.

Figure 1: Example of laser cleaning of a paper document.
3. Results and discussion

With chemiluminesmetry we showed, contrary to Rudolph et al.,³ that changes in substrate immediately after laser treatment can be observed. In a dynamic experiment, chemiluminescence activity of samples immediately after laser treatment is evident already at low (<100 °C) temperatures. This indicates the presence of reactive species, formed during the process of laser cleaning and gradually decomposed, as can be seen in Fig. 2, curves a, b, c. It is evident that the species is quite long lived in darkness at room conditions (22 °C), but is easily destroyed by oxidation (Fig 2, curve d). as a consequence, limited chemiluminescence emission, close to background, is observed at low temperatures (<100°C).

![Figure 2: Chemiluminescence emission in nitrogen atmosphere during dynamic experiments (temperature gradient: 2.5 °C/min) after a 15-min period of flushing, both in N₂ atmosphere. All samples were soiled and laser-cleaned (Nd:YAG 1064 nm, 1 J/cm²) and stored in darkness for: a) 20 min; b) 22 h; a) 95 h. Sample d) was, 98 min after the cleaning, oxidized in O₂ at 100 °C for 30 min and then subjected to the same chemiluminesmetric experiment.](image)

Results, obtained with size exclusion chromatography, chemiluminesmetry, FTIR, accelerated photo and thermal ageing experiments all support the fact that chemical changes do take place and will in long term destabilize structural integrity of the substrate. Light-induced ageing processes are of particular importance for objects which are exhibited after laser cleaning.

The data in Figure 3 demonstrate that as a result of laser cleaning, the yellow component b⁺ increases substantially. However, extensive bleaching of chromophores takes place even during irradiation with λ>340 nm, the difference amounting to 7 units in 7 days. Long-term instability towards chain-scission, however, is also impaired and the laser-treated material degrades more quickly than the original non-treated one. Similar results can be demonstrated for thermal ageing.

![Figure 4: Degree of polymerisation during accelerated ageing (80 °C, 65% RH) of a non-treated and a soiled and laser-cleaned (Nd:YAG 1064 nm, 1 J cm⁻²) cellulose sheet. The rate of thermal degradation at 80 °C, 65% RH is also significantly changed – it is evident that the stability of laser-cleaned paper will be impaired in the long term. It was already shown⁹,¹⁰ that laser cleaning at 532 nm may in several cases be preferable to 1064 nm, and that one pulse of 1 J/cm² is better than several pulses of lower fluence⁴. Considering that cellulose is a thermal insulator, the heat generated during interaction of light with particles of soiling, is accumulated in the treated area.](image)

4. Conclusions

Due to differences in type of soiling and type of paper itself, universal conditions for laser cleaning can not be put forward.

The research results obtained with an exaggerated model (high surface density of charcoal soiling, highly sensitive cellulosic material), indicate that laser cleaning of paper may result in its increased instability. However, it should be stressed that even if optimal laser cleaning conditions are achievable, with minimal yellowing, the cellulosic substrate will still be
destabilized in the long-term, both during thermal and photo ageing. It is doubtful whether large-area applications are thus acceptable, while laser cleaning of localised areas may still be the cleaning method of choice in certain instances (low mechanical stability, hindered access, unavailability of other treatments). Furthermore, since paper is a complex material, the behaviour of a particular artefact during laser cleaning is difficult to predict, and testing before use is essential.

5. References

COMPARISON BETWEEN STARCH AND METHYL CELLULOSE SURFACE COATING DURING THE LEAF CASTING TECHNIQUE

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1. Introduction

Starch¹ and water-soluble cellulose ethers², are important additives in paper production, in paper surface sizing and coating. They are as well used in paper conservation as adhesives, paper coatings or strengtheners, consolidates and also as cleaners.³ A research into the influence of starch and cellulose ether surface coating on the properties of paper formed during conservation by leaf casting was conducted within the framework of the applied research project⁴ “Optimization of conservation leaf casting technique”. In this context the first part of individual properties of starch types and starch layers were studied and determined. After having compared the results, we were able to confirm the assumption that starch properties depend mostly on its origin (wheat, potato, corn). This part was presented at the ICOM-CC meeting in Ljubljana on March 2004.⁵

2. Experimental part

In the next stage of the mentioned research project, paper samples were prepared in the same manner and with the same fibre composition as for the first part, the only difference was the coating where some methylcelluloses were applied and tested. Some typical physical properties of the tested samples were determined, and comparison with the results obtained with starch surface coated samples was performed. In the presentation the results of the comparison between starch and methylcellulose surface coatings applied during the leaf casting conservation technique, are presented. Due to financial restrictions only two samples of methylcellulose coating were possible to analyse. We selected one of the most frequently used products in paper conservation, a relatively low and medium viscosity was selected. The following samples of starches and MC were used:

Sample 1: Sudsterke potato starch (Helios),
Sample 2: Cerestar wheat starch , (Helios),
Sample 3: Cerestar corn starch (Helios),
Sample 4: Papiran SKM-42 corn cationic active starch (Helios),
Sample 5: Drei hasen Weizenstarke wheat starch (Laursen),
Sample 6: Jin Shofu Japanese wheat starch,
Sample 7: CULMINAL MC 2000 (Hercules),
Sample 8: CULMINAL MC 7000 (Hercules).

Measurements and analysis of surface coated paper samples were conducted at the Pulp and Paper Institute in Ljubljana, according to ISO and TAPPI standards and ICP methods:

– Basic physical-structural properties (grammage⁶, thickness, density, specific volume⁷, uniformity of the paper sheet – M/K-3D formation index⁸).
– Mechanical properties (tearing resistance⁹, bursting strength¹⁰, folding endurance – MIT¹¹, stiffness – Clark¹²)
– Surface properties (smoothness – Bekk¹³, porosity – Gurley¹⁴, contact angle – FibroDAT¹⁵).
– Optical properties (ISO brightness¹⁶, opacity¹⁷, light scattering and light absorption¹⁸).

3. Results and Discussion

1. Starches and MC surface coatings on paper influence only the paper uniformity, which is shown as improvement of the formation index. Other basic physical structural properties were not affected.

![Figure 1: The effect of starch and MC surface coatings on the uniformity of paper samples.](image)

2. Mechanical properties in general did not improve much with starch and MC, except the folding endurance. Starch samples showed less improved values. A distinct improvement in double folds was observed with 1% potato starch (sample 1).

The best results were obtained with samples coated with Culminal 7000 0.5% and Culminal 2000 1%. (fig. 2)

3. Measurements show that starch or MC surface coatings do not affect smoothness, but only porosity and hydrophilic properties. Results show that 1%
Durability of paper and writing

concentrations of potato (sample 1), corn (sample 3), Japanese wheat starch (sample 6), Culminal 2000 (sample 7) as well as 1% Culminal 7000 (sample 8) reduce porosity of paper structure. (Fig. 3)

4. In general application of starch and MC does not affect measured ISO properties. We noticed only some reduced values in opacity, which means higher transparency, on samples coated with 1% potato starch (Sample 1) and with 0,5% Culminal 7000 (Sample 8), all the others samples show no change in opacity.

Application of starch and MC on the surface of paper slightly decreases its hydrophilic properties. The surface becomes less wet absorbent, but still remains hydrophilic. The best results were obtained with 0,5 % Culminal 2000 (Sample 7). (Fig. 4)

4. Conclusions

With the comparison of analysed properties of leafcasted coated paper samples we examined the effect of starches and methylcellulose surface coatings on some typical physical properties used in paper testing. From the results conducted during the research we may be able to conclude that:

– Not all starches are suitable for surface coating application in the paper conservation leafcasting procedure.
– Potato starch coating (sample 1) show improved properties, but because of its great adhesion it is not adequate as coating during the leafcasting.
– Corn starches coatings (Sample 3 and 4) show no improvement on treated paper samples.
– Wheat starches (Samples 2, 5 and 6) show the best results among analysed starches.
– Starch and MC coatings improve paper formation.
– MC, compared to starches improves some surface properties especially the hidrophobicity (contact angle) and the porosity of paper.
– MC coated samples show the best results in folding endurance (double folds).

5. References


7. ISO 534 – Paper and board – Determination of thickness and apparent bulk density or apparent sheet density.

8. ICP method – M/K-3D Formation Index (M/K Formation tester/ floc analyzer).


12. TAPPI 451 – Flexural properties of paper (Clark stiffness).


15. TAPPI 558 – Surface wettability of paper (angle of contact method).


EXPERIMENTAL RESULTS OF AGED TREATED PAPER WITH SOME CONSOLI DANTS

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1. Introduction

Cellulose ethers polymers are typically used for, pharmaceuticals, foods, paints, paper sizing, printings and textiles. They consist of a wide diversity of polymers ranging from organic-soluble thermoplastic products to water-soluble food additives. They are more economical to produce than natural gums and starches as a result their importance has increased recently.1

In paper conservation, cellulose ethers have been used alone or combined with starch pastes for structural repair such as lining, hinging, and mending. Their moisture holding, surfactant and anti-redeposition properties made them useful as poultices for removing stains, old adhesives and other accretions. Dilute solutions of cellulose ethers polymers have been used for sizing or resizing paper and this has a direct application on this research. Cellulose ethers have also been used for consolidating flaking of friable paints on illuminated manuscripts and as a binder for cellulose powder fills.2

2. Effects of environmental conditions on the weight gain of the cellulose ethers

In order to study the effects of relative humidity on weight change the experimented cellulose ethers were exposed to 50% relative humidity and 21.3 °C. The purpose of this experiment is to study how much moisture is gained over time when exposed.

Exposed samples were weighed at time intervals until little or no measurable weight change is observed. Fig 1. shows how these materials absorb moisture when exposed to the air and gradually reach the equilibrium. Water-soluble ethers, e.g., Methocels and Klucels (Methyl Cellulose and Hydroxypropyl Cellulose), absorb more moisture than organic-soluble ethers such as Ethocels. Non-water soluble ethers, ethocel-10 and Ethocel-100, absorb nearly no moisture. Klucel-G and Klucel-M show an intermediate percentage of moisture absorption when compared with either Methocels or Ethocels.

3. Application of Methyl cellulose (Mothocel)

Cellulose ethers exhibited different degrees of thermal stability. In order to study the effect of heat, discoloration and weight loss changes were measured as an evaluation of the stability of the ethers. The powder forms of the ethers, as received from the companies, were exposed to 90 °C in air-circulating dry oven. Samples received even heat exposure. Samples were weighed at time intervals to determine the weight loss versus time. Feller mentioned that the amount of weight that polymers lose during heating usually indicates degradation and is a simple measure of long-term stability3 thermal aging was continued until distinct color changes were observed. Table 1 lists the weight loss% of the tested ethers.

Table 1: Percent Weight Loss % of Heated Ethers at 90°C versus time (hours).

<table>
<thead>
<tr>
<th>Material</th>
<th>112 Hours</th>
<th>1080 Hours</th>
<th>1872 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methocel-K100LV</td>
<td>1.97</td>
<td>2.67</td>
<td>5.98</td>
</tr>
<tr>
<td>Methocel-A15LV</td>
<td>2.39</td>
<td>3.08</td>
<td>7.44</td>
</tr>
<tr>
<td>Ethocel-10S</td>
<td>2.20</td>
<td>3.25</td>
<td>5.55</td>
</tr>
<tr>
<td>Ethocel-100S</td>
<td>0.68</td>
<td>4.48</td>
<td>7.75</td>
</tr>
<tr>
<td>Klucel-G</td>
<td>0.69</td>
<td>14.80</td>
<td>17.91</td>
</tr>
<tr>
<td>Klucel-M</td>
<td>3.34</td>
<td>20.12</td>
<td>22.19</td>
</tr>
<tr>
<td>Whatman Paper#1</td>
<td>2.98</td>
<td>4.79</td>
<td>9.22</td>
</tr>
<tr>
<td>Total Absorption</td>
<td>0.68</td>
<td>1.86</td>
<td>2.6</td>
</tr>
</tbody>
</table>

In brief, Methocels show almost no color change and very little weight loss when exposed to heating over quite a long time, certainly long enough to observe distinct color and weight changes for all of the tested materials. These results suggested that they are fairly stable materials.
3.1 Changes of mechanical properties during thermal ageing

The experiment included three Methylcelluloses, Methocel-A4C, Methocel-A15LV and Methocel K100LV. As mentioned before, Methocels absorb about 3% of its original weight of moisture when conditioned at 50% relative humidity and 23°C. Although thermal aging does not affect the color over more than 1872 hours, aged Methocels powders desorbs about 6–7% of the original weight.

Stress-strain curves of the treated and aged samples show that as the aging time increased, both the strain and the stress to failure decreased as shown in Fig 2.

![Figure 2: Breaking Stress (psi) versus Time Aging (Hours) at 90 °C and 75.3 RH of Treated Whatman Paper#1 with Cellulose Derivatives.](image)

Aged treated samples with Methocel-A15LV exhibited little color change when compared to other treated samples. Figure 3 includes the yellowness index YI E313 of the humid thermal aged treated and control samples. While treated samples with Methocel exhibited a little more color change than control alone, as seen in Figure 3, they underwent a color change that far less than treated samples with either Kymene-557H or with gelatin.

![Figure 3: Yellowness Index, ASTM-E313, of the Aging, at 90°C and 75.3% RH, of the Treated Whatman Paper#1.](image)

3.2 Light stability

Both treated and control samples were exposed to light aging under intense Ultraviolet lamps at a distance of about 20 cm between the lamp and the samples. They were exposed for more than 12 weeks at which decline in strength properties were observed. Figure 4 summarizes these results, in which stress and strain to failure are plotted versus aging time in weeks of both materials Methocel-A4C and Methocel-A15LV. Exposure to ultraviolet for 12 weeks reduced the strength of all samples to approximately the same value.

![Figure 4: UV – Light Aging Effects on the Breaking Strain (in./in.) of the Treated Whatman Paper#1.](image)

4. Application of ethyl cellulose (Ethocels)

4.1 Changes of mechanical properties during thermal ageing

From Figure 5, it is obvious that although the aging hours increased up to 700 hours, the strain to failure of the aged treated samples decreased only from about 0.025 to 0.015. This means that aging up to this number of hours reduced only the extensibility of the treated samples but the ultimate resistance to stress values are nearly the same.

After 1670 aging hours, it seems that both, the paper and the consolidant, are no longer resistant to the aging
conditions. Stress-strain curves in Figure 5 show that humid thermal aging stiffened the treated paper with this material eventually reduced the strength of the sample aging while at the same time increased the stiffness only at 1000 hours of exposure.

Treated paper samples with Ethocel-10S suffered little color change in comparison to Kymene-557H or even to Gelatin as seen in Figure 3 which plot the yellowness index E313 of the humid thermal aging effects on the color change of the treated aged and control samples. Samples treated with Ethocels and exposed to ultraviolet light exhibited no measurable color change even after 12 weeks of exposure. This suggested that in these materials color stability is not good indication of mechanical stability.

5. Application of gelatin

Animal glues and gelatin are binders and adhesives with broad applications in the paper manufacturing industry. They are used in both surface sizing and coatings of papers. It is well known that gelatin is one of major sizing materials in paper industry with its advantages and disadvantages.

5.1 Changes of mechanical properties during thermal ageing

Figure 6: Breaking Stress (psi) versus Time Aging (Hours) at 90 °C and 75.3% RH of Treated Whatman Paper#1.

Figure 6 shows that gelatin treated samples, before humid thermal aging, acquired not only considerable strength, but also exhibited much more extensibility when compared to the untreated (Control) samples.

3.2 Light stability

Ultraviolet light aging does not change the color of the treated samples with gelatin at all up to 2060 hours, the numbers of hours that decreased the strength properties to less than 50%, as shown in Figure 7.

Figure: 7 Effects UV-Light Exposure on the Stress-Strain Curves of Whatman Paper No#1 Treated with Gelatin.

On the other hand, humid thermal aging causes more serious color change to the gelatin-treated samples than the control. The color change was the in the second order of all the experimented materials in this research as seen in Figure 3.

In conclusion, although treated samples with gelatin exhibit the highest values of strength, comparing to all of the experimented materials within this research, they gradually suffered observable degrees of color change as a result of humid thermal aging.

6. References

1. Introduction
The aim of this experimental study was to propose the methods of the qualitative classification of historical books from 19th and 20th centuries from the point of view of their next preservation. A special selection of book collection before the next deacidification, conservation and strengthening processes is not necessary. The secondary effects and partial restrictions are published only1-3. It would be appropriate to develop a simple and fast realizable method for considering the books state. This method could also predict books behavior in the technological steps of preservation.

2. Experimental
Collection of 100 books of 20th century, kindly provided from Slovak National Library in Martin, was studied. The following parameters were measured: square weight, thick of paper, the content of paper pulp, pH of cold extract, surface pH of paper, the degree of sizing, folding endurance, tensile strain by subsistent norms (ISO, STN)4-10 and lignin content by spectrophotometric measurements of absorption at 280 and 457 nm (M40 with photometric ball, Carl Zeiss Jena), surface pH by indicator papers (Macherey-Nagel), performance stability from steel point. 15 measurements were performed (at 3 pages localized in different places of book block and at 5 different zones on one page) per one book. The following mathematical methods were used for statistical evaluation: analysis of variance (ANOVA), point estimators of parameters in the model of analysis of variance, nonparametric statistics – the Kruskal Wallis test, multivariante analysis of variance (MANOVA), correlation, cluster analysis.

3. Results and discussion
3.1 Acidity of paper
The acidity of ligno-cellulose materials was determined by 3 various methods of the pH value measuring. The statistically significant difference was achieved between them, but their correlation coefficient was determined as very high: 0.95–0.96. The dependence of pH value on the age of books was determined and is showed in Fig. 1. The following results were obtained by statistic evaluation: the position of the measured place on page influences the pH value, the location of the page in the book does not influence the pH value, the book age influences the pH value. It was found out that the text part was the most acidic area, internal edge near the back of the book was the least acidic and the margins had almost the same pH values.

3.2 Mechanical properties and degree of sizing
Results of mechanical properties measurement – tensile strength (tensile index Xt), folding endurance (number of DF), break through endurance (puncture depth PD) always in the machine direction (MD) and cross direction (CD) and their relations to the degree of sizing have shown, that all of mechanical properties mutually displayed statistically significant correlation, especially in case of MD with higher coefficient of correlation (0.45–0.75). That signifies that one of the measurements (semi-destructive method in longitudinal line) is sufficed in practical monitoring. The degree of sizing didn’t show correlation with other mechanical properties.

We expected improvement of the mechanical properties with shorter age of books. The hypothesis confirmed with the exception of some cases. The illustration of mechanical properties monitoring is in Fig. 2.

3.3 Lignin
Dyeing experiment using fluoroglucinol was used to estimate lignin content (%L) and compared with the spectral method (determination of remission at 280 – \(R_{280}\) and 457 nm – \(R_{457}\)). The correlation of these methods was significant with correlation coefficient 0.61 and dependence was following: \(\%L = 26.52 – 1.14 R_{280}\).

![Figure 1: Average of pH of 20th century books sorted by their age. Standard deviation was ± 0.1 for cold extraction and surface pH method and ± 0.2 for pH indicator method.](image-url)
4. Summary and conclusion

The other parameters showed neither statistical significance nor correlation with mentioned properties. The classification of books based on acidity measurements (by indicator), mechanical properties measurements (by steel point) and lignin content estimated (by spectrophotometry) enabled their categorization into four groups (Fig. 3). Four kinds of next book protection were proposed. There were 14% of books in a very bad state and hand intercession was needed, 31% should be treated by deacidification and strengthening, 49% should be treated by deacidification only and just 6% of books were in good state and no protection was needed. Monitoring of book state in dependence of date of their origin is showed in Table 1.

Table 1: Categorization of 20th century books into the classes A–D.

<table>
<thead>
<tr>
<th>Years</th>
<th>Number of books in class A</th>
<th>Number of books in class B</th>
<th>Number of books in class C</th>
<th>Number of books in class D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900–1919</td>
<td>4</td>
<td>9</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>1920–1939</td>
<td>6</td>
<td>9</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>1940–1959</td>
<td>1</td>
<td>5</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>1960–1979</td>
<td>3</td>
<td>5</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>1990–2000</td>
<td>0</td>
<td>3</td>
<td>12</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 2: Average of fold endurance of 20th century books sorted by their age.

Figure 3: Classification of books required protection; A – intercession of restaurators, B – deacidification and strengthening, C – deacidification only, D – without protection.

5. References

5. STN ISO 534 Paper and board. Determination of thickness.
8. STN 500374 Testing of pulp and paper. Surface pH measurement of pulp and paper.
DEACIFICATION OF AGED NEWSPRINTS

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The study was aimed to the influence of paper deacidification on the stability of graphic information of offset newsprints during the ageing. Wood-pulp newsprint paper naturally aged for about 20 years (50 g/m²) and high quality filter paper Whatman (Cat. No. 1001 917, 85 g/m²) as a reference were used. Samples of papers were printed with coldset offset inks Rollotemp produced by Michael Huber GmbH, München.

Nontreated papers and deacidified papers were tested. Samples of paper were deacidified by pouring into 2% solution of Methoxy Magnesium Methyl Carbonate in Methanol and drying on a free air. The standard techniques of accelerated ageing – moist heat (80 °C and 65% relative humidity), UV-A radiation (radiation intensity 29 W/m², illumination intensity 60 000 lux, average temperature of sample 31–36 °C, 11–17% relative humidity, distance of samples from the source 19 cm), daylight (samples were exposed to the light of standard sunlight through window’s glass, radiation intensity 3–25 W/m², illumination intensity 4770–39500 lux, average temperature of sample 23–27 °C, 32–37% relative humidity) and office light (samples were exposed to the light of standard office illuminating fluorescent tube, radiation intensity 0.0031 W/m², illumination intensity 600 lux, average temperature of sample 15–18 °C, 18–22% relative humidity, distance of samples from the source 150 cm) – were applied in the stability investigation of original and deacidified papers.

Deacidification of nonprinted samples leads to the improvement or does not significantly affect the mechanical properties of Whatman paper after accelerated ageing. On the other side, the deacidification in most cases leads to the downgrade of the mechanical properties of the newsprint paper after accelerated ageing, e.g. the folding endurance is significantly lower for deacidified samples after accelerated ageing (Figure 1). This downgrade was probably caused by significant lowering of the pH of the newsprint samples containing lignin after deacidification (pH of the cold extract of nontreated samples – 5.20; pH of the cold extract of the treated samples around 9.7). The values of pH of cold extract were obtained according to the ref.5.

The brightness of samples of newsprint paper (original as well as that after accelerated ageing) is significantly lower than the brightness of the corresponding samples of Whatman paper (Figure 2). In most cases, the deacidification treatment does not significantly affect the brightness of the samples of Whatman paper and leads to the further lowering of the brightness of the samples of the newsprint paper.

The optical properties of the samples of Whatman paper and newsprint paper printed by standard process inks cyan (C), magenta (M), yellow (Y) and black (K) were...
Durability of paper and writing

Whatman paper is various and depends on the particular ink and type of accelerated ageing. The color differences $\Delta E_{\text{CMC}}$ of samples printed by yellow ink are shown on Figure 3.

Comparing with nontreated samples, the deacidification treatment using 2% solution of Methoxy Magnesium Methyl Carbonate in Methanol leads to the downgrade of mechanical properties and lowering of brightness of the newspaper samples subjected to several types of accelerated ageing, while optical properties of color prints on these samples were not change significantly.

References

1. Introduction

Photograph collections have a dual value. Individual photographs and negatives are historic and authentic objects of their time. They represent the technology and processing of the past. Primarily the values in photograph collections are considered to be informative values. Nevertheless, it is of importance to survey the condition of the collection as the first step in collection management.1

Photograph collections in museums, libraries and archives are usually very large containing several thousands of objects or even more. Therefore thorough individual survey of objects is too time consuming. Methods for surveying large amounts of photographic objects have been developed recently.1-4 No standard for surveying of large collections has still yet been made.2

Statistic approach is often used in surveying large collections of books and archival materials.5 Random sampling is not always a good option due to the very specific deterioration behaviour of photograph materials. Several studies have presented the different deterioration phenomena characteristic for photographic materials.6-10 Many different deterioration factors are present, both internal (e.g. bad processing, acid hydrolysis of acetate film base) and external (e.g. climatic) factors. Due to the specific laminated structure and very sensitive image layer deterioration behaviours of photographic materials are specific.

2. Method

This work has started with in 2002 and it has already been used by the conservation students of our Institute in condition surveying of different photograph collections. It has been also in use on the surveying of Uno Wegelius collection of 856 glass plate negatives. The method will also be adapted for book and archival materials in the education of paper conservator students of our Institute. The surveying method consists of categorisation of damages types and damage amounts.

An essential part of the surveying method is a Condition Survey Atlas for giving details of the categories and an EXCEL form, where the results are presented. This poster will concentrate to the condition survey of silver gelatine glass plate negative collections.

2.1. Categorisation of damage types

Damages of glass plate negatives are divided in 6 groups according to the most usual damages. They are:

- A – damages caused by biologic factors
- B – emulsion damages, both caused by mechanical or climatic reasons
- C – silver mirroring
- D – yellowed or bleached silver image
- E – dirt or other foreign material present
- F – damages of the base material

2.2. Categorisation by amount of damage

It is common to use numbers from 0 to 3 to indicate the amount of damage.1-3

- 0 – no damage
- 1 – slight damage, no need for conservation
- 2 – moderate damage, need for conservation; should be controlled
- 3 – severe damage, need for acute conservation

2.3. Data of survey results

The survey data will consist of three different files. The results of the survey are written on Excel writing file. From writing file the results will be automatically transferred to the Survey Printing File. The program will calculate the total amount of different damage types and also the total amount of damage severeness (table 1). From those results one can plan the active and preventive conservation needs for future care. For one file the information of 200 negatives can be written.

The form was planned by István Kecskeméti and realised by a student of paper conservation Ilkka Heikkinen in autumn 2002.

With this surveying method one can survey the condition of 500–800 glass plate negatives per day, depending on how they are reached from their storage envelopes.

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| Table 1: The results of different damages and the severity of damages. |
|-----------------|---|---|---|---|
|                 | 1  | 2  | 3  | Totally: |
| A: biological   | 0  | 3  | 1  | 4  |
| B: emulsion     | 84 | 44 | 0  | 128 |
| C: silver mirror| 126| 39 | 14 | 179 |
| D: bleac/yell   | 14 | 3  | 0  | 17 |
| E: dirt         | 2  | 0  | 0  | 2  |
| F: base material| 0  | 0  | 0  | 0  |
| Totally:       | 226| 89 | 15 |     |

3. Condition Survey Atlas

In order to interpret the survey results by the same way by different individuals an illustrated Condition Survey
Atlas was created. In this Atlas each damage category with letter and number are described. Several photographs belonging to most categories have been taken to make the identification of damages more precise. During the planning of Atlas no sampling from collections was made; Uno Wegelius collection of 856 glass plates was surveyed as a whole.

4. Discussion
This Condition Survey Atlas is planned for surveying the condition of one specific photographic technique at a time. Most of the catalogued collections are organised and stored by different techniques. The main purpose of the Atlas is to create a surveying system to get more information of the deterioration of large collections. This will help to plan the needed conservation treatments. This survey system can be adapted easily to other photographic techniques and also to book and archival materials. It is possible to use this Condition Surveying Atlas to survey whole collections or to choose parts of larger collections by random sampling.

5. References
VIISCOSITY MEASUREMENTS. MARTIN EQUATION VERSUS MULTI-POINT METHODS

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1. General considerations

Chemists tend to regard viscosity as a specific property of fluids (both liquids and gases), but for a physicist viscosity is rather a coefficient used in the equations of flow. This physical point of view explains why experimental determination of viscosity of cellulose solutions in organic solvents greatly depends on the applied method (equation, type and geometry of the viscometer), and a necessity of standardization of these measurements is obvious. At present, national standards require that the intrinsic viscosity of cellulose is calculated according to one-point Martin equation from data obtained with a viscometer of strictly determined geometry. This method is fast and sufficiently reliable but it is used only in paper industry and preservation science. Generally, the intrinsic viscosity of polymers should be determined by one of multi-point methods based directly on the following equation:

\[
[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c D}
\]

where: \([\eta]\) – intrinsic viscosity of polymer, \(\eta_0\) – viscosity of solvent, \(\eta\) – viscosity of solution, \(c\) – concentration of solution, \(D\) – shear velocity.

Polymer handbooks give a general dependence of viscosity of a polymer solution on its concentration:

\[
\frac{\eta - \eta_0}{\eta_0 c} = [\eta] + k_1 [\eta]^2 c + k_2 [\eta]^3 c^2 + k_3 [\eta]^4 c^3 + ... \quad (2)
\]

From this equation the most commonly known multi-point equations can be derived – those of Huggins, Kraemer, and Schulz and Blaschke. Practical application of these equations needs much tedious laboratory work and usage of series of viscometers of varying geometry in order to be in accordance with the requirement of shear velocity approaching zero.

2. One-point Martin method

In 1951 Martin suggested the use of a much simpler one-point method, but no information about the origin of his equation was given in the paper. An attempt of reconstruction of the probable path of mathematical considerations, used in order to arrive at the final equation, will be presented below.

This seems to be very simple. When higher-order terms in equation (2) are neglected, one obtains the well known Huggins equation

\[
\frac{\eta - \eta_0}{\eta_0 c} = [\eta] + k_1 [\eta]^2 c = [\eta] (1 + k_1 [\eta] c) . \quad (3)
\]

After applying logarithmic transformation to this equation one arrives at its other form

\[
\ln\left(\frac{\eta - \eta_0}{\eta_0 c}\right) = \ln [\eta] + \ln (1 + k_1 [\eta] c) \quad (4)
\]

and taking into account the approximation:

\[
\ln(1 + x) \approx x \quad (5)
\]

the final result is obtained:

\[
\ln\left(\frac{\eta - \eta_0}{\eta_0 c}\right) = \ln [\eta] + k_1 [\eta] c . \quad (6)
\]

This is the logarithmic version of the Martin equation. But there is a trap hidden in these calculations. One must remember that some numerical errors are generated through approximate formulae. For example, this specific approximation in eq. (5) generates a 10% relative error when \(-0.2 < x < 0.2\). Let’s have a closer look at the consequences. Both standard and the second Martin publication require fulfillment of the inequality \(2.5 < [\eta]c < 3.5\). If we take into account only smaller of these limits and the value of Martin constant \((K \equiv k_1)\) equal to 0.3, it is easy to observe that the obtained value of the expression \(K[\eta]c = 0.75\) is much higher than the allowed value of \(x\) in the approximation (5). Therefore the generated numerical error greatly exceeds 10%. The conclusion seems to be obvious: though derived from the same basic equation (2), from which various multi-point equations are stemming, Martin equation cannot be treated as a basis for multi-point viscosity measurements.

Nevertheless, the Martin one-point method gives reproducible results when used in the case of cellulose solved in cupriethylenediamine. Therefore equation (6) must be regarded as an empirical equation of limited applicability. However, its unquestionable simplicity and strictly determined geometry of viscometer, as well
as strictly defined experimental conditions, make this method a perfect tool for rapid determination of intrinsic viscosity of cellulose\(^3\)\(^,\)\(^4\).

3. Experiments

Being fully aware that the Martin equation cannot be used for multi-point viscosity determination, we nevertheless tried to compare it with two other multi-point equations – that of Huggins, see eq. (3) and Kraemer:

\[
\ln \frac{\eta}{\eta_0} = [\eta] - k'' [\eta]^2 c .
\]  \hspace{1cm} (7)

which can be also derived from equation (2) by applying the approximate formula (5). The measurements have been done on samples of two model papers P1 and P2 (described in publication\(^12\)). The preliminary results, presented in Table 1, were both interesting and unexpected.

<table>
<thead>
<tr>
<th>Type of paper</th>
<th>P1 ((\pm) 1σ)</th>
<th>P2 ((\pm) 1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huggins equation</td>
<td>233 \pm 25</td>
<td>644 \pm 12</td>
</tr>
<tr>
<td></td>
<td>(r = 0.9976)</td>
<td>(r = 0.9931)</td>
</tr>
<tr>
<td>Kraemer equation</td>
<td>354 \pm 44</td>
<td>626 \pm 5</td>
</tr>
<tr>
<td></td>
<td>(r = 0.7169)</td>
<td>(r = 0.9953)</td>
</tr>
<tr>
<td>Martin equation (multi-point)</td>
<td>331 \pm 40</td>
<td>655 \pm 13</td>
</tr>
<tr>
<td></td>
<td>(r = 0.9725)</td>
<td>(r = 0.9868)</td>
</tr>
<tr>
<td>Standard Martin equation</td>
<td>618</td>
<td>599</td>
</tr>
</tbody>
</table>

Table 1: Intrinsic viscosity of cellulose calculated by various equations. For multi-point methods correlation coefficients are given.

It seems that mutual accordance of the obtained values of intrinsic velocity depends on the type of paper being studied. For paper P1 the results obtained by multi-point equations are much lower than the value calculated according to the standard\(^3\)\(^,\)\(^4\). This is not the case with paper P2, where, unexpectedly, all applied formulae lead to very similar values. This phenomenon undoubtedly deserves further studies – possibly not only on cellulose solutions in cupriethylenediamine, but also for other polymers.

4. References

EXPERIMENTAL VERIFICATION OF ZOU, UESAKA AND GURNAGUL FORMALISM, BASED ON KINETIC DATA OBTAINED FOR VARIOUS KINDS OF PAPER

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1. Introduction
Application of Arrhenius equation in predicting paper and pulp permanence, where a multiple-reaction system with different activation energies should be taken into account, has been seriously questioned by many authors. However, Zou and co-workers1 achieved a better understanding of the apparent activation energy even in the case of multiple parallel reactions, and justified the extrapolation based on Arrhenius plot. Their approach was a very promising one, but, unfortunately, this publication was not widely recognized among the researchers working in the fields of papermaking and preservation science. Strong experimental evidence of validity or falsity of this approach is still lacking.

The equation used in paper1 is based on a well known and widely used Ekenstam equation2 and has the following form:

\[
\frac{1}{DP} - \frac{1}{DP_0} = t \cdot A_a \exp \left( \frac{E_a}{RT} \right)
\]

where

\[
A_a = A_{a0} + A_{a2} [H_2O] + A_{a5} [H^+] [H_2O].
\]

Symbol \([H_2O]\) denotes the moisture content in paper. As the concentration of hydrogen ions in paper cannot be measured, the value of \([H^+]\) was recalculated from the experimentally determined pH value of paper. The parameters \(A_{a0}, A_{a2}, A_{a5}\), as well as the activation energy \(E_a\), should be empirically determined for the investigated kind of paper. However, they are not independent, and if one wants to use the equation for a different kind of paper, it is necessary to find the suitable values simultaneously. One can try, however, to find at least an approximate prediction of the investigated paper ageing behaviour using the original set of values published in the second part of the cited publication3. This is exactly what we did. We tried to use the parameters of Zou and co-workers equation to the papers differing from the material used in the original experiments described in the literature1,3.

2. Types of papers used
We decided to check the applicability of Zou, Uesaka and Gurnagul formalism, taking our kinetic data obtained for the model P1 paper (containing more than 95% of cellulose from coniferous trees and 0.45% of ash) at temperature 90 °C and at various relative humidities (from 10 to 75%).4. Samples of paper P1 have been obtained from TNO, Delft.5 It should be stressed here that two different reams of P1 paper, differing slightly in the original value of polymerization degree, have been obtained from this source.

Another set of well documented kinetic data can be taken from the report of Kaminska, Bégin et al.6. The authors used in their experiments two other kinds of paper – BNSWK softwood ISR paper #1 (Bleached Northern Softwood Kraft fibre, rosin sized) and SW-BCTMP softwood ISR paper #3 (Bleached ChemiThermoMechanical Pulp fibre, unsized). The temperature range used by Kaminska and Bégin was 65–90 °C, and the relative humidity range was 65–72%.

For comparison, one of the kinetic runs obtained by Zou, Uesaka and Gurnagul has been chosen in order to check applicability of the same equation parameters (averaged over temperatures and humidities) to a single curve. The samples used in the experiments of Zou were those of softwood bisulfite pulp (BBSP) originating from various Canadian paper mills and formed into standard handsheets (60 g/m²).

3. Results and Discussion
The most important data concerning the kinetic results are presented in Table 1. Typical curves have been shown in Fig. 1.

The reader should be aware that the residual standard deviation (RSTD) values given in Table 1, though obtained as a result of linear regression analysis, have been recalculated so as to show differences between experimental data and theoretical curves in the natural system of coordinates: DP versus time.

The worst results of fitting the discussed model to the experimental data have been obtained for Kaminska and Bégin paper SW-BCTMP. The remaining results were quite promising. Most of the investigated kinetic curves were quite satisfactorily predicted by the model, though in almost all cases the experimental points were situated below the calculated curve, this meaning that real degradation rate was somewhat higher than the calculated one. Experimental degradation progressing faster than that predicted by the discussed model could be explained by the fact that the model assumes a...
Table 1: Selected experimental details of kinetic results obtained for various kinds of paper. The Kraków data have been obtained for P1 paper originating from different paper reams.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Paper type</td>
<td>BBSP</td>
<td>BNSWK</td>
<td>SW-BCTMP</td>
<td>P1</td>
<td>P1</td>
</tr>
<tr>
<td>Temperature range</td>
<td>90 °C</td>
<td>65–90 °C</td>
<td>65–90 °C</td>
<td>90 °C</td>
<td>90 °C</td>
</tr>
<tr>
<td>RH range</td>
<td>75%</td>
<td>65–72</td>
<td>65–72</td>
<td>10–45</td>
<td>23–75</td>
</tr>
<tr>
<td>DP₀ value</td>
<td>1369</td>
<td>2475</td>
<td>1858</td>
<td>921</td>
<td>997</td>
</tr>
<tr>
<td>Number of kinetic curves</td>
<td>4422</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean value of Residual Standard Deviation (RSTD) in DP units</td>
<td>72</td>
<td>122</td>
<td>188</td>
<td>69</td>
<td>35</td>
</tr>
</tbody>
</table>

Figure 1: Kinetic curves calculated according to Zou, Uesaka and Gurnagul model (lines), as fitted to the experimental data (points) obtained in various laboratories at temperature 90 °C and relative humidity close to 75%.

The constant concentration of hydrogen ions during the degradation process, whereas our own experimental results clearly show that pH is lowered during the artificial ageing tests, thus resulting in the acceleration of acid hydrolysis process.

4. Conclusion

The results presented here, though not conclusive enough, speak strongly in favor of Zou, Uesaka and Gurnagul formalism. It seems possible to apply the values of parameters experimentally obtained by these authors for the rough estimation of kinetic behaviour of papers originating from different sources. Of course, better results will be, most probably, obtained if a set of equation parameters is experimentally determined for the specific kind of paper being investigated. Another improvement in the original model could be achieved by taking into account variation of the hydrogen ion concentration in the course of accelerated ageing tests.

5. References

DEGRADATION OF PAPER AS STUDIED BY FIBER LENGTH MEASUREMENTS AFTER HYDRODYNAMICAL TREATMENT

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1. Introduction

Comprehensive characterization of deteriorating papers is a prerequisite of selecting the best methods for their preservation. In this context, it is important to learn how macromolecular changes influence mechanical properties of paper.

Properties of cellulose chains determine the properties of cellulose fibers. A decrease in the degree of polymerization of cellulose lowers mechanical resistance of fibers, thus making them susceptible to shortening due to mechanical treatment. Consequently, mechanical properties of paper are also changed. A scheme of this cause-and-effect chain of the degradation process can be drawn:

- temperature and relative humidity
- polymerization degree (DP)
- fiber properties: fiber strength, fiber length (after standard pretreatment)
- mechanical properties: MP, paper breaking length, tear resistance, double folds
- time

Studies on the dependences DP = DP(t) and MP = MP(DP) exist in the literature, but description of a possible relation between fiber length and DP is hard to be found. Characterization of paper degradation through the studies of fiber length has several practical advantages:

a) a small amount of paper is necessary for the measurement (0.1 g sample, about 14 cm², would suffice);
b) paper samples covered with print, as well as those containing lignin, can be studied;
c) the measurements are fast.

2. Experimental

2.1 Samples

The experiments were carried out on a sample of model paper P1 (containing more than 95% of cellulose and obtained from TNO, Delft¹), previously subjected to accelerated aging⁵. Some samples had been impregnated with aluminum sulphate prior to accelerated aging⁶ in order to achieve an effect of degradation more advanced than that obtained for the non-impregnated samples after the same degradation period.

2.2 Equipment

Morphological properties of fibers were determined with a MorFi LB-01 fiber analyzer, produced by Techpap, France. The analysis is done on a fiber network, so that the measurement occurs in the natural unrestrained environment of fibers. This approach allows for a reliable statistical measurement of thousands of fibers at high speed and accurate determination of important characteristics of their shape.

2.3 Defibration procedure

The samples of degraded paper had to be defibered prior to a measurement in a simple domestic blender used as a disintegrator. Direct action of the blender knives, as well as the action of water whirl produced by the rotation of knives, were the defibering agents. In order to minimize the destructive action of knives, the defibration process (of total duration time equal to 3 minutes) was done in cycles: blender switched on for 5 seconds, then blender switched off for 10 seconds.

2.4 Fiber length measurements

The length of fibers was measured automatically in the MorFi apparatus by a computer analysis of images of the suspension flowing through a flat cell observed by a digital CCD video-camera. The analysis of morphological properties of fibers performed by MorFi LB-01 provided arithmetical average length of fibers (the value most sensitive to the effect of shortening of degraded fibers during their mechanical treatment), expressed by the equation

\[ FL = \frac{\sum z_i \cdot l_i}{\sum z_i} \]

where \( z_i \) is the number of fibers in a given class of length, and \( l_i \) is the mean length of fibers in the given class. Additionally, a determination of the degree of cellulose polymerization (DP), for all samples tested by MorFi LB-01, has been done viscometrically, in accordance with the SCAN-CM 15:88 standard.

2.5 SEM measurements

Another method of defibering of samples consisted in a gentle shaking of paper sample in a small bottle partly
filled with water. After defibration, suspensions composed of separate fibres were obtained. From these suspensions small handsheets (1 cm² in diameter) were made. The length of fibres could be measured from the photographs of handsheets, made by Scanning Electron Microscope.

3. Results and Discussion

The dependence of both measured quantities – degree of cellulose polymerization (DP) and average fibre length (FL) – on time has been shown in Figure 1. Both curves are similar and running approximately in parallel, thus confirming existence of correlation between polymerization degree and fiber length.

However, this correlation was established only for paper samples containing cellulose with polymerization degree below 450, as illustrated by Figure 2.

It has to be stressed that a decrease in the arithmetical average length of fibers is an effect of weak mechanical treatment of sample, being the result of water whirl only (results of action of the blender knives was regarded as negligible). This decrease is due to the presence of sensitive places in the structure of degraded fibers. These places are distinguished by a very weak mechanical strength. It can be postulated that for DP values below 450 the number of weak points in fibers is so great that even a delicate mechanical treatment can break off the fibers.

When a dependence of average length of fibers on the polymerization degree of cellulose is drawn for all samples impregnated with aluminum (Figure 3), an existence of a logarithmic relation can be supposed. Such a hypothesis has been forwarded by Akcetin and Verschraege⁴. However, more experimental data in the region of lower DP values are necessary in order to obtain a more unequivocal confirmation of this supposition.

A comparison has been made between the values of fiber length obtained from SEM photographs and those measured with MorFi LB-01. Both values were of the same order of magnitude. The differences fall within the interval of (+10 ÷ –33)% of the value obtained from MorFi LB-01. If the action of knives was a critical source of shortening of fibers, then the values of fiber length obtained from the analyzer would be significantly lower.

4. Conclusions

Determination of properties of cellulose fibers can be useful in paper degradation studies. However, essential decrease in arithmetical average length of fibers, correlated linearly with the decrease in cellulose DP values was observed only for paper samples aged for a long time, or under conditions increasing the rate of hydrolysis of cellulose chains. It is proposed that measurements of arithmetical average length of cellulose fibers can be used as an indicator of paper condition in books and printings, because for this kind of measurement only a small piece of paper is needed – as compared with other methods used in conservation practice.
5. References


4. D. Akcetin, L. Verschraege, Relation between the degree of polymerization, the fiber strength, and the breaking elongation, Textilis 1974, 10, 16.
CONTROL OF AQUEOUS PAPER TREATMENTS WITH ION CHROMATOGRAPHY

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1. Introduction
There are several aqueous conservation treatments for paper materials in use: cleaning/washing with water, deacidification/neutralisation treatments and aqueous methods for the stabilisation of iron gall ink containing paper. The effectiveness of these processes has been studied mainly by analysing changes in paper properties.1-4 With few exceptions, the only common treatment control was provided by determination of pH.5

The purpose of this study was to test the usability of IC (ion chromatography) for the control of washing of paper materials, for the monitoring of deacidification with calcium hydroxide and sodium phosphate, as well as in studies of phytate treatments.

Sampling for the IC analyses can be performed non-destructively, by taking samples directly from treatment solutions, or destructively, by making extracts of the treated papers. This paper presents some preliminary results of IC analyses of washing and conservation treatment solutions. More results will be published later.

2. Experimental
2.1 Ion chromatography
IC is a liquid-chromatographic technique in which the principle of separation involves ion-exchange. It is used for qualitative and quantitative analyses of ionic components in complex matrices. The separation proceeds between the stationary phase with functional groups, and the mobile phase, which moves through the column. The ionic components of a sample are separated on the basis of their different affinities for the stationary phase. Factors that control the separation include column type (length, resin type, particle size), eluent, its concentration and flow rate. Detection limits (depending on the detector) under normal operation conditions are in sub-ppm to ppm range.6,7

The Metrohm 761 compact high-performance ion chromatography system, was used with Dialysis (754 IC) unit to analyse both anionic and cationic samples. As a pre-treatment, the dialysis unit separated high molecular (colloidal) substances from the injected solutions.

For anionic analyses Metrosep A Supp 5-100 (6.1006.510) Column, size 4.0 × 100 mm and particle size 5.0 µm was used with 3.2 mmol/L Na₂CO₃/1.0 mmol/L NaOH eluent with suppression. The separating phase of the column consisted of polyvinyl alcohol coated with quaternary ammonium groups. The separated ions were detected using a conductivity detector. Conditions for anionic analyses were: Injection volume 20.0 µL, flow rate 0.70 m L/min, temperature 20.0 °C and pressure 13.2 MPa. The anionic analyses were calibrated to detect and quantify sulphate, phosphate, chloride and fluoride anions.

For the cationic analyses the Metrosep C 2-250 (6.1010.230) cation column, size 4.0 × 250 mm and particle size 7.0 µm was used with 4.0 mmol/L tartaric acid and 1.0 mmol/L dipicolinic acid eluent. Conditions for cationic analyses were: injection volume 20.0 µL, flow rate 1.2 m L/min, temperature 20.0 °C and pressure 13.2 MPa. The cationic analyses were calibrated to detect and quantify sodium, ammonium, potassium, calcium and magnesium cations.

2.2 Samples
Rag paper, sample A (cotton linters, 1840’s) and lignin containing mechanical pulp, sample B (newspaper, 1920’s) were used. 2 × 1.5 g of each was washed separately in purified (Millipore, Elix™) water (500 mL) in a beaker for 15 min and the washing (20 °C) solutions were analyzed with IC after dialyses.

Two batches of 0.27 mmol/L calcium phytate solutions (solution I and solution II) 2 L each, were made according to Neevel’s recipe from p.a grade phytic acid, calcium carbonate in purified water and pH of solutions was adjusted to pH 5.6 (WTW pH Meter 330) with ammonium hydroxide.8

3. Results and Discussion
The IC chromatograms (Figure 1) show three identified water-soluble anionic substances, which were washed out from paper samples. IC analyses offer direct information on the amount of water-soluble sulphates, which are washed out during the aqueous process.

More sulphates washed out from old rag paper, sample A (2.7 mg/L) than from newspaper, sample B (1.4 mg/L). The SD (standard deviation) value for sulphate cation analyses is ±0.3 mg/L. Purified water itself contained sulphate only in trace amount. Of course, IC analyses cannot reveal the origin of sulphate and it is obvious that internal and external sources of sulphates can be different in different papers.9
Durability of paper and writing treatment. In the deacidification/neutralisation processes are very often performed with saturated calcium carbonate and ammoniac. They are mixtures of calcium-, and ammonium phytate containing both soluble and insoluble complexes and ions. In the formation of calcium-phytate complexes other cations (in this case ammonium ions), if present in the same solution, can intervene by forming both solid and soluble species. It is evident, that pH measurement combined with the solubility information of calcium phytate solution, is not a sufficient control for this kind of complex aqueous mixtures.

The IC offers a possibility to analyse both soluble cations and anions from these treatment solutions and also provides an opportunity for studying changes in ion composition during aqueous stabilisation treatments.

Table 1: Ion contents of calcium phytate solutions I and II. Error is given as standard deviation.

<table>
<thead>
<tr>
<th>Calcium phytate solution</th>
<th>[PO₄³⁻] (mg/L)</th>
<th>[Ca²⁺] (mg/L)</th>
<th>[NH₄⁺] (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>470 ± 8</td>
<td>92 ± 4</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>II</td>
<td>323 ± 8</td>
<td>117 ± 4</td>
<td>16 ± 1</td>
</tr>
</tbody>
</table>

In paper conservation, aqueous deacidification processes are very often performed with saturated solutions of calcium hydroxide, which turn to calcium carbonate or with calcium carbonate, which is almost insoluble in water. Clear solutions over precipitates are used for the deacidification without knowledge of exact concentrations of soluble calcium cations or other ions, which form the basis of the chemical conservation treatment. In the deacidification/neutralisation reaction cations (Ca²⁺, Mg²⁺) are important, because they take part in salt formation. They will be also adsorbed on paper and give alkaline reserve. Concentrations of cations in neutralising solutions and loss of cations from solution during sorption, as well as possible washing out of cations and/or anions, can be studied by the IC.

Adsorption of ions/salts can be monitored also from paper extracts after treatment processes by destructive IC analyses.

There are, anyhow, some limitations for IC analyses: use of chemicals of a high degree of purity (p.a.), while for preparation of solutions and eluents water of high purity is needed.

4. Summary

The preliminary results show that IC is a very useful tool for the study and control of aqueous treatments of paper. With this method one can follow the removal of sulphates and other ions from paper into water used for washing. Also the changes in ion concentrations (ion take up and wash out) in treatment solutions, used for stabilisation and neutralisation, can be examined.

With IC (either anionic or cationic), can achieved low detection limits and low sample consumption: typical sample volume is 20 µl (even smaller samples are possible). Repeatability, resolution, as well as linearity of calibration are unique for each cation and anion. The method was statistically evaluated. There are also many chromatographic parameters: dead volume, retention times, net retention times, standard deviation of peaks of individual components, selectivity (the separation efficiency of chromatographic system), which need to be controlled before using IC routinely.

Anyhow, even routine analyses must be made under the control of a chemist.

5. References

8. J. G. Neveel, (Im)possibilities of the phytate treatment. The iron gall ink meeting, Newcastle 4th–5th September, Postprints, University of Northumbria, Newcastle upon Tyne, 125–134.


THE CONSERVATION AND RESTORATION OF THE MANUSCRIPTS “LA BASTILLE”

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1. Introduction

Workshops always have to deal with the treatment of a large number of manuscripts containing iron gall ink. The CTBnF has tried to find a way to treat this kind of document without damaging the ink. The use of water to clean or leafcast the paper is sometimes necessary, and we have tried to study its effect on the ink, particularly on the iron ions.

2. History of the manuscripts

The Bastille archives date from 1660 to 1786, and concern prisoners and jail administration. They were stolen and scattered on the 14th of July during the French Revolution1. Now conserved at the “Bibliothèque de l’Arsenal”, this enormous collection (about 20,000 documents), preserves some evidence of its own history as it is in poor condition and difficult to read by researchers.

3. Condition of documents

The documents are in various states of degradation but most of them are folded, incomplete, full of dust and mud, and sometimes have been attacked by mould or bacteria.

Most of the inks on the treated documents are in good or mediocre condition (Figure 2), and they are not sensitive to water. Unfortunately others are in poor condition (Figure 3), particularly when they have suffered from a water damage.

4. Conservation and Restoration

Even though some of the documents are in good condition, the sheer quantity of them and the presence of iron gall ink force us to make a choice between different treatments. The use of water (immersion) is sometimes the only viable alternative if one wishes to wash, flatten and leafcast the documents to render them legible and preserve them.

Figure 1: Document 10217 A-2-37 before treatment.

Figure 2: Iron gall ink in mediocre condition.

Figure 3: Iron gall ink on a water-damaged document in poor condition.

Figure 4: Document 10217 A-2-37 after leafcasting.

Figure 5: Leafcasting of a document damaged by iron gall ink.
Leafcasting has many advantages, for example, it puts no stress on the borders because the technique uses no adhesives but recreates fiber bonds and it is a good way to strengthen paper degraded by microorganisms. It is a rapid treatment that preserves every piece of the document. Compared to lining, there is nothing attached to the whole surface of the document. This technique boasts excellent legibility and reversibility.

5. Long term control of the ink

The use of water evokes up some questions: is this treatment appropriate for this kind of ink despite the fact that it is in good condition and this is not a bleeding ink? According to B. Reissland\(^2\), an aqueous treatment may have side effects: it can activate an acid hydrolysis, or it can make iron ions move on the paper surface or it can discolour the ink. It is also established that iron ions are harmful to paper as they catalyse the oxidation\(^3\). In order to control the effects of water treatments on the iron ions we have used “the indicator papers for iron ions” developed by the Netherlands Institute for Cultural Heritage\(^4\).

5.1 Bathophenantroline spot tests

Firstly, test papers containing the indicator bathophenantroline are prepared. The principle is that water-soluble iron salts migrate into a dampened indicator strip that is brought in contact with the surface of the document. The bathophenantroline forms an intensively magenta-coloured complex with iron (II)-ions (there is no risk of bleeding from the indicator bathophenantroline during the contact because the indicator is not water-soluble.)

Procedure:
- We have prepared small pieces of the indicator papers (containing bathophenantroline).
- The indicator paper has been dipped in distilled water (removing the excess water on a blotting paper).
- We have placed the indicator on the ink, covered it with a piece of plastic foil and we have pressed it with a finger for 30 seconds.
- The indicator paper was removed from the object. Magenta colour of the strip indicated the presence of iron (II) ions.

5.2 Hydroxylamine hydrochloride spot test

Secondly, hydroxylamine hydrochloride has been used to show the presence of iron (III)-ions in the ink.

Procedure:
- The test papers used for the bathophenantroline spot test have been cut in two pieces.
- A half of this test paper has been dipped in hydroxylamine hydrochloride.
- The hydroxylamine hydrochloride reduces the iron (III)-ions in iron (II)-ions and the test paper becomes magenta.

The more iron (II)-ions and iron (III)-ions there are in the paper, the more magenta coloured the test papers become.

6. Results

The indicator strips were used to evaluate the effects of aqueous treatments on iron gall ink. The formation of magenta-coloured complex was not observed after aqueous treatments involving large quantities of water, as is the case during washing or leafcasting. We can thus assume that some of the soluble iron(II) ions and iron(III) ions are washed from the paper.

In order to control the ageing stability of paper, we have collected our results in tables (figure 6). A picture is inserted in the table to report the area tested with the spot tests. After some years we will control if the ink is still in good condition. By repeating the same tests on the same areas we will be able to see if some soluble iron ions could be detected.

![Figure 6: Tables of spot tests using bathophenantroline and hydroxylamine chloride.](image)

7. Conclusion

It was necessary for the workshop to find a rapid and secure way to conserve and treat this enormous and important collection. Thanks to these simple spot tests, we can control the presence of free iron in the ink after treatment. And, as it is not water-soluble ink, we can say that washing and leafcasting in this case is a good solution to treat this documents without damaging the ink.

8. References

The principal tasks of archives and libraries – as keepers of irreplaceable source of cultural and information values – is to make accessible these materials for users and also to preserve this heritage for future generations. As paper is a principal information carrier and its degradation can cause the loss of “memory of mankind” only an integrated effort of paper education, research, science, conservation and paper industry will be able to preserve this cultural heritage.1

The biggest problems in archives and libraries are caused – paradoxically – by modern papers produced from the 2nd half of the 19th up to the recent years. The new technology of paper-making introduced in 1850, involved paper formation in an acidic environment. This was a crucial milestone from the point of permanence and durability of paper, its degradation and preservation in archives and libraries. It is a self-degradative effect of acidic paper; “time bomb”, as it is often called the limited lifetime of machine-made paper with acidic rosin sizing with addition of alum has been threatening the great part of the cultural paper heritage. The present state of knowledge confirms that paper degradation in the course of its ageing is the result of hydrolysis (acidic, alkaline) and oxidation of cellulose by internal agents presented in paper in close co-influence of contaminated atmosphere, humidity and light on one hand and cross-linking and fibres embrittlement on the other hand. Thermal, biological and mechanical destruction can occur as well. In most cases, however, a combination of all above mentioned effects causes degradation of cellulose macromolecule, hemicellulose and lignin which result in decrease of fibres strength, mechanical properties, creation of brittleness, fragility and colour changes (yellowing, darkening) of paper.

1. Problem holders

47 state archives in the Slovak Republic keep altogether 22 345 archival fonds and collections representing total scope of 157 700 running meters of material. In archives custody there are 44 236 middle-age charters dating back before year 1526, 945 269 office books, about 138 000 maps, plans and drawings; documents are stored in more than 1 million covers and boxes, etc.2 It is estimated that about 80–85% of total holdings are documents created on paper from the period 1850–1970, i.e. on acidic paper with very low ageing resistance and thus potentially liable to self-degradation processes.3

Situation in Slovak libraries can be illustrated on an example of the Slovak National Library in Martin. The total number of book volumes until year 1900 is 1,2 million, of which 684 000 are on acidic paper. Of 900 000 volumes produced on hand-made paper 470 000 ones are acidic – 117 500 volumes of them are in acute jeopardy. 300 000 volumes are on wooden paper; 214 000 volumes are on acidic paper – 107 000 volumes are in acute jeopardy. Much worse is situation concerning books after year 1900. The Slovak National Library keeps 2,4 millions of book titles of which 2 280 000 are made of acidic paper. 1 140 000 book volumes are in acute jeopardy.4 In other Slovak libraries – scientific, public, special and academic – is kept about 43,6 millions of library units. On the basis of statistical data it can be stated that the situation in these libraries is even worse because most of their collections are books, journals, newspaper and other units produced after 1850 and 1900 on wooden and acidic paper. It means that the distribution of library units compared to the Slovak National Library is shifted more to the period of “acidic paper production”.

From this brief review it is obvious that the situation in cultural heritage preservation – of which archives and libraries represent very significant and irreplaceable part – is really very grave. It has to bear in mind that preservation of such heritage requires also considerable financial costs.

2. Problems solution

There are two principal groups of problems to be solved in paper preservation. The first solution must deal with acidic documents and books, i.e. acidic paper written or printed in by different inks from the above mentioned period which create the majority of collections in archives and libraries and are already kept in these institutions. As the quantity of acidic books and records is enormous only mass-scale deacidification processes will be able to solve the most serious problems. Various methods of mass deacidification treatment are available nowadays and an extensive applied research still continues in this field.
The second solution must deal with creation of new documents and books themselves. It is very obvious that use of permanent and durable paper and writing and printing inks provides the best solution and the way, how to preserve paper cultural heritage of present for future generations.

3. Legislative provisions

Preservation and protection of cultural heritage all over the world are covered by different legislative provisions on international and national levels. The Slovak Republic belongs to countries in which legislative background provides an excellent base for preservation – worth of mentioning are at least the Declaration of the National Council of the SR (NC SR) on preservation of cultural heritage from February 2001, The Act of the NC SR no. 395/2002 on archives and registries and no. 183/2000 on libraries.

4. National Program

The Department of Chemical Technology of Wood, Pulp and Paper covers in its educational programme also problems of paper ageing and preservation; research activities in paper permanence and durability started at the Department already in 1980.6,7 During the last several years several diploma works – completed at this Department and also at the Department of Graphic Arts and Applied Photochemistry – were devoted to problems of preservation of cultural heritage – permanence and ageing behaviour of some pulps and papers, deacidification of acidic paper, interaction of paper and printing inks, their permanence and ageing resistance, etc. All these works were performed in close cooperation with the Slovak National Archives and Library.

The systematic effort of the authors started in 19898 and later on of the organizations namely the Slovak National Archives and the Slovak National Library for preservation of archives and library paper cultural heritage together with activities of the Department of Chemical Technology of Wood, Pulp and Paper, STU Bratislava and the Slovak Academy of Science resulted in the national programme and one particular project “Program of preservation, stabilisation and conservation of classical information carriers in the Slovak Republic – KNIHA SK”9,10.

The basic aims of the project can be summarized as follows:

– increasing quality of university and continuing education of professionals for the field, including engagement of graduate and postgraduate students of chemical technology into projects on stabilisation of LC carriers of information;
– concentration of the scientific capacity in the field of technology of preservation, stabilization and conservation of lingo-cellulosic (LC) macromolecular materials in the Slovak Republic;
– creation of specialised shared national virtual library and inter-active shared knowledge space on the problems of preservation of LC materials of the Slovak Republic for all project participants;
– improvement and verification of method for qualitative classification of endangered library & archives materials according to historical and technological criteria from the point of searching the possibilities for increasing of capacity and decreasing of risks during their machinery treatment;
– new knowledge and new methods proposal for preservation of library & archives materials;
– new information on indoor quality environment for long-term storage of library & archives materials.

5. Acknowledgements

The authors acknowledge the support of the Project KNIHA.SK granted by the Ministry of Education of the Slovak Republic and the grant VEGA 1/0061/03.

6. References

CHARACTERISATION OF INK COMPONENTS IN ANCIENT MANUSCRIPTS USING FTIR SPECTROSCOPY

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1. Introduction
Degradation of paper and parchment has long been a line of scientific research because of the destruction it can produce in libraries and archives. Serious damage can be caused by iron gall inks.

Different parameters seem to be involved in the destructive process: paper characteristics, ink composition, and other compounds.

Knowledge of reaction mechanisms in original ink components is crucial to understand the damage caused to paper and parchment¹-⁶. Therefore, characterisation of final ink products may help us to understand better the mechanisms and consequently to avoid degradation.

Considering ink components (tannins, iron sulphate and gum Arabic) as natural products which contain impurities, it is reasonable to find several inorganic elements (Cu, K, Zn ..) together with iron. In the same way carbohydrates from tannins and gum Arabic develop an important role when oxidation and hydrolysis processes affects to the ink, as well as the paper support itself.

FTIR spectroscopy was used to characterise ink components in ancient manuscripts.

One of the most important problems related to this kind of samples is the small amount of ink that may be removed from original manuscripts. This is why microscopic techniques are required.

Different methodologies have been used in order to obtain good quality infrared spectra. Reflection techniques, such as attenuated total reflectance (ATR) and transmission techniques have been compared. Both methodologies are coupled to an IR microscope, due to the usually tiny amount of ink contained on manuscripts. For transmission techniques, we need to remove some particles from the surface of inks with a tungsten needle, and transport them to a diamond cell. At the same time, it is necessary to try to avoid paper or parchment. ATR techniques are not destructive at all. The ZnSe crystal of the objective is pressed against the sample and a single reflection penetrates it slightly.

The technique was tested using several manuscript samples with ink, which show different degree of corrosion, blackness and amount of settled ink.

A large number of inks have been analysed and different oxalate salts have been characterised. Good correlation between acidity of ink and oxalate anions has been observed. Iron (II) sulfate has also been detected in some samples.

Figure 1: An image of one of the samples used in our research, where the corrosion effect can be seen.

2. Apparatus
A Bomem MB-120 infrared spectrometer was used. The instrument has a Glowbar source, a KBr beamsplitter and a DTGS detector. A Spectra-tech IR Plan Microscope, which has a liquid nitrogen cooled MCT detector and an ATR objective of ZnSe, is attached to the spectrometer.

Transmission infrared microscope spectra were measured by accumulating 100 scans at a resolution of 4 cm⁻¹. ART infrared spectra were measured by accumulating 200 scans at a resolution of 8 cm⁻¹.

Spectral range was from 4,000 to 720 cm⁻¹. The spectral data were processed with the GRAM/386 program from GALACTIC.

3. Results
Both methods used in this study, transmission and reflection techniques, give the same information and are equally useful for all samples analysed. Poor quality spectra are usually obtained when non-degraded samples of paper are measured with the ATR microscope. Usually, several attempts have to be made, because the crystal often touches a non-smoothed region containing fibres and empty areas. As degraded ink samples have a bigger and more homogeneous surface, the ATR spectrum is normally easier to obtain.
Spectra of inks on parchment are normally better samples to analyse than on paper, whether removing particles for the transmission method or pressing the ATR crystal.

These results mean that the ink composition is the same, not only on the surface but also in the region in contact with the paper support.

Distribution of iron in the paper involves iron (II) and iron (III) ions, which can be found as different compounds in the ink spectra. In the same way, calcium from the paper alkaline buffering remains in the sample as calcium carbonate, calcium sulphate or calcium oxalate. Inks from parchment show more contribution of this calcium compounds. Degradation of natural extracts of tannins and gum arabic brings about organic salts. Although spectra of inks have important bands of water and iron sulphate that overlap other compounds, it was possible to identify bands placed in free zones.

Figure 2: Transmission spectrum of a parchment sample from the XIIIth century: Calcium oxalate and calcium carbonate can be measured on the surface of the ink.

There seems to be a correlation between pH and colour, changing from black, dark to light when pH increases (Surface pH measurement, TAPPI T 529 om-99).

Corrosion also changes from very strong corrosion at very low pH to strong corrosion, poor corrosion and no corrosion when pH increases.

Comparing the oxalate salts with these results above, we can see that iron potassium oxalate appears at low pH values, from 2.5 to 6.2. Higher pH values, from 6.5 to 6.7, clearly indicate calcium oxalate, even though this salt coexists with iron potassium oxalate and iron oxalate in some samples.

Calcium oxalate seems to be related to samples with no corrosion and higher pH values.

In general, big peaks of K and Fe using SEM-EDX (JSM 840 (Jeol Ltd.) with Scanner AN 10000 (LYNK SYSTEMS) with Be window) confirm iron potassium oxalate. Big peaks of Ca correlate with calcium oxalate (samples were cover with carbon and analysed on surface).

Several samples analysed by GC-MS showed oxalic acid in their composition.

4. Conclusions

FTIR allows a rapid analysis of samples of ink on paper or parchment, using both transmission and reflection microscopic techniques.

According to the sample’s pH, corrosion and colour, different compounds are detected in the ink. Calcium oxalate, calcium carbonate, iron sulfate, iron oxalate and iron potassium oxalate were identified.

These findings contribute to a better understanding of the mechanisms of the reactions involved in inks and inks’ degradation.

5. References

Investigation on iron-gall inks

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In restoring some paper manuscripts at the State Central Archives in Prague, a number of species, which were clearly visible under a stereomicroscope and whose origin was not known, were found on the surface of lines of iron-gall inks. Available spectral analytical methods – Raman spectroscopy, FTIR and X-ray fluorescence – were employed to investigate these species.

On the basis of the results of the analyses, these species can be divided into two groups: The first group consists in crystalline products formed directly on the surface of the iron-gall ink. The second group consists in foreign substances that were most probably introduced to the ink lines as a blotting powder used by the writer.

The first group includes crystals formed directly in the ink line. They can grow to a size of up to several tenths of a millimetre. They occur in very corrosive inks and are mostly found in the inner parts of the book block (where the measured pH is in the range 2–3). They probably require a favourable microclimate for their growth. The crystals are mostly white, or slightly yellow or brownish. Information on crystal formations appears only sporadically in the literature, frequently in connection with deacidification processes. Historical inks have been found to contain, e.g. calcium or magnesium sulfates or oxalates,1,2 after deacidification carbonates too.3,5 A manuscript with one type of iron-gall ink, where numerous crystals were found, was subjected to spectral analysis (Land Rolls 27, 1651, D22). The chemical composition of the crystals was studied using X-ray fluorescence microanalysis and FTIR. It was found that the crystals contain calcium and phosphorus. FTIR indicated that an organic phase participated in their formation, where the calcium salt of an unspecified organic acid was identified. On the basis of the results obtained by FTIR, it is apparent that the crystal formations do not consist of a single compound, but rather of a mixture of several products (a crystalline protein was also identified). More detailed study was prevented by the very small amount of material available for the analyses. The crystals are most probably formed as a consequence of degradation processes of the cellulose fibres due the effect of the corrosive ink.

In addition to salt formations, some inks also sporadically contained flat sparkling particles of irregular shape, which looked reddish under the microscope. Archivists were of the opinion that these could be gold flakes that could have been intentionally mixed in the ink. It was found by X-ray fluorescence analysis and FTIR that this is an amorphous, transparent substance in which very fine red particles are scattered, which were identified as ferric oxide on the basis of the Raman spectra. No connection with the corrosive ink has been found.

In restoring a number of manuscripts of the State Central Archive in Prague (Fund of the Upper Mining Office in Jáchymov, Book No. 831 of 1753–1883, Book No. 832 of 1784–1820) and the State Regional Archives in Prague (Kováň 1, register of births and deaths of 1723–1765), a mixture of coloured particles was found in the sections of the books and ink lines, which can be classified in the second group on the basis of their character. Blue particles predominated and were found in mixtures with black, grey or white or transparent particles. As the presence of these mixtures was repeated in a number of books and the amounts were not negligible, their elemental composition was found using X-ray fluorescence microanalysis.

Table 1: Elemental composition of the analysed particles.

<table>
<thead>
<tr>
<th>Type of solid particle</th>
<th>Elemental composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue glassy particles</td>
<td>Si, K, As, Ca, Fe, Co, Ni, Cu, Zn</td>
</tr>
<tr>
<td>Black particles (type I)</td>
<td>Pb, trace amounts of Ca</td>
</tr>
<tr>
<td>Grey particles</td>
<td>Zn, trace amounts of Fe</td>
</tr>
<tr>
<td>Black to brown-black (type II)</td>
<td>Zr, Nb, Si, Sn, Ca, Ti, Mn, Fe, W</td>
</tr>
<tr>
<td>White to transparent particles</td>
<td>Si, small amount of Ca</td>
</tr>
</tbody>
</table>

The blue particles were identified (also using an optical microscope) as blue potassium glass, which was also found in other studied manuscripts. Because of the arsenic content, it can be assumed that the source of the cobalt for production of the glass is safflorite (CoAs3), which occurs in various veins together with nickel, or smaltine (CoAs4) or cobaltite (CoAs6). These minerals are found in Bohemia in the Krušné Mts. Because of the relative contents of cobalt and arsenic in the glass, smaltine seems most probable. The light particles, which consist practically only of silicon dioxide, were used in the form of fine sand to blot the wet ink. The other types of particles have not yet been precisely defined; if a sufficiently large sample of material is available, it will be employed for identification by X-ray diffraction.

An Eagle µProbe X-ray fluorescence spectrometer was used to study the elemental composition of the particles in the historical ink. In this connection, it is useful to...
point out the ability of the spectrometer to carry out non-destructive distribution elemental analysis, which could also be interesting for study of corrosion of inks.

This application permits monitoring of the elemental distribution either along a line (LineScan) or on a surface (Mapping). The scanning technology designated as mapping has the great advantage that three kinds of information can be obtained from the measured area: the elemental composition at any point indicated by the cursor on the measured surface, the elemental composition on a line of any length and orientation on the surface, and the elemental composition over a rectangular area of any size or location (the maximum size is given by the size of the measured area). Special software enables the creation of spectral maps (pictures), in which it is possible to depict the distribution of a pre-selected element in the framework of the measured area, where the magnitude of the intensity of the fluorescent radiation of this element is expressed either through various intensities on a grey scale from black (minimum) to white (maximum) or coded in a coloured scale. Thus, a single measurement of the surface of a sample can yield the spectral maps for the individual elements and direct information not only on the distribution, but also on the concentrations of the given element over the surface.

The poster depicts the analysed crystal formations in the inks and foreign material present in the ink lines, accompanied by a brief description of the studies carried out. The poster is supplemented by depiction of the distribution of elements in historical inks in the form of spectral maps.

We would like to thank Ing. Miroslava Novotná, CSc. for the FTIR analysis and Raman spectroscopy and Doc. Ing. Martin Maryška, CSc. for optical microscope images (Institute of Chemical Technology in Prague).

References

NEW EVALUATION METHODS OF PAPER DETERIORATION: STUDY OF BRITISH PARLIAMENTARY PAPERS IN THE COLLECTION OF NATIONAL MUSEUM OF ETHNOLOGY, JAPAN

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The National Museum of Ethnology, Osaka, Japan, received in 1998 a donation of approximately 13,000 volumes of British Parliamentary Papers from Kyocera Co. Ltd, on the condition that they be made available to researchers. However, due to the fragility of paper, perusal of a part of these papers is either very difficult or impossible. We are conducting research to elucidate at what stage of damage we have to start a strengthening treatment. In other words, how can we evaluate the state of paper deterioration? Only when these points are clarified, we can select an appropriate strengthening method.

In the first part, the present condition of the British Parliamentary Papers is summarized. This investigation has been conducted on samples from 47 Papers.

In the second part, our ongoing research to find out appropriate testing methods to evaluate the state of paper deterioration is presented. This study has been conducted on 9 samples of discarded books from the National Diet Library.

1. Present condition of the British Parliamentary Papers

The double fold test has been carried out on each of 47 of the Papers, selected from different periods. The composition and degree of deterioration of papers have then been examined using small pieces of paper, detached during a double fold test. Most of samples from the first half of the 1800s are composed of linen and those from the last half of the century showed an increased ratio of esparto as well as an addition of cotton rag, Manila hemp and ground wood pulp. Softwood chemical pulp began to appear around the 1880s and became the mainstream material by the 1900s. Samples from the time of World War II showed a great portion of non-wood fibres. Samples after World War II showed the use of softwood and hardwood chemical pulp (Figure 1).

Zero-span tensile strength (Figure 2) shows the strength of one fibre. Results of a measurement of Zero-span tensile strength indicate that, on the whole, the samples of paper from the first half of the 1800s are comparatively strong, while those from the last half of the 1800s to the first half of the 1900s tend to be comparatively weak. As the analysis of fibre composition shows, the use of ground wood pulp may be a cause of deterioration in the papers of this period.

2. Evaluation of deterioration of paper from discarded books

2.1. Visual evaluation

The year and country of publication and fibre composition of natural aged discarded books are summarized in Table 1.
Table 1: Year and country of publication, and fibre composition of studied books.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date and country of publication</th>
<th>Fibre composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1942, Japan</td>
<td>Groundwood pulp (70%), softwood sulfite pulp (30%)</td>
</tr>
<tr>
<td>B</td>
<td>1952, Japan</td>
<td>Groundwood pulp (75%), softwood sulfite pulp (25%)</td>
</tr>
<tr>
<td>C</td>
<td>1918, Japan</td>
<td>Groundwood pulp (40%), softwood sulfite pulp (40%), cotton rag (20%)</td>
</tr>
<tr>
<td>D</td>
<td>1943, Japan</td>
<td>Groundwood pulp (85%), softwood sulfite pulp (15%), cotton rag (trace), unknown (trace)</td>
</tr>
<tr>
<td>E</td>
<td>1949, Japan</td>
<td>Groundwood pulp (65%), softwood sulfite pulp (35%), unknown (trace)</td>
</tr>
<tr>
<td>F</td>
<td>1943, Japan</td>
<td>Groundwood pulp (25%), softwood sulfite pulp (75%), straw (trace)</td>
</tr>
<tr>
<td>G</td>
<td>1949, Japan</td>
<td>Groundwood pulp (80%), softwood sulfite pulp (20%)</td>
</tr>
<tr>
<td>H</td>
<td>1948, Japan</td>
<td>Groundwood pulp (85%), softwood sulfite pulp (15%)</td>
</tr>
<tr>
<td>I</td>
<td>1932, Mexico</td>
<td>Groundwood pulp (50%), softwood sulfite pulp (45%), cotton rag (5%)</td>
</tr>
</tbody>
</table>

Visual evaluation was first conducted from a restoration standpoint. A restorer has been asked to group book samples into 3 classes: samples which necessitate conservation treatment, samples which do not necessitate conservation treatment, and intermediate samples.

In addition to performing the conventional double fold test, we devised a new evaluation method that we tentatively call the rolling test, using cylinders of different diameter: from 40 mm to 5 mm in diameter, with an interval of 5 mm. According to this method, a paper is first rolled around a cylinder of 40 mm in diameter. If the page is rolled safely, without wrinkles, tears or any kind of resistance, the same test is performed using a narrower cylinder, and so on. As soon as a sign of resistance appears, the rolling test was stopped. This test was done in two different manners: rolling parallel to the page (from 40 mm up to 10 mm in diameter), and rolling from a corner forming an angle of 45 degree to the page (from 40 mm up to 5 mm in diameter) (Figure 3). See Table 2 for results.

2.2. Pyrolysis Gas Chromatography (PyGC)

If a paper sample is pyrolysed at 300 °C, it decomposes slowly, generating levoglucosan as the main decomposition product. However, deteriorated samples from paper I (Table 2) are quickly thermally decomposed even at 300 °C. In addition to levoglucosan, its oxidized product levoglucosenone was clearly observed. This result suggests that the oxidation of cellulose contributes greatly to the deterioration of paper.

Visual evaluation was first conducted from a restoration standpoint. A restorer has been asked to group book samples into 3 classes: samples which necessitate conservation treatment, samples which do not necessitate conservation treatment, and intermediate samples.

In addition to performing the conventional double fold test, we devised a new evaluation method that we tentatively call the rolling test, using cylinders of different diameter: from 40 mm to 5 mm in diameter, with an interval of 5 mm. According to this method, a paper is first rolled around a cylinder of 40 mm in diameter. If the page is rolled safely, without wrinkles, tears or any kind of resistance, the same test is performed using a narrower cylinder, and so on. As soon as a sign of resistance appears, the rolling test was stopped. This test was done in two different manners: rolling parallel to the page (from 40 mm up to 10 mm in diameter), and rolling from a corner forming an angle of 45 degree to the page (from 40 mm up to 5 mm in diameter) (Figure 3). See Table 2 for results.

Comparing the pyrograms of samples taken from the middle of a paper with those of samples from the edges of the same page (3.5 cm and 7 cm from centre, and at the extreme end of the page), we found that the peak of levoglucosenone was relatively much higher at the edges (Figure 4).

3. Summary

Determinations of mechanical properties, by zero-span tensile strength performed on detached pieces of 47 of the British Parliamentary Papers might have given more alarming results than if they had been performed on a whole page. Nevertheless, the results illustrate well the overall present paper condition.

To evaluate if a book requires a conservation treatment, the state of degradation of an entire page is taken in consideration. We believe that the rolling test is an effective one for visual evaluation and deserves further attention, as it can be carried out on a larger surface of the page, and is much less destructive than a double fold test. The data in Table 2 seem to indicate that (with the exception of sample B) if a paper cannot be safely rolled around a cylinder of 20 mm in diameter, it requires precaution during handling.

The PyGC is also effective for evaluation of paper deterioration. By using the relative peak areas of
levoglucosan and levoglucosenone as an index, a rapid evaluation of the degree of deterioration of paper seems possible using a tiny sample, without damaging the original.

4. References


Figure 4: Pyrograms of (a) filter paper (reference), (b) deteriorated paper (centre), (c) deteriorated paper (3.5 cm from centre), (4) deteriorated paper (7 cm from centre), and (e) deteriorated paper (edge). Pyrolyzer: Frontier Lab PY-2020D, pyrolysis temperature: 300 °C, gas chromatograph: HP6890, column: Ultra ALLOY ±5, oven temperature, 50 °C – 5 °C/min – 280 °C, detector: flame ionization detector, injection temperature: 280 °C, detector temperature: 300 °C, sample weight: ca. 300 µg.