ISSN 0034-5806

RESTAURATOR

International Journal for the Preservation of Library and Archival Material

Volume 16 · Number 1 · 1995

MUNKSGAARD · COPENHAGEN

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RESTAURATOR (ISSN 0034-5806) is published quarterly by Munksgaard International Publishers Ltd., 35 Nørre Søgade, P.O. Box 2148, DK-1016 Copenhagen K, Denmark. USA subscription price is USD 141.00 including airspeed delivery. Application to mail at second class postage pending at Jamaica, NY 11431. USA POSTMASTER for North American subscribers: send address changes to Publications Expediting Inc., 200 Meacham Avenue, Elmont, NY 11003. Airspeed and mailing in the USA by Publications Expediting Inc. Printed in Denmark by P.J.Schmidt A/S, Vojens.

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Restaurator, 1995, 16, 1–9
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RESTAURATOR
ISSN 0034-5806

The Battelle Mass Deacidification Process Equipment and Technology

by J. LIERS & P. SCHWERDT

It has long been widely acknowledged that paper produced industrially since the middle of the nineteenth century is endangered by decomposition.

What causes this decomposition process? Since 1826 the traditional gelatine sizing of paper began to be to replaced by rosin sizing invented by Illig. Using this method, acid aluminium sulphate, which releases sulphuric acid, enters the paper. The acid decomposes the cellulose fibres by catalysing a hydrolysis reaction.[1]

Additionally, in the second half of the nineteenth century, wood became the main raw material for paper-making. Wood contains 15–30% lignin. The decomposition of lignin produces organic acids that speed up the ageing process.[2]

Unsuitable storage conditions such as excessive heat and humidity and inadequate air conditioning accelerate the decomposition process as well. It may take only 50–80 years until a book or document can no longer be handled.

In the 1940s, the first deacidification methods were developed by Schierholtz[3] and Barrow & Sproull[4] and improved in the following years. The general idea of these methods is to neutralize the acids contained in the paper by an aqueous solution of earth alkali salts (such as barium or calcium bicarbonate) or earth alkali hydroxides. Such deacidification methods are based on the individual treatment of each document. Methods of this type are used frequently by restorers but require much time and labour. The treatment of books on a large scale, such as for an entire library, therefore requires a new kind of process.

In the early 1970s, the first mass deacidification processes, the diethyl zinc (DEZ) process[5] and the Wei T'o process[6,7] were developed. Whereas the DEZ process works with gaseous diethyl zinc, the Wei T'o process uses a solution of methoxy magnesium methyl carbonate as the deacidification compound. In the following years these processes were improved and some new ones developed.[1]

In 1987 the German Library began looking for a method to deacidify their books. An test comparing several mass deacidification treatments showed that none of the existing methods was able to effectively treat all library materials without adverse affects.[8]

The Battelle Institute in Frankfurt was therefore engaged to develop a new mass deacidification process. The basis of their research was the Wei T'o process. The first paper deacidification facility that worked with a substantially improved version of this method was put into operation at Battelle in 1990. After a further improvement of the Battelle deacidification method, a facility for the German Library was built in 1993. After a three-month test at Battelle, the equipment was moved to Leipzig and rebuilt in the basement of the German Library. On June 22, 1994 the Battelle mass deacidification equipment was put into operation.

The Battelle Mass Deacidification Process

The equipment

The main components of the equipment are the treatment unit, two vacuum pumps – for pre-drying and post-drying, a solvent recovery unit and the storage

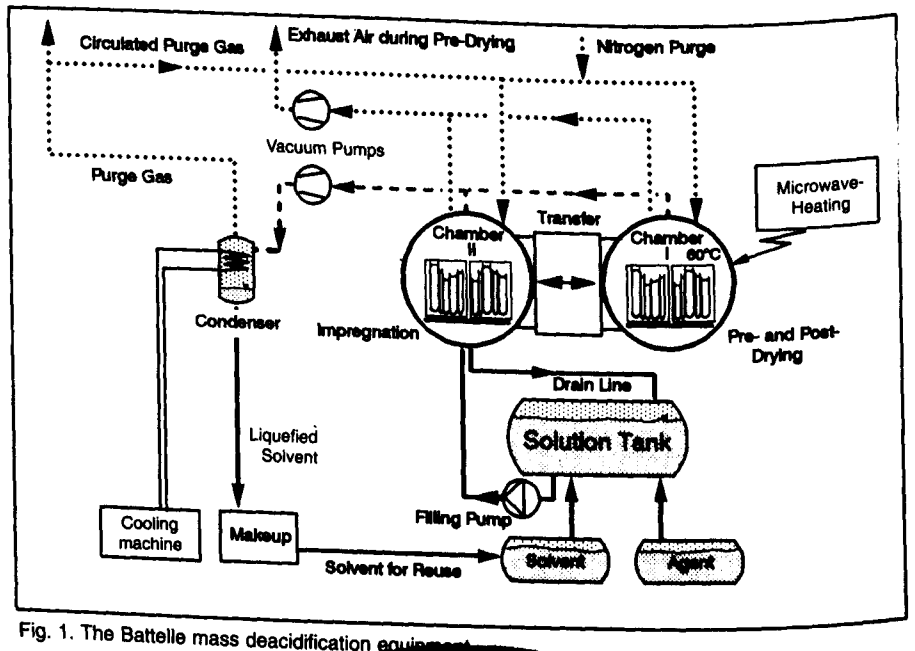
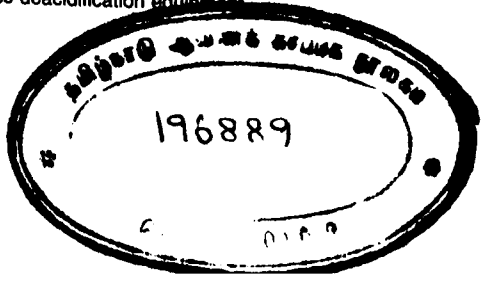


Fig. 1. The Battelle mass deacidification equipment



tanks (Fig. 1). Because the solvent used (hexamethydisiloxane) is flammable, the deacidification equipment has to be explosion-proof. The mass deacidification facility in the German Library has a modular design and allows the installation of a planned additional treatment unit.

The treatment unit (Fig. 2, 3) consists of two chambers – the drying chamber (chamber I) and the impregnation chamber (chamber II) connected by a transfer unit. The chambers have a cylindrical shape with a diameter of 60 cm and a length of 4.5 m.

The drying chamber is equipped for microwave heating. Additionally, the two chambers and the transfer unit contain facilities to move a slide with book baskets (Fig. 4, 5) in the chambers and to transport the book baskets from the drying chamber into the impregnation chamber and back. The treatment unit is directly connected to the vacuum pumps. They realize a vacuum down to 1 mbar in the treatment chambers. The vacuum system for post-drying is directly coupled with a condenser to recover the solvent.

The storage tanks are located outside the German Library and lie underground. They consist of 4 tanks with a total volume of 50 m^3. This number of tanks permits recirculation of the used chemicals and a variation of the concentration of the deacidification compound. The tanks are sealed with nitrogen to

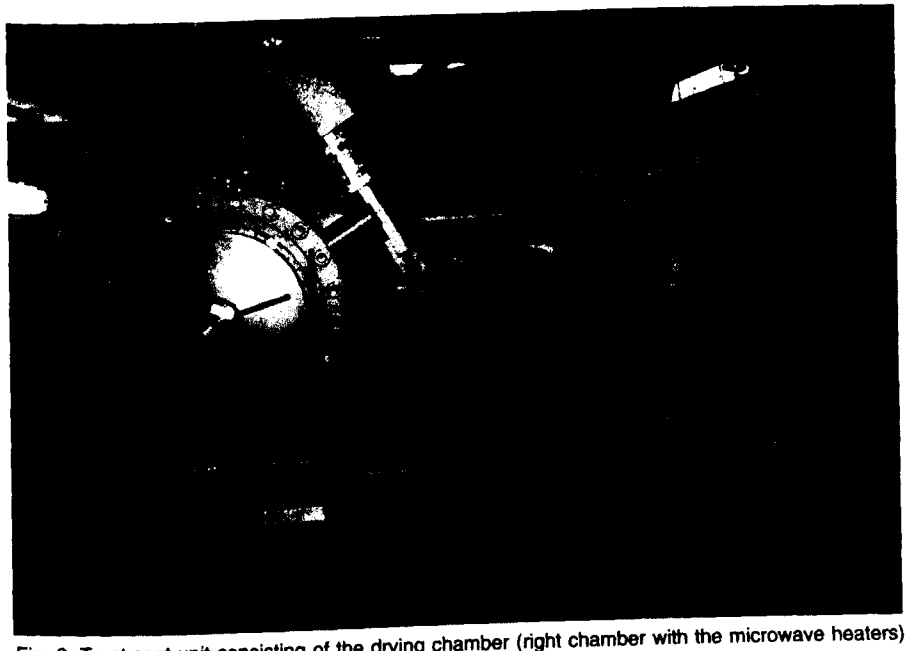


Fig. 2. Treatment unit consisting of the drying chamber (right chamber with the microwave heaters) and the impregnation chamber (left chamber) connected by a transfer unit

Fig. 3. Impregnation chamber

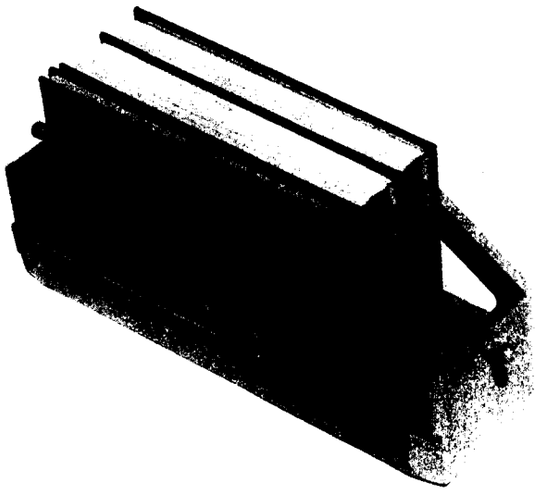


Fig. 4. Book basket with books

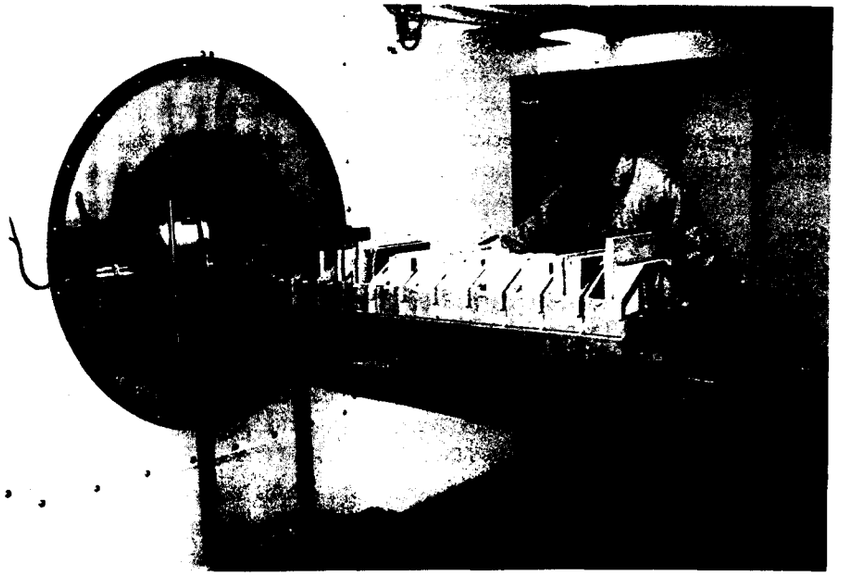


Fig. 5. The slide with 15 book baskets is moved into the drying chamber at the beginning of the treatment

prevent vapour leakage and also to keep air from flowing in when the volume in the tanks changes.

Because of the solvent recovery and the recirculation of the used chemicals, this equipment allows closed circulation of the chemical compounds.

The process control of the equipment takes place via a stored-program controller (SPS) produced by Siemens. This program control is suitable for complex industrial controlling problems. The whole process is displayed on and operated through a visual display system on a monitor. The SPS allows automatic, semi-automatic and manual control of the equipment.

The treatment

For the deacidification treatment the books must be selected and cleaned. Covers that contain metal are unsuitable for the deacidification treatment. Treatment of such materials is a topic of research at the moment.

The books and documents to be treated are placed in plastic baskets on a slide and moved into the drying chamber. After the drying chamber is closed the deacidification treatment can be started.

To prepare the paper for deacidification, its normal moisture content of 7–8% by weight must be reduced to about 1% in a pre-drying step.

Customarily, books are dried in a warm air dryer and in a vacuum dryer with conventional heating (such as the MMC-drying procedure). This drying procedure is not very efficient, requiring about 36 hours, because of the poor heat transfer in the vacuum. Battelle therefore developed a new technology for book and paper drying – a vacuum dryer combined with microwave heating. This warms the books rapidly and evenly in a vacuum.

However, glow discharge effects could be initiated by microwaves in a strong vacuum and would lead to strong local heating of equipment components inside the drying chamber. These plasma effects create a conflict between the need for low pressure to ensure thorough and fast drying on the one hand and the danger of glow discharge effects by high vacuum on the other hand. It is therefore necessary to control the microwave power dependent on the pressure in the drying chamber to prevent glow discharge effects.

Infrared sensors monitor the temperature of the books in the different baskets and control the microwave heating. In this way, even books containing different kinds of paper are dried evenly. The infrared sensors ensure that the temperature of the book surface does not rise above 50°C. Previous experiments have shown that, by keeping this surface temperature, the temperature inside the books does not rise over 60°C. To achieve even warming of the books by microwave heating, the book slide has to be moved permanently.

Upon reaching either the temperature limit or the time limit for pre-drying, the baskets are automatically transferred to the impregnation chamber. It takes about one to two hours to pre-dry the books.

Impregnation starts after all baskets have entered the second chamber. Both chambers are completely evacuated before the impregnation begins. Through this process all the air is extracted from the pores of the paper.

When chamber II is filled with the alkaline solution, the papers absorb very quickly the liquid like a "sponge", even though the books and documents are enclosed in the baskets. The pre-drying step and vacuum impregnation guarantee that the solution quickly enters all pores of the paper. The impregnation process takes only a few minutes.

After chamber II is drained, the book baskets are transferred back to chamber I. The deacidification solvent is pumped back into the storage tanks and can be reused.

The impregnated books contain solvent in the range of their dry weight. Therefore the saturated books must be dried. The post-drying process takes place in a vacuum with simultaneous microwave heating as in the pre-drying step. Because of the evaporation enthalpy of the solvent, a temperature drop of the treated

material in the vacuum takes place. However, effective warming by microwave heating prevents the books from freezing and allows fast post-drying. This process requires about half an hour.

The exhaust vapour from the drying chamber is cooled in the solvent recovery unit and the obtained condensate is collected and recycled. After post-drying the chambers are ventilated and the books are removed from chamber I.

The whole deacidification process takes about 3 hours. It is possible to deacidify 50 books per run. It is planned to increase the capacity by further optimization of the drying steps. By expanding the equipment to 4 chambers and by working in two shifts, the capacity could be increased to about 1000 books per day. The planned second treatment unit would allow semicontinuous operation.

The chemical process

The complete chemical background of the Battelle mass deacidification treatment has already been published by Wittekind.[9] This article therefore is restricted to a few important chemical details.

The chemicals used in the solvent phase of the Battelle deacidification process are ethylates of magnesium and titanium and iso-propylates of titanium. These alkoxides are dissolved in hexamethyldisiloxane. Whereas the ethylate of magnesium acts as the deacidification compound, the alkoxides of titanium are only solvents.

By using the environmentally safe hexamethydisiloxane as the solvent, it was possible to substitute conventionally used chlorofluorocarbons (for example by the Wei T'o process).

Hexamethyldisiloxane is compatible with all materials commonly used in books and archival materials. This colourless organic silicon compound has no effect on adhesives, plastics, printing inks or dyes. It leaves no odour and produces no marks or changes in the treated books.

From the deacidifying process the alkoxides of magnesium and titanium remain finely distributed in the paper. The acids are neutralized by the alkoxides of magnesium, but the complete chemical process of producing the alkaline buffer takes more time. This process consists of the reaction of the alkoxides with the water and with the carbon dioxide of the air by producing magnesium carbonate and ethanol. Because of the formation of ethanol, the treated books have to stay in a separate room for about 14 days before they can be moved to the stacks.

The deacidification process not only results in the effective neutralization of the acids in the paper but also raises the pH value to around 8 to 9. This process also gives an alkaline buffer to the paper, which consists of 1 to 2% magnesium

carbonate. Thus the treated paper is additionally protected against the further formation of acids. The first results of treatments using the Battelle deacidification method have been published by Wittekind.[9]

Conclusion

With the Battelle mass deacidification equipment the German Library has an excellent tool for saving their stock of books for acid deterioration. This new process allows the effective deacidification of a large number of books and archival materials. It has no adverse effects on the treated materials and is environmental safe. Therefore this new technology is a milestone in the preservation in libraries and archives.

Acknowledgement

The whole project of developing and building the first German mass deacidification process was founded by the *Bundesministerium für Forschung und Technologie* (Federal Ministry of Research and Technology).

Summaries

The Battelle Mass Deacidification Process Equipment and Technology

A new kind of mass deacidification process has been developed by the Battelle Institute in Frankfurt am Main. The Battelle mass deacidification treatment is a substantially improved version of the Wei T'o process and uses a solution of alkoxides of magnesium and titanium in hexamethyldisiloxane as the deacidification compound. After a successful test period, the Battelle equipment was set up in the German Library in Leipzig and has been in operation there since June 1994.

Le procédé de désacidification de masse Battelle

Une nouvelle méthode de désacidification de masse a été développée par l'Institut Battelle à Francfort-sur-le-Main. Le traitement de désacidification de masse Battelle est une version largement améliorée du procédé Wei T'o et utilise une solution d'alkoxydes de magnésium et de titane dans de l'hexaméthyldisiloxane comme agent de désacidification. Après une période d'essai réussie, l'équipement Battelle a été installé dans la Bibliothéque allemande de Leipzig et y est en activité depuis le mois de juin 1994.

Das Battelle-Massenneutralisierungsverfahren Einrichtung und Technologie

Eine neue Methode der Massenneutralisierung wurde vom Battelle-Institut in Frankfurt entwickelt. Es stellt eine von Grund auf verbesserte Version der Wei T'o Methode dar. Das neutralisierende Agens sind Alkoxide von Magnesium und Titan gelöst in Hexamethylendisiloxan. Nach erfolgreichem Abschluß der Testperiode wurde die Battelle-Anlage in der Deutschen Bücherei in Leipzig aufgestellt. Sie arbeitet dort seit Juni 1994.

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Restaurator, 1995, 16, 10–30
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RESTAURATOR
ISSN 0034-5806

The Effect of Oxidation on the Subsequent Oven Aging of Filter Paper

by PAUL M. WHITMORE & JOHN BOGAARD

Introduction

A detailed understanding of the chemistry of cellulose degradation is key to efforts to slow the deterioration of papers. The dominant degradation paths must be identified in aging papers, for not only will this aid in devising appropriate monitors for the progress of natural aging, but it is also essential to establish the validity of accelerated aging test methods, which are intended to speed the natural aging processes exactly to make accurate predictions of future performance. The internal (paper manufacture or composition) and external (paper environment) risk factors that may affect the rate of deterioration must also be characterized, for control of these risk factors becomes the route by which the degradation can be slowed.

It is worth noting that the complete picture of paper degradation is likely to be complex, and it may not be possible to devise preservation strategies with only part of this picture in focus. For example, the notion that a particular paper component (such as acidity or lignin) compromises paper stability may be difficult to establish when papers having differing contents of the putative hazard may also differ in many other, perhaps critical, ways. Similarly, efforts to establish the correlation of paper condition and a particular risk factor by surveying collections of published materials must generally rely on comparisons of papers that differ in many ways, and distinguishing such correlations can become dependent on understanding all of the important factors that may be affecting the overall degradation rates.

In an earlier publication[1] we described the application of an analytical approach designed to provide a more detailed picture of cellulose chemistry occurring in degrading paper, particularly the chemical reactions that shorten the cellu-

lose chains and eventually cause loss of strength and flexibility in the sheet. This method, based on the studies of cellulosic textile fibers by Dobbelstein & Valk,[2] relies on the quantitative comparison of selected conventional assays of chain scissions and the carbonyl and carboxyl groups formed during the degradation. We used this procedure to study the cellulose chemistry occurring in filter paper treated with acid and oxidants as well as in filter paper exposed to light and aged in humid and dry ovens. These studies demonstrated the carbonyl end group formation during hydrolytic scission and also provided insight into the course of "random" oxidation that occurs on exposure to light and chemical oxidants and may also occur on exposure to atmospheric oxygen or oxidizing air pollutants.

Although the results of that study indicated that a cellulose oxidation reaction could be characterized by the ratio of carbonyls and carboxyls formed to the number of chains broken, the analytical approach did not allow the determination of the position of these extra oxidation sites: specifically, the number formed along the chains as opposed to those formed at chain ends during the scission reactions. It has been suggested that the presence of these groups, especially carbonyls, along the chains may accelerate the subsequent degradation of the cellulose following the oxidation. Such postoxidation effects have been observed by many workers (for example, following light exposure of filter paper[3]), and this weakening of the chain due to the presence of oxidized groups has been dubbed weak link scissioning.[4] Despite their frequent observation and study, it is still impossible to predict the potential for weak link scissions following an oxidation procedure: the exact nature and position of oxidized products on the cellulose chain cannot be determined with current analytical tools, and the effect of these functional groups on scission reactions also remains poorly understood. The only method to estimate the "extra" degradation that results from oxidation procedures is to monitor the aging of each oxidized paper in an oven test.

Since our efforts to follow the course of cellulose oxidation suggested that the number of carbonyls produced in excess of new chain ends could be measured easily, we were interested in whether the amount of these "excess" carbonyls would be an approximate indicator of the weak link scissions that would occur upon subsequent oven aging of the oxidized sheets. We surmised that the amount of these excess carbonyls might, in fact, establish an upper bound on the weak link scissions that would be possible, assuming that some of these groups would not be effective at accelerating chain scissions due to their chemical nature, position on the glucose ring or location along the chain.

In this article we report the results of the humid oven aging of previously oxidized filter papers. The oxidized papers studied were the same as those reported in our earlier work, and the degree of oxidation was slight, so that further degradation could be monitored during the oven aging. Scission rates of the oxid-

ized cellulose were measured and compared with the scission rate of unoxidized cellulose. The amount of apparent weak link scissions was measured from the scission kinetics and compared with the measured excess carbonyls produced from the oxidation. Carbonyl and carboxyl group concentrations were also monitored and compared with the end group concentrations to explore the nature of the scission chemistry in the oxidized papers during the oven aging.

Experimental

The paper samples and analytical procedures have been described previously.[1] Briefly, the paper studied here was Whatman No. 42 filter paper. Analyses of the papers were performed after the sheets had been allowed to equilibrate at 23°C and 50% relative humidity (RH) for 24 h. Carbonyl contents were assayed using the hydrazine method,[5] and carboxyl contents with the standard methylene blue method.[6] Viscometric degrees of polymerization (DP_v) were determined by the standard measurements on cuene solutions, following pretreatment in sodium borohydride to minimize alkaline degradation of the oxidized samples.[7] For the simple molecular weight distribution demonstrated for cotton linter papers,[8] the number-average degree of polymerization (DP_n) can be taken as approximately half the DP_v.[9] Scissions of the cellulose chains, which are an equivalent measure of the number of new chains formed, were calculated from the DP_n using the formula described previously and subsequently converted to the same units as the functional group concentrations. In this study, the unaged and unoxidized filter paper had a DP_v of 1400–1500 and carbonyl and carboxyl contents of about 0.4 mmol/100 g and 0.5 mmol/100 g, respectively.

Sheets of the filter paper were subjected to various oxidizing treatments, including: 1 h of immersion in 0.1 M sodium periodate solution; 4 h in unbuffered 5% hydrogen peroxide; and 10 min in 3% sodium hypochlorite solution, buffered to pH=5 with acetate. All samples were thoroughly rinsed in deionized water after treatment and allowed to air-dry overnight. The oxidations with sodium hypochlorite solution were performed at two bath temperatures, one at room temperature and one at 5°C. This lower temperature slowed the oxidative action and allowed the production of very lightly oxidized sheets. The two sample sets oxidized with hydrogen peroxide were treated identically, except that the more heavily oxidized set was stored at 23°C and 50% RH for 11 days prior to oven aging to ensure that the oxidation reactions had reached completion.

In addition to these chemical oxidations, the filter paper was oxidized photochemically by exposure to the output of fluorescent lamps. Exposure to ultraviolet (UV) A light (Q-Panel UVA-351) produced the more heavily oxidized papers, whereas the lightly oxidized samples were produced by exposure to simulated

UV-free daylight, generated with high-output daylight fluorescent lamps (Sylvania F48t12/D/HO) filtered through UF-3 Plexiglas sheets. These filters transmit less than 10% of the intensity of wavelengths below 400 nm. The light intensity was measured periodically with a radiometer (International Light Model 700), and exposures were carried out at 23°C and 50% RH.

Following these oxidative treatments, samples were aged in humid ovens. For the chemically oxidized samples, the ovens were operated at 80°C and 65% RH. Due to a calibration error in the oven temperature-recording equipment, the light-exposed samples were aged at 75°C and 65% RH. Unoxidized control sheets were aged at the appropriate temperatures in separate oven tests to avoid possible contamination from the oxidized samples.

To determine the presence of rapid weak link scissions or any other alterations to the degradation of papers brought about by an oxidizing treatment, the rates of chain scissions for oxidized and unoxidized cellulose must be compared. However, this comparison is difficult for the Whatman filter paper studied in this work because the scission reaction slows down as it progresses, probably because of a range of reaction rates in locations of differing accessibility or local morphology. Thus one cannot compare a single scission rate for the oxidized papers with that of the unoxidized papers, but rather one must compare the scission rates of the oxidized and unoxidized pairs at an equivalent progress of the degradation reaction.

As there is no clear procedure as to how to best make this comparison, we have chosen to compare the scission rates of oxidized and unoxidized pairs that have the same average degree of polymerization. We do this graphically, by overlaying the scissions (as derived from the DP) in the oxidized and unoxidized papers during the oven aging treatments. However, at the start of the oven aging, the oxidized and unoxidized papers do not have the same DP, because the DP has usually decreased during the oxidizing treatments. Thus, we must compare the scission of the oxidized sheet to that of the unoxidized sheet having the same DP, and this can be achieved simply by offsetting the start of the oxidized paper degradation so that it overlaps with the aging of the unoxidized sheet, which has degraded to the same starting DP. This graphical procedure is tantamount to thermally preaging an unoxidized sheet so that it has a DP identical to that of the oxidized sheet and then monitoring the degradation rates of both sheets in further oven aging. To compare the scission rates of unoxidized and oxidized sheets when their DPs are equal, then, one must compare the slopes of the curves at equal vertical levels on the graph: that is, when their "scission contents" are equal.

Because both the unoxidized and oxidized sheets displayed steadily changing scission rates during the aging, a graphical method was chosen to compare the overall scission behavior of the unoxidized and oxidized sheets. The scission production of the unoxidized sheet is overlaid with the results for the oxidized sheet,

but for these graphs the oven aging times for the oxidized sheets are first multiplied by a scaling factor chosen so that a portion of the scission curve of the oxidized sheet is made roughly parallel to that of the unoxidized sheet. This scaling factor for the oven aging time represents the average scission rate increase of the oxidized sheet versus the unoxidized sheet over the period where the scission curves have been made parallel.

This is a particularly convenient graphical representation, for in addition to providing a comparison of the late-stage scission rates, the presence and approximate magnitudes of early-stage weak link scissions can be determined. By appropriate choice of the time-scaling factor for the oven aging of the oxidized papers, the late stage scission curve can be made parallel to that of the late stage of the unoxidized papers. When that has been achieved, the offset between the curves of the oxidized and unoxidized sheets can be estimated. Since this offset results from rapid scission production in the early stage of the oven aging of the oxidized sheets, the magnitude of this offset can be taken as the number of weak links introduced during the oxidation treatment.

Once the magnitudes of any weak link contributions have been estimated, these are compared with the excess carbonyls measured in the oxidation treatments, that is, the carbonyls that exceeded the number of new chain ends produced during the oxidation. Although one can determine these excess carbonyls using a graphical method as illustrated earlier,[1] it is also straightforward to simply calculate the difference between end groups and carbonyls produced in the oxidizing treatments.

Results

Periodate-oxidized cellulose

The results of the oven aging of the periodate-oxidized paper is shown in Table 1 and Fig. 1. As was observed in our prior work, the mild periodate treatment produces exclusively carbonyl groups, presumably in the form of 2,3 dialdehydes[10] with little concomitant chain scission or carboxyl group development. The excess carbonyl concentration for this paper was about 1.7 mmol/100 g, giving about 0.8 mmol/100 g of dialdehyde sites that might act as weak link units along the chains.

The data shown in Fig. 1 demonstrate no significant difference in the scission rates of the oxidized and unoxidized papers. This result is in accord with the work of Davidson,[11] who saw no increased instability toward acid hydrolysis in periodate-treated cellulose. Although it is clear that periodate is peculiar in its strong tendency to produce dialdehydes in cellulose, it also seems that if dialdehyde products contribute to the measured excess carbonyls created in an oxidizing treatment, one would overestimate the potential for weak link hydrolytic scissions.

Table 1. Oven aging following sodium periodate exposure

Hours	DP	Scissions, mmol/100 g	Carbonyls, mmol/100 g	ΔCarbonyls, mmol/100 g	Carboxyls, mmol/100 g	ΔCarboxyls, mmol/100 g	pH
A. Unoxidized							
0	1421	–	0.40	–	0.55	–	
163	837	0.61	0.99	0.59	0.49	−0.06	
499	595	1.21	1.58	1.18	0.51	−0.04	
836	503	1.59	2.03	1.63	0.55	0.00	
1172	446	1.90	2.63	2.23	0.58	0.03	
1508	382	2.36	3.28	2.88	0.70	0.15	
1844	344	2.72	3.90	3.50	0.86	0.31	
B. Sodium periodate, 1 hour							
Unexposed	1417	–	0.43	–	0.45	–	
0	1277	0.10	2.21	1.78	0.57	0.12	
24	1089	0.26	2.14	1.71	0.46	0.01	
72	978	0.39	2.16	1.73			
168	798	0.68	2.32	1.89	0.48	0.03	
360	649	1.03	2.57	2.14	0.50	0.05	
577	542	1.41	2.65	2.22	0.55	0.10	

Peroxide-oxidized cellulose

The results of the oven aging of peroxide-oxidized papers are shown in Table 2 and Fig. 2 and 3. As had been observed in our prior study, the unbuffered peroxide treatment alone produced mainly carbonyl groups on the cellulose. Chains were broken and carboxyl groups were formed in amounts roughly one-third that of the carbonyl group development. Thus, as indicated in Table 2, the peroxide-treated sheets contain cellulose chains having 2–3 times more carbonyls and slightly more carboxyls than unoxidized cellulose at the same DP.

Unlike the periodate-oxidized sheets, the peroxide-treated papers experience much more rapid chain scission chemistry than an unoxidized sheet throughout the course of the oven test (Fig. 3). Further, the rate of degradation in the oven is greater for the paper that has been oxidized to a greater degree. The functional group changes during the aging of the oxidized papers are consistent with hydrolytic scission of the cellulose: carbonyls are produced in about the same amounts as new end groups (shown in Fig. 2), with a relatively minor increase in carboxyl concentrations. Since this suggests that the degradation chemistry during the oven

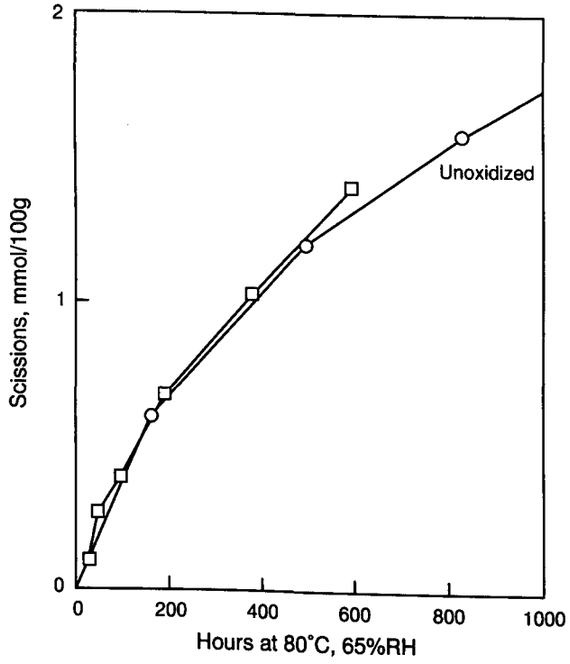

Fig. 1. Rate of scission production in Whatman No. 42 filter paper that has been chemically oxidized by sodium periodate and then thermally aged at 80°C and 65% RH

aging of oxidized and unoxidized cellulose is predominantly hydrolysis, it is reasonable to interpret the different late stage degradation of the papers (after any weak link scission behavior) as being hydrolysis occurring at different rates.

The graphical comparison of the scission kinetics is shown in Fig. 4, in which the oven aging times for the oxidized papers have been scaled to become parallel to the late-stage scission of the unoxidized sheet. The scale factors necessary to achieve this correspondence indicate that the lightly oxidized sheet is degrading about two times faster, and the more heavily oxidized paper about three times faster, than the unoxidized sheet. In addition to the effect of oxidation to accelerate the late stage hydrolysis, the scission kinetics of the oxidized sheets in Fig. 3 also show an early period of rapid chain breaking, which is not observed for the unoxidized sheets. The amount of these weak links can be estimated in Fig. 4 by the vertical offset between the oxidized and unoxidized scission curves: these offsets are about 0.7 mmol/100 g for the lightly oxidized sheet and about 1.1 mmol/100 g for the more heavily oxidized. These amounts are roughly equivalent to

Table 2. Oven aging following hydrogen peroxide exposure

Hours	DP	Scissions, mmol/100 g	Carbonyls, mmol/100 g	ΔCarbonyls, mmol/100 g	Carboxyls, mmol/100 g	ΔCarboxyls, mmol/100 g	pH
A. Unoxidized (same as Table 1A)							
0	1421	–	0.40	–	0.55	–	
163	837	0.61	0.99	0.59	0.49	−0.06	
499	595	1.21	1.58	1.18	0.51	−0.04	
836	503	1.59	2.03	1.63	0.55	0.00	
1172	446	1.90	2.63	2.23	0.58	0.03	
1508	382	2.36	3.28	2.88	0.70	0.15	
1844	344	2.72	3.90	3.50	0.86	0.31	
B. Hydrogen peroxide, 4 hours							
Unexposed	1402	–	0.37	–	0.45	–	
0	969	0.39	1.35	0.98	0.70	0.25	5.3
19	790	0.68	1.66	1.29	0.77	0.32	
74	578	1.26	2.42	2.05	0.77	0.32	
140	496	1.61	3.14	2.77	0.84	0.39	
332	395	2.25	4.01	3.64	0.93	0.48	
476	360	2.55	4.07	3.70	0.95	0.50	4.8
C. Hydrogen peroxide, 4 hours							
Unexposed	1379	–	0.54	–	0.48	–	
0	810	0.63	2.46	1.92	0.92	0.44	5.0
23	595	1.18	2.88	2.34	1.01	0.53	
75	436	1.94	3.77	3.23	1.01	0.53	
149	369	2.45	4.43	3.89	0.96	0.48	
315	307	3.13	4.89	4.35	0.98	0.50	
504	272	3.64	5.24	4.70	1.08	0.60	4.85

the calculated excess carbonyl contents (that is, the carbonyls in excess of the new chain ends) produced during the peroxide oxidations, which were about 0.6 mmol/100 g and 1.3 mmol/100 g for the lightly and heavily oxidized sheets, respectively. By an analogous scaling of the oven aging times (not shown in Fig. 4), the scission during this early period is occurring roughly 6–8 times faster for the lightly oxidized sheet, and about 12 times faster for the heavily oxidized sheet, than for the unoxidized sheet at the same DP.

Acidic hypochlorite-oxidized cellulose

The results of the oven aging of hypochlorite-oxidized papers are shown in Table 3 and Fig. 5 and 6. As observed in our earlier study, the acidic (pH=5) hypo-

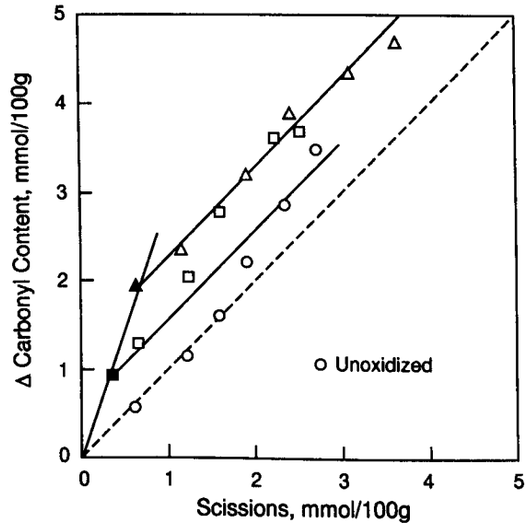

Fig. 2. Carbonyl *vs* scission production in Whatman No. 42 filter paper that has been chemically oxidized by hydrogen peroxide, then thermally aged at 80°C and 65% RH. Filled symbols represent oxidized samples before oven aging. The dashed line represents one carbonyl produced per scission.

chlorite oxidation produces predominantly carbonyls on the cellulose chains, and in this case about five times as many carbonyls as scissions and carboxyls were produced during the treatment. As for the peroxide-treated sheets, the cellulose chains in the hypochlorite-oxidized papers contain many more carbonyls and a few more carboxyl groups than unoxidized cellulose having the same DP.

The results for the oven aging of the hypochlorite-oxidized papers shown in Fig. 6 demonstrate the same behavior seen for the peroxide-oxidized papers: faster degradation for the oxidized sheets than for an unoxidized sheet, and the degradation is faster for the more heavily oxidized paper. The functional group development in the later stages of the aging is consistent with hydrolytic changes for the lightly oxidized sheet, but the carbonyl production and significant increase in carboxyl concentration for the more heavily oxidized sheet are less well described as being due to strictly hydrolytic reaction.

The comparison of the unoxidized and oxidized degradation rates with scaled aging times is shown in Fig. 7, and the late-stage degradation occurs 2 and 3 times faster for the lightly and heavily oxidized sheets, respectively. The weak link degradation occurring early in the oven aging is estimated by the offset between these degradation kinetic curves, approximately 0.4 mmol/100 g and 1.0 mmol/100 g for the lightly and heavily oxidized sheets, respectively. This is slightly less

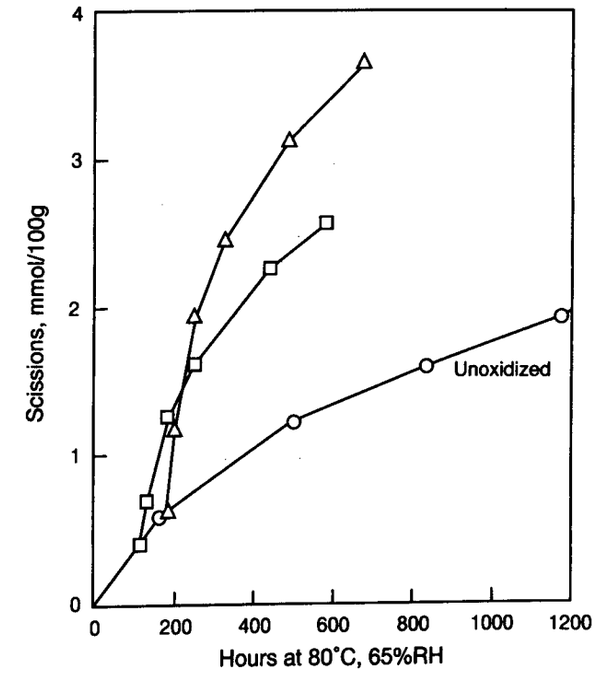

Fig. 3. Rate of scission production in Whatman No. 42 filter paper that has been chemically oxidized by hydrogen peroxide and then thermally aged at 80°C and 65% RH.

than the number of excess carbonyls produced during the oxidizing treatments, which measured about 0.8 mmol/100 g and 4.0 mmol/100 g for these two papers. Scission rates during the weak link period are estimated to occur about 6 times faster for the lightly oxidized paper than for the unoxidized.

Light-exposed cellulose

The results of the oven aging of photo-oxidized papers are shown in Table 4 and Fig. 8 and 9. The lightly oxidized sheet was exposed to the filtered daylight fluorescent source, and the heavily oxidized sheet to the UVA fluorescent source. As observed in our earlier work, exposure to near-UV or short-wavelength visible light tends to produce the same result as peroxide exposure: about 2–3 times more carbonyls than scissions produced during the oxidation. These exposures also caused a slight decrease in the measured carboxyl concentrations during the oxidation.

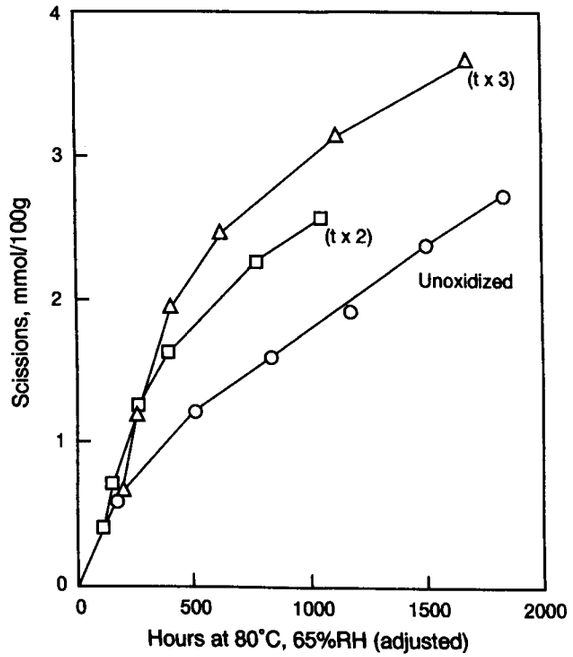

Fig. 4. Same as Fig. 3, except the oven aging times for the oxidized sheets have been multiplied by the scaling factor shown

As seen for the other oxidized papers, the scission kinetics in Fig. 9 show the light-exposed sheets degrade more rapidly than unoxidized paper in subsequent oven aging, and the more heavily oxidized sheet (exposed to UVA) degrades more rapidly than the lightly oxidized paper (exposed to visible light). The functional group development during the oven aging bears resemblance to the result for hypochlorite-oxidized sheets: the lightly photo-oxidized paper produces apparently hydrolysis products, one carbonyl per chain scission and few carboxyls, whereas the heavily oxidized sheet produces irregular carbonyl growth and carboxyls during the oven aging.

The scaled aging time comparison of oxidized and unoxidized sheets is shown in Fig. 10. Late-stage degradation seems to occur about 1.7 and 2.5 times faster for the lightly and heavily oxidized papers, respectively. The weak link scissions occurring in the early stage of oven aging are 0.2 mmol/100 g and 0.5 mmol/100 g for these two oxidized sheets. This is again slightly less than the corresponding contents of excess carbonyls following the photo-oxidation, measured to be

Table 3. Oven aging following sodium hypochlorite exposure

Hours	DP	Scissions, mmol/100 g	Carbonyls, mmol/100 g	ΔCarbonyls, mmol/100 g	Carboxyls, mmol/100 g	ΔCarboxyls, mmol/100 g	pH
A. Unoxidized (same as Table 1A)							
0	1421	–	0.40	–	0.55	–	
163	837	0.61	0.99	0.59	0.49	−0.06	
499	595	1.21	1.58	1.18	0.51	−0.04	
836	503	1.59	2.03	1.63	0.55	0.00	
1172	446	1.90	2.63	2.23	0.58	0.03	
1508	382	2.36	3.28	2.88	0.70	0.15	
1844	344	2.72	3.90	3.50	0.86	0.31	
B. Sodium hypochlorite, pH=5							
Unexposed	1459	–	0.41	–	0.47	–	5.3
0	1214	0.17	1.36	0.95	0.47	0.00	4.8
50	652	1.05	2.11	1.70	0.50	0.03	
146	556	1.37	2.47	2.06	0.56	0.09	
308	466	1.81	2.89	2.48	0.58	0.11	
500	391	2.31	3.61	3.20	0.76	0.29	4.8
C. Sodium hypochlorite, pH=5							
Unexposed	1433	–	0.38	–	0.50	–	
0	700	0.90	5.26	4.88	1.34	0.84	5.0
19	521	1.51	5.02	4.64	1.63	1.13	
74	428	2.02	6.09	5.71	1.48	0.98	
140	374	2.44	6.71	6.33	1.78	1.28	
332	307	3.16	7.70	7.32	2.03	1.53	
476	282	3.52	7.61	7.23	2.66	2.16	4.45

approximately 0.3 mmol/100 g and 1.0 mmol/100 g. Scission rates during the early stage are estimated to be about five times faster for the filtered daylight-oxidized paper than for the unoxidized sheet.

Discussion

The results of this study indicate that the concentrations of excess carbonyls created during oxidative treatments seem to correlate reasonably well with the magnitudes of weak link scissions observed during subsequent oven aging. With two exceptions (see previously), the late-stage degradation appears to be predominantly hydrolytic, and our graphical analysis that compares the late-stage aging of oxidized and unoxidized sheets (and allows measures of the weak link scissions) seems justified. This correlation of excess carbonyls and weak link scissions suggests that most of the ex-

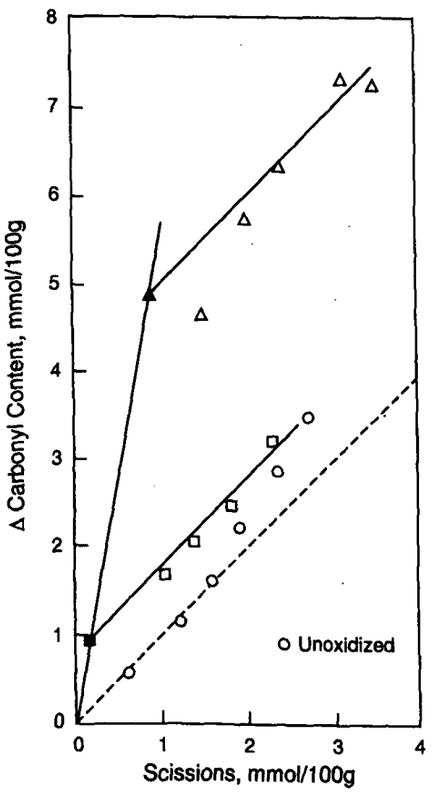

Fig. 5. Carbonyl *vs* scission production in Whatman No. 42 filter paper that has been chemically oxidized by sodium hypochlorite and then thermally aged at 80°C and 65% RH. The filled symbols represent oxidized samples before oven aging. The dashed line represents one carbonyl produced per scission.

cess carbonyls are located along the chains rather than at chain ends, and that most of these excess carbonyls also function to accelerate the chain scissions at adjacent links. This result is consistent with frequent observation of greater alkali solubility following oxidation, which also suggests significant numbers of oxidized sites along cellulose chains.[12] The two exceptions to this correlation were observed in the aging of sheets heavily oxidized with hypochlorite and with UV light exposure. Although it is easy to imagine many possible explanations for this, it is noteworthy that these samples also showed functional group development throughout the oven aging that suggested nonhydrolytic chemical reactions occurring. Although it is possible that other chemical reactions may be operating to affect carbonyl concentrations in an

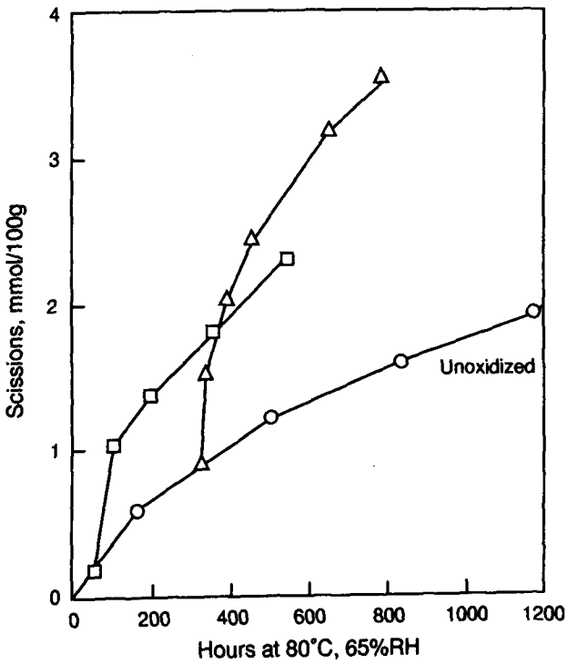

Fig. 6. Rate of scission production in Whatman No. 42 filter paper that has been chemically oxidized by sodium hypochlorite and then thermally aged at 80°C and 65% RH

unusual way, it is also possible that weak link scissions may still be occurring throughout the aging of the heavily oxidized sheet. If that is the case, our graphical analysis, which assumes that the weak link scissions are rapidly completed and that the late-stage degradation can be compared, may be inappropriate. Consequently, we may be grossly underestimating the magnitude of the weak link scissions for these heavily oxidized papers.

During the weak link scission period of the peroxide-oxidized papers, scissions occurred several times faster than late-stage hydrolytic scissions at oven temperatures. If the weak link scissions are also accelerated by the same factors as the late stage scission for the oxidized papers, then the scission rates during the initial rapid stage are faster by factors of about 3–4. This compares well with the weak link hydrolytic scission rates observed by Marchessault & Rånby,[13] which were estimated to occur about twice as fast as normal hydrolytic scissions. It should be noted that this is not equivalent to weak links breaking at twice the rate of normal links, for the weak links are present at concentrations roughly 500–1000 times

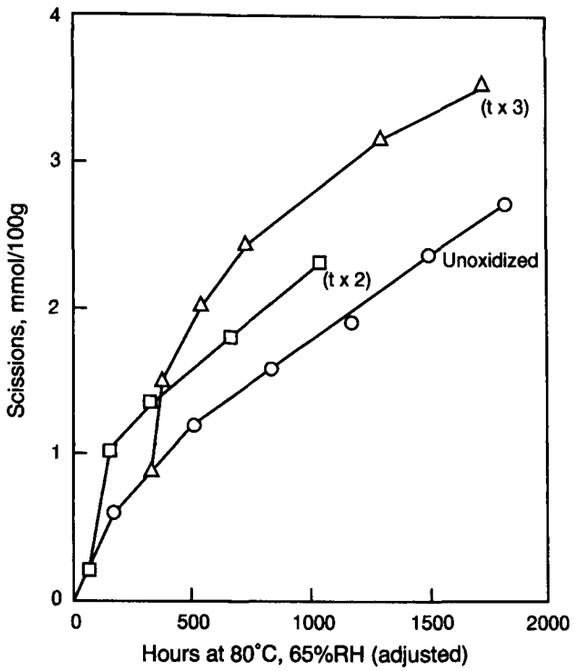

Fig. 7. Same as Fig. 6, except the oven aging times for the oxidized sheets have been multiplied by the scaling factor shown.

less than that of unbroken normal links, and for a first-order reaction the rate will be proportional to the reactant concentration. Thus, if the weak links are breaking at rates comparable to the scission rate of normal bonds, their intrinsic reactivity (that is, the first-order rate constant) must be orders of magnitude greater than that of the normal bonds. This significant increase in rate constant may not be irreconcilable with the observation of overall scission rates being only a factor of 2–4 faster during the weak link period.

Even after the rapid degradation during the initial weak link scission period, the aging of the oxidized papers continues to be slightly faster than of the comparable unoxidized sheets. This could be due to: 1) faster hydrolysis from acids produced during oxidation or during oven aging of carbonyls formed during oxidation; 2) further hydrolytic scissioning of links that are weaker than the unoxidized link but not as weak as early-stage weak links; 3) a small contribution from another scission route, such as oxidative scission of modified links; 4) a slight alteration in accessibility or fiber morphology with oxidation; or 5) a combination

Table 4. Oven aging following light exposure

Hours	DP	Scissions, mmol/100 g	Carbonyls, mmol/100 g	ΔCarbonyls, mmol/100 g	Carboxyls, mmol/100 g	ΔCarboxyls, mmol/100 g	pH
A. Unoxidized							
0	1444	–	0.40	–			
18	1216	0.16	0.53	0.13			
42	1172	0.20	0.68	0.28			
70	1059	0.31	0.70	0.30			
115	1026	0.35	0.74	0.34			
163	981	0.40	0.75	0.35			
337	822	0.65	0.95	0.55			
498	765	0.76	1.13	0.73			
673	697	0.92	1.37	0.97			
B. Filtered daylight fluorescent light, 1177 hours							
Unexposed	1398	–	0.46	–	0.52	–	
0	1232	0.12	0.89	0.43	0.41	−0.11	
26	971	0.39	1.06	0.60	0.36	−0.16	
50	893	0.50	1.10	0.64	0.45	−0.07	
74	839	0.59	1.19	0.73	0.44	−0.08	
190	736	0.80	1.50	1.04	0.43	−0.09	
335	646	1.03	1.83	1.37	0.52	0.00	
C. Ultraviolet A light, 213 hours							
Unexposed	1490	–	0.42	–	0.66	–	
0	866	0.60	2.06	1.64	0.59	−0.07	
23	712	0.91	2.35	1.93	0.69	0.03	
49	640	1.10	2.68	2.26	0.73	0.07	
99	580	1.30	2.89	2.47	0.91	0.25	
191	523	1.53	2.80	2.38	1.08	0.42	
338	466	1.82	3.10	2.68	1.09	0.43	

of the above. The most plausible explanation may be rapid hydrolysis induced by acids produced in oxidation or later during oven aging: the functional group development generally indicates hydrolytic reaction, and there is evidence that the oxidized sheets have a slightly greater acid content than the unoxidized paper.

It should be noted, however, that for heavily oxidized sheets there was evidence of nonhydrolytic chemistry occurring, specifically in the production of acidity. This carboxyl development has rarely been observed except in the very late stages of degradation of unoxidized filter paper, and it may occur only when the concentration of carbonyl groups becomes quite high. In any case, the oxidative treatment causes a filter paper of a particular DP (or strength) to thermally age in a distinctly different way than without prior oxidation. Such observations may yield

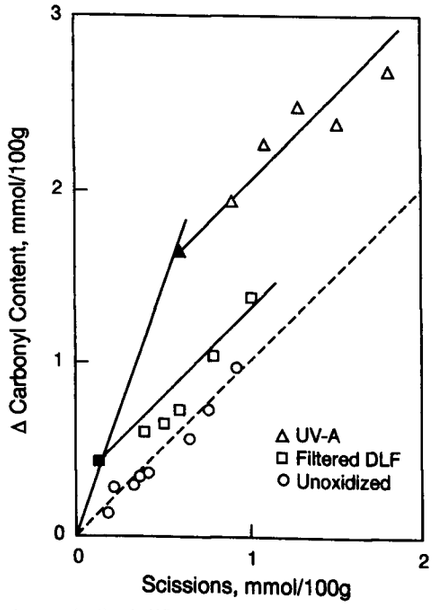

Fig. 8. Carbonyl *vs* scission production in Whatman No. 42 filter paper that has been photochemically oxidized and then thermally aged at 75°C and 65% RH. Filled symbols represent oxidized samples before oven aging. The dashed line represents one carbonyl produced per scission.

insights into the possible relationship between aging studies of filter papers and the aging of art and book papers.

Finally, it is appropriate to address the fundamental issue of whether any of this weak link degradation observed in oven aging will occur rapidly, or dominate the aging behavior, at room temperature. An answer to this question requires at least knowledge of the temperature dependence of the weak link scission reaction. Because of the continued controversy about the nature of the observed weak link scission chemistry, there is to date no reliable measure of the temperature dependence of the rapid initial chain breaking, particularly in heterogeneous (that is, solid state rather than solution-phase) reactions. As a result, at this time any assertion that such rapid weak link scissions observed in oven tests will also occur in room temperature aging remains mere speculation.

Conclusion

The research reported here was not designed to examine the after-effects of conservation bleach treatments, which would be formulated differently and would

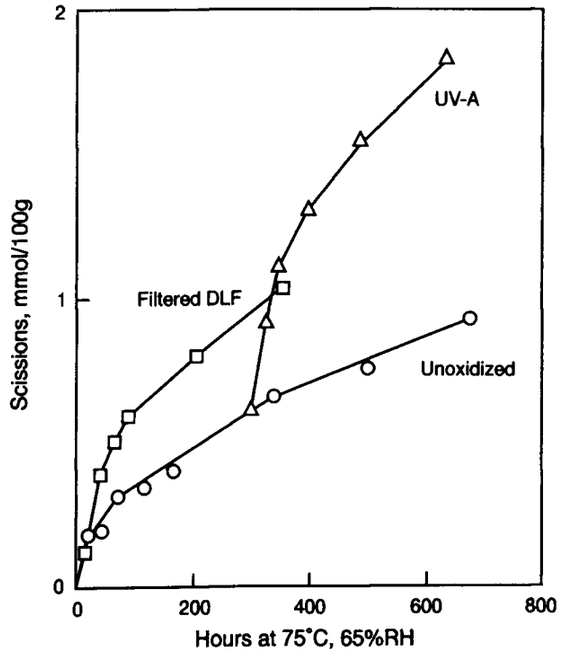

Fig. 9. Rate of scission production in Whatman No. 42 filter paper that has been photochemically oxidized and then thermally aged at 75°C and 65% RH.

not be so severe. Rather, these studies are intended to explore the nature and consequences of other cellulose oxidation reactions, for example, atmospheric and photochemical oxidation. These processes not only have a significant tendency to degrade cellulose during oxidation but the result of the oxidation reaction seems to be a cellulose whose long-term stability may be compromised further in two ways. Modification of the cellulose chain creates weak links that seem more easily broken than links in the unmodified cellulose, and the amount of these weak links seems to be at least approximated by the excess carbonyls produced during the oxidation. Also, the oxidation can create acidity, which exacerbates the normal hydrolytic breakdown of the cellulose.

An important implication of this study is the possibility that the degradation of a paper is determined not only by its acid content or cellulose DP but also by its content of such modified weak links, which essentially create a cellulose that may, at least for a time, tend to degrade more rapidly. Thus, just as fiber morphology and accessibility are known to affect the rate of hydrolytic degradation of cellulose,

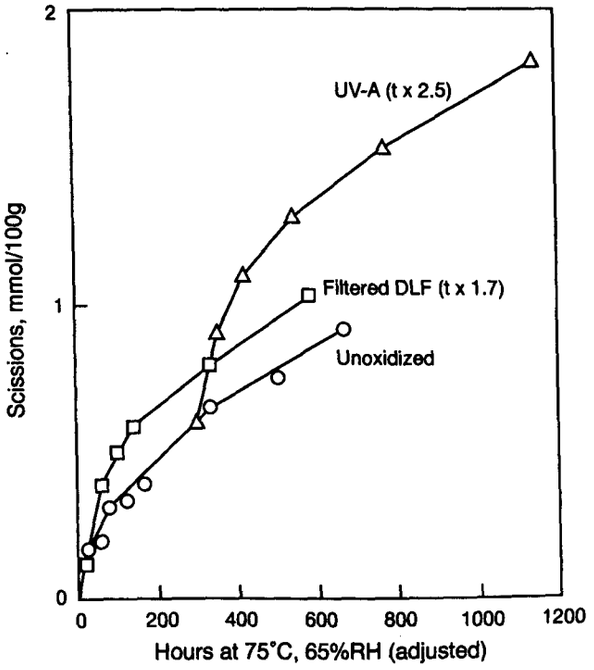

Fig. 10. Same as Fig. 9, except the oven aging times for the oxidized sheets have been multiplied by the scaling factor shown.

the presence of these modified groups can also alter the observed degradation rate of cellulose. As a result, there should be no presumption that two papers having equal cellulose DP and equal acidity will degrade at the same rate, and it is possible that the degree of oxidation of the cellulose may be an important determinant of the overall degradation rate.

ACKNOWLEDGEMENTS

This work was performed at the Research Center on the Materials of the Artist and Conservator at Carnegie Mellon University. The financial support of the Andrew W. Mellon Foundation is gratefully acknowledged.

SUMMARIES

The Effect of Oxidation on the Subsequent Oven Aging of Filter Paper

It has been observed that oxidation of cellulose can affect the rate at which thermal chain scissions subsequently occur, an effect thought to result from the weakening of the chain at the site of the oxidized groups formed along the chains during the oxidation. This study examines the possibility that the number of such functional groups in excess of the chain ends formed during the oxidation provides an estimate of the weak links created along the chain that will break rapidly during subsequent thermal aging. In these experiments, filter paper that had been chemically or photochemically oxidized was aged in a humid oven. Scission kinetics during the degradation of the oxidized papers were measured and compared with that of unoxidized papers. For all papers except the most heavily oxidized, the magnitude of the early weak link scissions in the oven is comparable to the measured excess carbonyls produced during the oxidizing treatments. The oven aging of the oxidized sheets also demonstrated faster hydrolytic degradation even after the weak link period, which may be the result of increased acidity following oxidation of the cellulose.

Effet de l'oxydation sur le vieillissement accéléré ultérieur de papier filtre

On a observé que l'oxydation de la cellulose peut modifier la vitesse à laquelle les scissions thermiques de chaînes se produisent ensuite, un effet attribué à l'affaiblissement de la chaîne à l'endroit des groupes oxydés formés le long des chaînes pendant l'oxydation. Cette étude examine la possibilité que le nombre de ces groupes fonctionnels qui dépassent des extrémités de la chaîne formées pendant l'oxydation fournit une estimation des liaisons faibles formées de long de la chaîne et qui casseront rapidement au cours du vieillissement thermique postérieur. Dans ces expérimentations, du papier filtre préalablement oxydé chimiquement ou photochimiquement a été vieilli dans une étuve humide. Les cinétiques de la scission au cours de la dégradation des papiers oxydés ont été mesurées et comparées avec celles de papiers non oxydés. Pour tous les papiers, à l'exception de celui le plus fortement oxydé, la magnitude des scissions des premières liaisons faibles en étuve est comparable à celles des groupes carbonyles excédentaires produits pendant les traitements d'oxydation. Le vieillissement accéléré des feuilles oxydées a également montré une dégradation hydrolytique plus rapide, même après le stade des liaisons faibles, qui peut être la conséquence d'une augmentation de l'acidité après l'oxydation de la cellulose.

Der Einfluß einer Oxidation auf die nachfolgende Ofenalterung von Filtrierpapier

Es wurde beobachtet, daß eine vorher durchgeführte Oxidation von Cellulose das Ausmaß des danach stattfindenden thermischen Abbaus beeinflußt. Als Ursache wird die Schwächung der Übergangsstellen im Kettenmolekül als Folge der Bildung von oxidierten Gruppen in den Ketteneinheiten angenommen. Es wird die Möglichkeit untersucht, daß die Anzahl dieser oxidativ gebildeten Gruppen in Relation zu den oxidativ gebildeten Kettenenden eine Abschätzung der Schwachstellen erlaubt, die bei nachfolgender Wärmealterung sehr schnell brechen werden. Filterpapier, das chemisch bzw. photochemisch voroxidiert war, wurde bei feuchter Wärme gealtert. Die Kinetik des Kettenbruches bei der Alterung wurde mit der von nicht voroxidiertem Papier verglichen. Für alle Papiere, mit Ausnahme der am stärksten voroxidierten, besteht ein Zusammenhang zwischen rasch eintretendem Kettenbruch an »Schwachstellen« im Sinne des Versuchs und den oxidativ im Überschuß gebildeten Carbonylgruppen. Die voroxidierten Blättern zeigen bei der Ofenalterung auch ein stärkeres Ausmaß an Hydrolyse, was als Folge der durch die Voroxidation gebildeten Acidität gedeutet wird.

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Restaurator, 1995, 16, 31–44
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RESTAURATOR
ISSN 0034-5806

An Investigation of the Hygroscopicity of Parchment Subjected to Different Treatments

by J. DERNOVŠKOVÁ, H. JIRASOVÁ, J. ZELINGER

Introduction

When assessing the causes of damages to parchment and taking decisions about the protection and conservation of literary works on parchment, one should always bear in mind one of its basic properties: hygroscopicity, which is the ability to absorb and release water, and the humidity content related to the hygroscopicity. Similarly to water contained in leather, water in parchment is present in three forms: free, associated and bound. Bound water acts as protection against denaturation, whereas associated and free water are reserve sources.[1] Proteins in their natural conformation have good steric conditions for noncovalent interactions, which, though not possessing high energy, can nevertheless affect the structural stability on the level of the secondary, tertiary and quaternary structure. Water molecules that participate in the noncovalent bonds form a hydration shell in the region of amino acid side chains and, being attached to the protein molecule by hydrogen bonds, contribute to structural stability.[2]

If fibrous proteins lose too many hydrogen bonds, they denature, are not capable of being rehydrated and shrink. The changes in hygroscopicity correspond with those in the supermolecular structure of collagen and the interfibrillar mass. The water-retaining ability strongly affects the durability of the material. The water content in parchment influences its weight, dimensions, elasticity, microbial resistance and the like.

For written and mainly illuminated parchments, frequent changes in the relative air humidity (RH) and alternate dimensional changes in parchment may damage the colour layer, i.e., its pulverization, cracking and peeling. The RH changes give rise to shear stress at the phase boundary due to the different sorption of moisture by the substrate and by the paste used in the illumination.[3]

This study focuses on the difference in hygroscopicity of a new and a historical parchment and the effects of conservation treatment, such as soaking in methanol used to remove the residues of inadequate disinfection in the Czech Crown Archives,[4] soaking in ethanol and softening with synthetic spermaceti. The effects of natural and synthetic polymers used as pastes, parchment-consolidating agents, glues and colour layer fixatives were also examined. The natural polymers were represented by the egg white, gelatine and gum arabic present in the parchment materials of central Europe. The synthetic polymers selected for this study were those possessing stable properties and mostly already in use in conservation treatment.[3,5] To compare the results of sorption and desorption of materials, both a new parchment and untreated and treated historical parchments were subjected to scanning electron microscopic (SEM) analysis.

Experimental

Sample preparation

Type of parchment

- Modern parchment: goat, not prepared for a writing use, that is, only slightly ground on the hairy side. Producer: ERGON (Jaroměř, Czech Republic).
- Historical parchment: goat, prepared for writing, that is, ground on both sides, before mid-sixteenth century. Origin: central Europe, before about 1550.

Chemicals

Fixing agents:

- Paraloid B72: ethylmethacrylate/methylacrylate copolymer manufactured by Rohm and Haas, Philadelphia, USA. 2% by weight in acetone.
- Tylose MH300: methylhydroxyethylcellulose, manufactured by Hoechst, Germany, 2% weight in water. Viscosity of the remaining solution: 300 mPa · s.
- Klucel G: hydroxypropylcellulose produced by Hercules, USA, 2% weight in ethanol. Viscosity of the resulting solution: 150–400 mPa · s.
- Sokrat 6402: anion active dispersion of a pure acrylic powder, manufactured by Chemické závody a.s., Czech Republic. The commercial product contains 49–51% dry matter. It was diluted with ethanol to 2%, viscosity about 40 mPa · s.
- gelatine, food quality, in water. Viscosity about 2–3 mPa · s.
- egg white in water. Viscosity about 1.5–2.5 mPa · s.
- gum arabic in water. Viscosity about 1–2 mPa · s.

Solvents:

- Pure ethanol.
- Pure methanol.

Softening agent:

- synthetic spermaceti: mixture of ester of lauric acid and higher alcohols: cetyl- and myristyl-. Manufactured by Setuza Lovosice, Czech Republic. 2% weight in 1:9 toluene:ethanol.

Preparation procedure

Samples of new parchment (squares 4×4 cm) were conditioned at 56% RH, t= 25°C, for seven days and weighed. All fixing agents and the softening mixture were applied to the samples twice by coating. Other parchment samples were immersed in a solution of synthetic fixatives (one minute), and some samples were immersed in alcohol (60 min). After the deposit had dried, the samples were conditioned under the same conditions.

The samples of historical parchment were irregular in shape and were half the size of the new parchment samples; the preparation procedure was the same.

Measuring the humidity sorption and desorption

The method is used to follow the time dependence of the sorption and desorption of humidity by parchment with varying RH, in our case from 20% to 98% RH. If sorption and desorption proceed up to equilibrium, a complete sorption and desorption isotherm is obtained.[2]

Samples of parchment treated with a solution of the respective compound were conditioned at 20% RH for seven days, after which their mass and the dimension of two sides were measured. The samples were then placed in a 98% RH medium in which the sorption of humidity took place. The mass increase of the samples was measured during the sorption process. The sorption measurement ended when the mass remained constant. The samples dimensions were measured again, and the samples were again placed in a 20% RH medium, where humidity was desorbed. The decrease in the sample mass was recorded during the desorption process. The sorption and desorption of the sample proceeded at 25°C.

SEM analysis of selected samples

Samples of untreated parchment and of historical parchment treated with synthetic and natural fixing agents were examined. The samples were sprayed with

Table 1. Humidity sorption of modern and historical parchment as result of raising the relative humidity of the surrounding air from 20% to 98%

Agent	Methods	Humidity sorption of modern parchment %	%	historical parchment %	%
1 No treatment		28,1	difference	45.5	difference
2 Gum arabic	two coatings	27.0	−1.1	46.2	0.7
3 Egg white	two coatings	27.9	−0.2	49.2	3.7
4 Gelatine	two coatings	27.4	−0.7	47.2	1.7
5 Tylose MH 300	two coatings	28.9	0.8	49.6	4.1
6 Paraloid B72	two coatings	28.0	−0.1	50.5	5.0
7 Klucel G	two coatings	28.6	0.5	54.3	8.8
8 Sokrat 6402	two coatings	28.3	0.2	42.5	−3.0
9 Softening mixture	soaking	24.6	−3.5	50.5	5.0
10 Methanol	soaking	29.9	1.8	57.6	12.1
11 Ethanol	soaking	31.6	3.5	61.4	15.9
12 Tylose MH 300	soaking	29.7	1.6	50.7	5.2
13 Paraloid B72	soaking	29.8	1.7	44.7	−0.8
14 Klucel G	soaking	28.2	0.1	44.7	−0.8
15 Sokrat 6402	soaking	30.4	2.3	54.1	8.6

a conductive gold layer about 50 nm thick and analyzed using an SEM Tesla BS 343 Pearl apparatus in the State Restoration Workshops in Prague.

Results and Discussion

The results of measurements are summarized in Table 1 and Fig.1 for the modern parchment and the historical parchment respectively. Fig. 2 compares the shape of the humidity hysteresis curve and the humidity sorption and desorption rate for the untreated modern and the historical parchment.

The results of the measurements reveal large differences in the humidity sorption and desorption for the historical and the modern parchment. The historical parchment shows a distinctly higher and quicker sorption, and its humidity hysteresis curve is steeper. The different sorption properties of the two types of parchment are probably due to the different structure and properties of the historical and the modern parchment.

The sorption capacity of the parchment is probably affected by many factors, which may include the molar mass of the parchment, its origin and age, the content of filling agent and fat components, compactness and degradation of

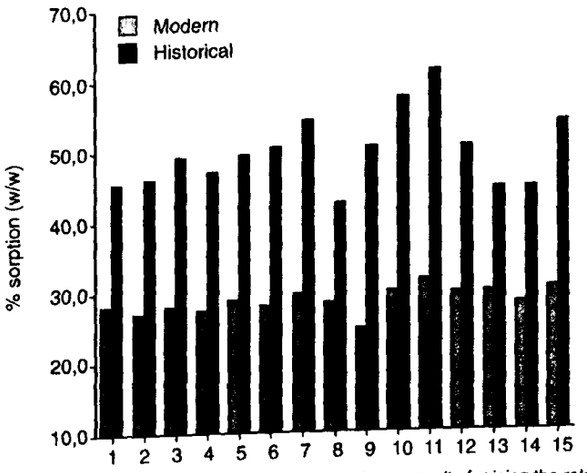

Fig. 1. Humidity sorption of modern and historical parchment as a result of raising the relative humidity of the surrounding air from 20% to 98%.

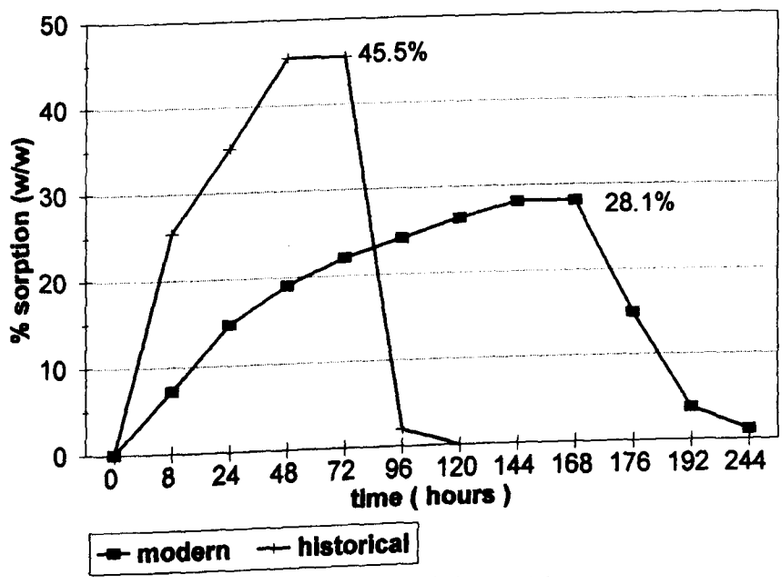

Fig. 2. Humidity hysteresis curve of modern and historical parchment.

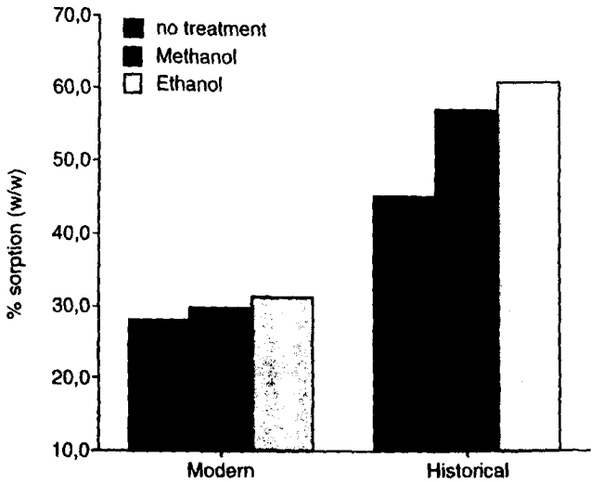

Fig. 3. Humidity sorption of modern and historical parchment soaked in alcohols.

structure, porosity and water permeability of the parchment and its surface treatment.

In the investigation of the humidity sorption and desorption, the samples of untreated historical and modern parchment are regarded as standards. The results obained for parchment samples treated with a certain compound are adequately evaluated by comparing them with these standards. A fixing agent that brings about the smallest change in the humidity sorption and desorption compared with untreated material can be regarded as providing positive results. From the conservation standpoint, it is important that the differences in hygroscopicity between the locally fixed area and the surrounding parchment area be minimal.

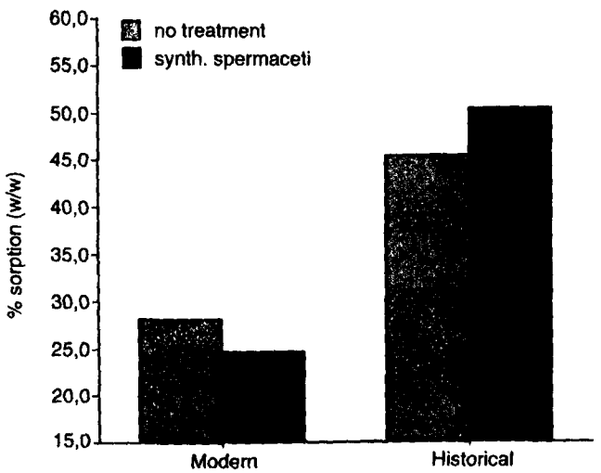

Fig. 4. Humidity sorption of modern and historical parchment coated twice with synthetic spermaceti.

The relative equilibrium humidity sorption value of untreated modern parchment is 28.1% (Table 1). Samples of new parchment reach the maximum sorption within 144 hours, whereas desorption takes 76 hours.

The sorption value of untreated historical parchment is 45.5% (Table 1). Samples of historical parchment reach the maximum sorption within 48 hours, the only exception being samples soaked in pure alcohol, where sorption takes 72 hours. All samples are desorbed within 48 hours.

In both types of parchments under study, the humidity sorption increases distinctly after the parchment has been soaked in pure ethanol and methanol (Fig. 3). Both alcohols and probably other polar organic solvents, if they contact the parchment, may open and loosen its structure, leading to a loss of free and bound water and, subsequently, to a higher humidity sorption. The effect of methanol is weaker.

The effect of the softening spermaceti mixture on the two types of parchment is not similar (Fig. 4), which is probably derived from the different structure and different properties of the historical and the modern parchment. The sorption value of the modern parchment decreases after treatment, obviously due to the

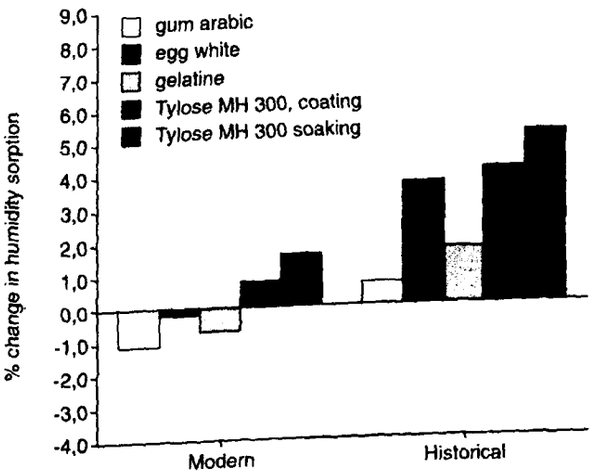

Fig. 5. Difference in humidity sorption of modern and historical parchment as a result of treatments with different water-soluble fixing agents (no treatment=0%).

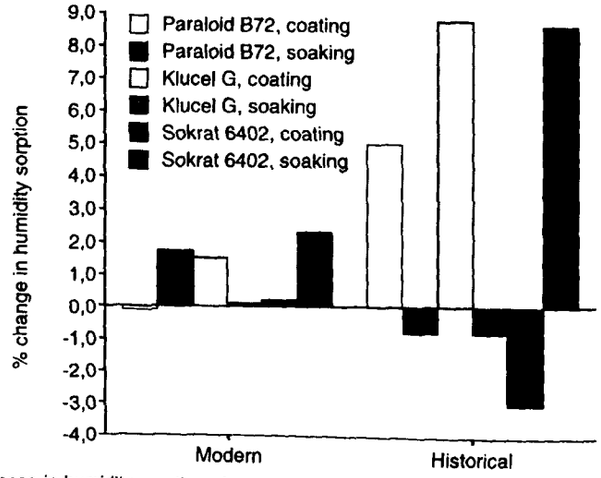

Fig. 6. Difference in humidity sorption of modern and historical parchment as a result of treatments with different solvent-soluble fixing agents (no treatment=0%).

surface being closed by the softening agent. Contrary to this, the sorption value of the historical parchment increases after softening, because in this case the effect of the organic solvent used predominates over the assumed hygrophobic effect of fat.

Interesting results are obtained by investigating the effect of fixing agents on the sorption in parchment. Generally, it can be said that the humidity sorption in the modern parchment undergoes a smaller change after treatment with fixing agents than that in the historical parchment. A change in sorption after the treatment with fixative that is not too pronounced compared with the standard untreated parchment (below 1%) is regarded as satisfactory.

Fig. 5 shows that natural fixatives applied as a coating of aqueous solution reduce the sorption in the new parchment nonsignificantly compared with the standard. The effect of synthetic fixatives on the sorption in the new parchment varies, however (Fig. 6). In three cases the change in sorption is below 1% with respect to the standard. In the case of Paraloid B72 and Sokrat 6402, a distinctly more pronounced increase in sorption can be observed after soaking the new parchment in a solution of the fixing agent. If there were not a contrary effect in the case of Klucel G, this might be understood as the result of the solvent.

Natural fixing agents raise the sorption in the historical parchment (Fig. 5). The rise in sorption is affected by the aqueous solvent, which may loosen structure of the material. The four synthetic or semisynthetic fixatives applied in a solvent cause a pronounced increase in the sorption of this material. In two cases (Paraloid B72 and Klucel G) this is only true after coating, whereas soaking results in a slight decrease. In the case of Sokrat 6402 the contrary is observed, and the decrease after two coatings is more pronounced.

At the maximum sorption in the new parchment, the increase in the side dimensions of the untreated parchment is 2.1%. With most of the treated samples the increase in dimensions is greater than in the standard. No dimensional changes have been measured for irregular samples of the historical parchment.

A comparison of SEM micrographs for untreated new and the historical parchment reveals a difference in their surface structure. Fig. 7 shows that defibered collagen fibrils are present on the surface of historical parchment and that the filler content is still quite high. Fig. 8 reveals a spore of mould found in the fibre. Fig. 9 and 10 show that the surface of the modern parchment is more compact. Each fixing agent used has altered the surface structure of the parchment. A suitable fixative could be a compound that envelops only collagen fibres of the parchment and reinforces them but on the whole does not strongly adhere to the surface of the parchment and brings about minimal changes in its surface structure. According to Fig. 11 and 12, of all the fixing agents applied, the smallest changes in the surface structure of the material were caused by the egg white and

Fig. 7. Micrograph of historical parchment. The wound unit in the left part of the picture is an indication for chalk of algae origin.

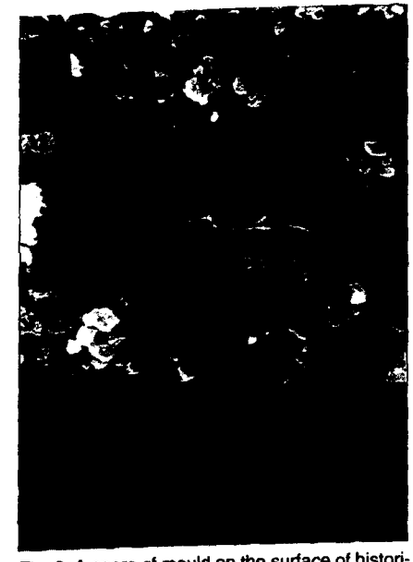

Fig. 8. A spore of mould on the surface of historical parchment.

Fig. 9, 10. Surface micrograph of modern parchment. In the upper part of Fig. 10 again an indication for chalk of organic origin can be seen.

Fig. 11. Historic parchment treated with egg white.

Fig. 12. Historic parchment treated with gum arabic.

gum arabic, which merely enveloped the collagen fibres. On the other hand, gelatine (Fig. 13) altered the surface structure of the parchment markedly compared with the fixing agents just mentioned. Fig. 14 and 15 show that cellulose ethers have no pronounced effect on the surface structure. These polymers, which are soluble in cold water, obviously can better penetrate into the collagen structure than, for example, acrylates. Of all the fixatives used, the greatest surface changes in the parchment are caused by acrylates: Paraloid B72 and Sokrat 6402 (Fig. 16, 17). It seems that they strongly adhere to the surface and envelop it. The different effects of the fixatives on the surface structure of parchment probably also depends on the molar mass of each fixative and on its particle size.

Conclusions

The humidity hysteresis curves for parchment show that the historical parchment possesses a markedly higher humidity sorption than the modern parchment: in our case sorption and desorption in the historical parchment proceeded three time faster. These differences can be explained by differences in the structure and properties of the historical parchment.

Fig. 13. Historic parchment treated with gelatine.

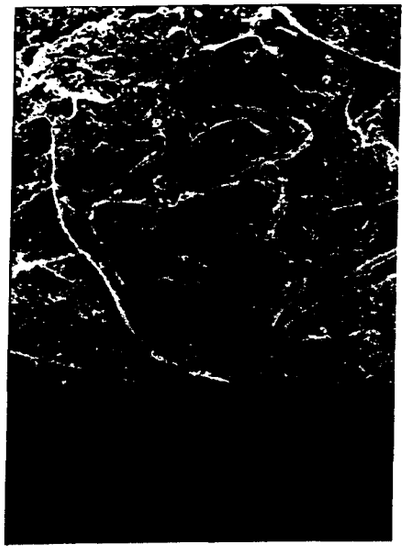

Fig. 14. Historic parchment coated twice with Tylose MH 300 2% w/w in water.

Fig. 15. Historical parchment coated twice with Klucel G 2% w/w in ethanol.

Fig. 16. Historical parchment coated twice with Paraloid B72 2% w/w in acetone.

The effect of the fixing agents and of the softening mixture used on the hygroscopicity of the historical and modern parchment was not always the same. A minimal change in the hygroscopicity of the modern parchment was brought about by hydroxypropylcellulose – Klucel G (2% in ethanol) applied by soaking and coating, by the acrylate copolymer Paraloid B72 (2% in acetone) applied by coating and by the egg white (2% aqueous solution) applied by coating. A minimal change in the hygroscopicity of the historical parchment was observed with the gum arabic (2% aqueous solution) applied by coating, with hydroxypropylcellulose – Klucel G (2% in ethanol) applied by soaking and with the acrylate copolymer – Paraloid B72 (2% in acetone) applied by coating. Soaking the parchments in alcohol, and particularly in ethanol, raised the humidity sorption. Treatment of the modern parchment by the softening mixture reduced the sorption, but with the historical material the effect of treatment was quite opposite.

Evaluated as a whole, the results of this study allow us to stress great differences observed in the properties and structure of the modern and historical parchment. It would be advisable to restrict the substitution of the historical material with modern parchment, both in the restoration work and in experimental measurements.

Fig. 17. Historical parchment coated twice with Sokrat 6402 (commercial dispersion diluted with ethanol to 2% dry matter).

Acknowledgement

We thank Dr Ivan Vančček, State Restoration Workshops, Prague, for the analyses using a scanning electron microscope and for important assistance in evaluating the results obtained.

Summaries

An investigation of the hygroscopicity of parchment subjected to different treatments

Modern and historical parchment (sixteenth century) was subjected to different treatments: soaking in alcohol to remove residues of disinfection treatment; applying a softening agent; or applying natural polymers, cellulose derivates or acrylics to consolidate the structure or to fix loose paint layers. Distinct differences in the change of hygroscopicity and in the manner of connection to the parchment were found.

The Hygroscopicity of Parchment Subjected to Different Treatments

Une étude des variations hygroscopiques de parchemin soumis à différents traitements

Du parchemin moderne et historique (16ème siècle) a été soumis à différents traitements: immersion dans de l'alcool pour enlever des résidus de traitement de désinfection, application d'un assouplissant ou application de polymères synthétiques, dérivés cellulosiques ou résines acryliques, pour consolider la structure ou fixer des couches picturales détachées. On a trouvé des différences significatives des variations hygroscopiques et de la liaison du fixatif au parchemin.

Eine Untersuchung zur Änderung der Wasseraufnahmefähigkeit von Pergament als Folge von konservatorisch/restauratortischer Behandlung

Modernes und historisches Pergament (16. Jh.) wurde verschiedenen Behandlungen unterworfen: Bad in Alkohol zum Entfernung von Desinfectionsmittelrückständen; Einbringen eines Weichmachers; Aufbringen von natürlichen Polymeren, Cellulosederivaten und Acrylaten zum Festigen der Struktur oder zum Fixieren loser Farbschichten. Es wurde eine deutlich unterschiedlich Veränderung des Wasseraufnahmevermögens und eine verschiedenartige Verbindung des Fixativs mit dem Pergament festgestellt.

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Restaurator, 1995, 16, 45–63
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RESTAURATOR
ISSN 0034-5806

The Degradation of Silk by Verdigris

by VINCENT DANIELS & MORVEN LEESE

Introduction

Some copper pigments can have a dramatic long-term effect on paper, causing severe degradation, and the ensuing embrittlement occasionally results in the apparent disappearance of areas of the pigmented sheet. For example, some Islamic miniature paintings were given a rectangular outline with verdigris paint. This outline often turns black and brittle, causing the central rectangular area containing the painting to fall out of the page. This phenomenon has received attention from conservation scientists, notably Gerhard Banik et al.[1,2]

It has long been known that this discoloration is caused by copper-containing pigments, especially those called verdigris, copper pigments that contain principally copper acetates. Discoloration of silk by green pigments on paintings in the British Museum's collection prompted a search of the literature on the effect of verdigris on proteinaceous fibres. It was soon found that practically nothing was known about this subject. This view was confirmed by a personal communication from Gerhard Banik. It was, thus, decided to investigate the problem. From a conservator's standpoint, the two principal questions were whether verdigris was as great a danger to silk as it was to paper and whether intervention was required from conservators when they saw discoloration on silk that might be attributed to verdigris.

The Literature

Although very little has been written on the effect of verdigris on silk, there are data on the effect of copper on wool and on cellulose and on the degradation of silk generally.

In an examination of the reaction of verdigris with cellulose, Mairinger et al.[1] attribute the degradation to auto-oxidation of cellulose accelerated by the presence

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of copper ions; the mechanism is a free radical process. Damage is accelerated by high levels of light, relative humidity and sulphur dioxide. Further work by Banik et al.[2] showed that cellulose fibres concentrate soluble copper at the lumen of the fibre (the hollow centre), where the concentration can reach 8–10%. For degradation to take place, copper must be able to penetrate the fibre by being present in a mobile soluble form as Cu^{+} and Cu^{++} ions. Low concentrations of copper ions are produced from the relatively insoluble carbonates malachite and azurite, and higher concentrations come from the compounds known collectively as verdigris, one of which is readily water-soluble. Verdigris is a name given to a range of copper acetate compounds. Normal or neutral copper acetate is $Cu_2(CH_3COO)_4 \cdot 2H_2O$ and basic copper acetate is $Cu(CH_3COO)_2 \cdot Cu(OH)_2 5H_2O$. Other compounds with variations on this stoichiometry can be obtained, such as $Cu(CH_2COO)_2 \cdot [Cu(OH)_2]_3 2H_2O$.

Banik found that the stability of verdigris-impregnated cellulose could be enhanced by a conservation treatment involving soaking in magnesium bicarbonate solution. As high relative humidity enhances the degradation of copper-impregnated cellulose, including that containing copper hydroxides, Banik also recommended that such material be kept "reasonably dry".

A survey[3] of the literature on the degradation of silk carried out in 1980 found no mention of the copper-enhanced degradation of silk, a reflection of the paucity of information on this topic. Bogle[4] has reviewed the effects of weighting agents on silk and found that copper chlorides have been suggested as catalysts for the oxidation of silk and the formation of red spots. Kuruppillai et al.[5] have performed valuable work on the kinetics of the degradation of silk under conditions of artificial ageing, with particular reference to changes in tensile strength on ageing in a dry oven at 150°C. Heating silk at 150°C was concluded to be a satisfactory method for assessing the long-term ageing properties of silk. First-order decay was observed for loss of tensile strength with time of ageing during which extra amino groups were formed. Samples deacidified with magnesium bicarbonate deposited from ethoxy magnesium ethyl carbonate in trichlorotrifluoroethane were not stabilized, but this was attributed to the low water content of the silk at 150°C.

Masri & Friedman[6] have reviewed the interaction of wool with transition metal ions. These data are of use because wool and silk are both proteinaceous fibres and copper is a transition metal. Binding of copper to wool is fast and efficient enough for wool to have been proposed as a material for cleaning water of copper contamination. In 24 h, wool took up 4% of copper from CuCl and 1.2% from $CuCl_2$ solution. A wide range of solution strength was used with 10–20 mmol of the copper salts in 50–100 ml of water (average of 0.72% of Cu). Alkylation and reduction of sulphydryl groups was brought about to elucidate the mechanism of

bonding of metals to wool. It was concluded that metal mercaptides were formed by reaction of metal ions with -S-H groups; no interaction was observed with disulphide groups. The ability of Cu (II) to catalyse oxidation of sulphydryl groups was noted.

Poupko et al.[7] mention the decarboxylation of $R\text{-}COO^{-}$ groups in proteins generally. This reaction is facilitated by the presence of inorganic ions, including copper. The reaction can be induced photochemically or thermally.

Compared with wool, silk has a low sulphur content. A typical sulphur content for wool is 3.5%, and for silk it is 0.2%[8]; thus, silk would not be expected to chemically bind with copper to the same extent as wool, but physical migration into the fibre can still occur. It is not known whether ageing of wool is accelerated by copper ions; however, Deasy[9], as a result of working on oxidation of the protein collagen, reports that "contamination of hides with transition metals (iron, copper, nickel, cobalt) etc. should be avoided as a practical measure to decrease oxidative degradation".

Bearing in mind the application of this work to Japanese paintings on silk, references were sought that referred to the pigments on these paintings. Fitzhugh[10] found malachite, Paris green and atacamite/paratacamite on Ukiyo-e paintings, but no other copper greens were identified. There was no X-ray diffraction evidence to support the use of verdigris (basic copper acetate). However, Banik et al.[1] reported that X-ray diffraction identification of verdigris on paper was only possible in a small number of the samples he attempted to analyse, as most samples appeared to be amorphous. Gettens[11] considered that verdigris was recognized as an unstable pigment by the Japanese and therefore was never used on paintings. None was found in the Freer Gallery collection. He also states that verdigris is injurious to both paper and silk. Areas of Ukiyo-e paintings with malachite are quite commonly darker on the backs of paintings. These areas were accentuated in ultraviolet light, but there was no evidence of weakening of the silk or paper support. Observations by British Museum conservators support these findings and that degradation of silk by copper pigments of any kind is not widespread.

AIMS

The experimental aims of this work were:

- to determine whether the rate of degradation of silk was enhanced by verdigris;
- if the rate of degradation was increased, to determine whether conservation treatments were available that could retard the degradation; and
- to compare the rate of degradation of silk with that of paper given a similar concentration of copper contaminant.

Experimental

The work of Banik et al. concluded that degradation by verdigris is chiefly caused by the presence of copper ions. The rate of degradation could also be enhanced by acetic acid produced by the hydrolysis of verdigris. As there appeared to be little difference between the degradation enhancement effects of the various copper acetate pigments on cellulose, impregnation of silk substrates and paper in this work was performed with the well characterized, easily available and water-soluble, normal copper acetate. An experiment using a sparingly soluble type of copper acetate pigment in a binder would not be expected to produce the desired reaction in a dry oven accelerated ageing test, as migration of copper ions into the fibre is an essential part of the deterioration, and such migration would not take place because of the lack of water.

Degradation of silk may be followed by measuring a mechanical property (such as tensile strength) or a chemical property (such as the content of amino groups, molecular weight etc.); of these techniques, tensile strength was chosen, as the work of Kuruppillai et al.[5] had determined this to be a reliable indicator, and it could be measured with in-house apparatus.

Verdigris on paper may be stabilized by the use of magnesium bicarbonate aqueous solution, as recommended by Banik et al.[2]. Banik & Ponahlo[12] suggest that complexing agents for copper might also be used as a means of arresting the degradative effect but have done no work on this. Benzotriazole is one such complexing agent widely used on copper alloy corrosion. It forms a linear complex with copper ions, rendering them relatively unreactive. Thus, benzotriazole and magnesium bicarbonate were compared as stabilizing agents for verdigris on silk.

For tensile testing, a silk yarn was chosen that broke under tension in a reproducible manner and gave a small scatter of results. The yarn used was 100% silk and undyed and was manufactured by Cucirini Cantoni Coats, Milan. A seventeenth-century book was also used for tensile testing when comparisons with cellulose were required. There is a current trend away from straightforward tensile strength measurements for assessing the mechanical properties of paper while ageing to tensile energy absorption and extension before break, but in this work tensile strength was used to enable direct comparisons to be made with the silk data.

In this report, the experimental work was carried out by Vincent Daniels, and the data were analysed by Morven Leese using methods described by Miller & Miller.[13]

Preparation of samples

Solutions containing copper acetate at 2%, 4% and 6% w/w were prepared. Silk yarn samples was soaked with these solutions for 30 min, removed and laid on

glass sheets and lightly blotted with paper tissue. They were then allowed to dry. Silk blanks were prepared by soaking the yarn in distilled water instead of copper acetate solution. A set of paper samples was prepared in a similar way to the silk samples. The resulting samples contained increasing amounts of copper acetate as the solution increased in strength; this could be observed directly by the increasing blueness of the samples.

Determination of copper concentrations

A colorimetric method[14] was used to measure the concentration of copper in the samples. Copper was extracted from the fibre by treating 1 or 2 cm in 1 M hydrochloric acid (50 ml) for 30 min. The resulting solution was shaken with 0.01% zinc dibenzylthiocarbamate in carbon tetrachloride (10 ml) for 30 s. When the layers had separated, the yellow solution obtained was transferred to a cuvette and its optical density measured at 435 nm. Data for a calibration curve were obtained by using standard copper sulphate solutions. The quoted useful working range of the test is 7–40 μg of copper.

Tensile testing

For tensile testing, the rate of elongation was 200 mm/min using an initial inter-jaw distance of 50 mm. The relative humidity of the room where the tensile tester was housed was 45–50%. To minimize the errors obtained in tensile strength testing, ageing was usually carried out until a 50% decrease in strength was obtained. This keeps the overall change in strength high compared with the experimental errors.

Kinetic analysis

Kuruppillai et al.[5] found that the tensile strength of silk decreased in a first-order or exponential manner, and thus:

$$T_t = T_0 \, e^{-kt}$$

where T_t is the tensile strength at time t, T_0 is the initial tensile strength, t is time of ageing and k is a constant called the rate constant.

Taking natural logarithms

$$\ln T_t = \ln T_0 - kt \qquad (\ln X = \log_e X)$$

Thus a graph of ln T_t against time will be a straight line of slope $-k$. The rate constant is calculated to give a numerical value to the rate of loss of strength.

The variation of reaction rate with temperature is often governed by the Arrhenius equation; although this only strictly applies to homogeneous chemical reactions, it may usefully be applied to other systems.

$$k = Ae^{-} E_a/RT$$

where A is a constant, called the pre-exponential factor, E_a is the experimental activation energy, T is the absolute temperature (273+°C) and R is the gas constant.

Taking natural logarithms

$$\ln k = \ln A - E_a/\mathrm{RT} \text{ or } R \ln k = R \ln A - E_a/T$$

Thus, a graph of $R \ln k$ against $1/T$ gives a straight line of slope $-E_a$, the units being cal/mol or J/mol, depending on the units used for R.

The numbers obtained for $1/T$ are usually very small; for example,

$$100°\mathrm{C} = 373°\mathrm{K},\ 1/T = 0.002681.$$

Thus, it is often more convenient to draw a graph of $R \ln k$ against $1000/T$, where the term for 100°C is now 2.681 and the slope of the graph is now $-E_a$ in units of kcal/mol or kJ/mol instead of cal/mol · °C J/mol. This is convenient, as the values of E_a are typically around 25 kcal/mol or 100 kJ/mol for slow reactions.

Artificial ageing

Ageing was carried out in an oven with no humidity control. The nominal temperatures on the controls were calibrated using a mercury-in-glass thermometer. The actual temperatures of ageing are thus not always the round numbers one might expect to see.

To give an idea of a typical data set, the values for tensile strength in (newtons) of untreated silk are reproduced here: 73.5, 74, 73.5, 76, 76, 73.5, 74, 73.5, 73.5, 73.5; mean 74.1, standard deviation 1.02. The spread of the preceding results is very small compared with the results one might be accustomed to with tests on the tensile strength of paper. Thus, only 10 silk yarn samples were tested for tensile strength for each data point on a graph, whereas at least 20 were used for the work on paper.

In this work extensive use was made of the fact that the decay of tensile strength

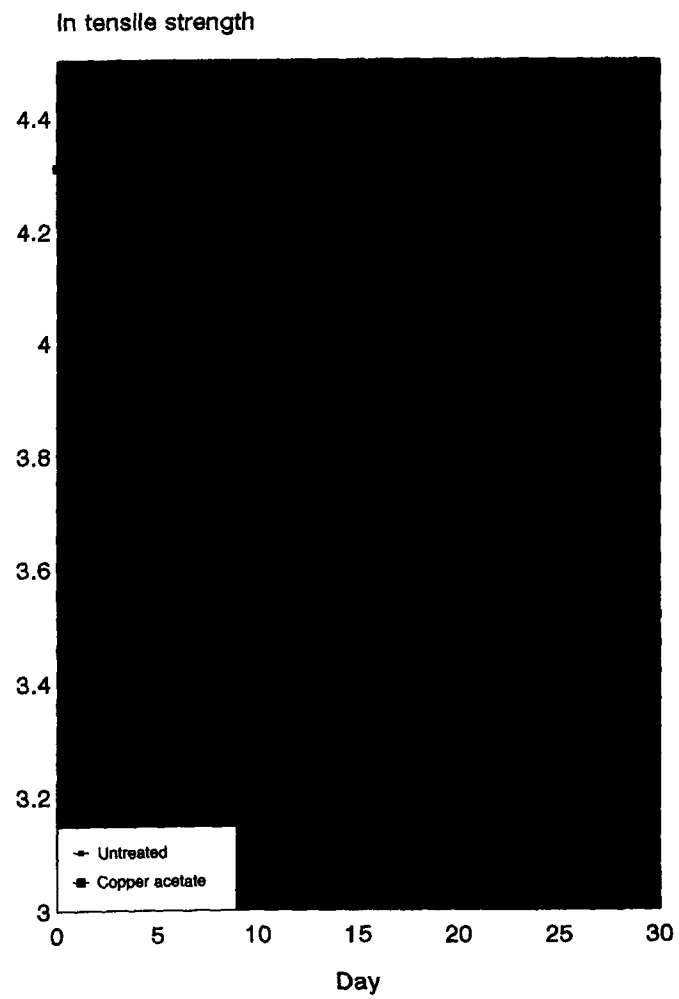


Fig. 1. Typical loss of tensile strength of silk yarn with and without impregnation by 2% copper acetate solutions (113°C)

is exponential. To illustrate this, Fig. 1 shows a graph of ln (tensile strength) plotted against time. Two straight lines are shown for ageing at 113°C, of silk before and after impregnation with 2% copper acetate.

Effect of copper concentration

Samples of silk with varying amounts of copper acetate in them were aged in an oven at 130°C for 71 h. Eleven tensile strength measurements were obtained for each data point. Tensile strength measurements of "untreated" (actually water treated) silks and of silks treated with copper acetate solution were obtained, both before and after ageing.

Rate constants were calculated for the degradation for each concentration of copper and a graph plotted of rate constant versus concentration of copper in the fibre.

In the calculation of the rate constant in this experiment, two data points were used; thus k could be calculated from

$$-k = (\ln T_t - \ln T_0)/t$$

Influence of temperature

The rate constants for the degradation of silk yarn before and after treatment with 2% copper acetate were determined. The experiment was performed at four different temperatures between 100°C and 145°C (eight regressions in all). The standard errors of the slopes of the lines are the result of a least-squares fit. In most cases there were measurements at 3–4 time points. The errors quoted for these rate constants thus include both measurement error and any lack of fit in the line.

Effect of stabilizing treatments

Three solutions were selected for stabilization treatment: magnesium bicarbonate, methyl magnesium carbonate and benzotriazole. Magnesium bicarbonate solution was prepared by bubbling carbon dioxide through a suspension of magnesium carbonate (light) in distilled water. A solution of 0.66% magnesium bicarbonate was produced. Methyl magnesium carbonate was a commercially available solution (Archival Aids). This was analysed and yielded 0.21% of magnesium carbonate. Both of the above analyses were performed by placing measured quantities of solution in a Petri dish; after evaporation the dishes were left for 24 h until conversion to magnesium carbonate was thought to be complete (constant weight). For benzotriazole impregnation, a 5% solution in industrial methylated spirit (ethanol) was used. Silk previously soaked in 4% copper acetate and dried was aged for 24 h at 100°C before being immersed in the stabilizing treatment

for 60 s. In practice, most stabilizing mixtures would be applied by brush; a short period of exposure to liquid stabilizing agent was therefore used as an approximation to this treatment. After immersion, samples were lightly blotted with tissue and allowed to dry. The rate constants were determined at 100°C.

Comparison of silk and paper ageing

Although conservators recognize that the effect of verdigris on paper is a problem, the same cannot be said of silk; the reason for this could be that the rate of reaction is very much slower on silk than it is on paper. It was therefore, desirable to do some experiments to determine the rate of loss of tensile strength of paper impregnated with copper acetate. An Italian book paper dated approximately 1670 was used. Strips 1.5 cm by 10 cm were cut and mixed to ensure that any unevenness in the pages was randomly distributed among the strips tested. Impregnation with 4% copper acetate and subsequent ageing at 100°C was similar to that of the silk samples.

The rate constants were calculated for loss of tensile strength of the samples tested with and without impregnation by copper acetate.

RESULTS

Effect of copper concentration

The copper content of samples of yarn soaked in copper acetate were determined. Fig. 2 is a calibration graph relating copper concentration in the analytical solution with optical density. When evaporation of soluble salts occurs on porous substrates there is usually a concentration of salts at the surface. The results presented here in Table 1 are the average concentrations of copper, throughout the fibre.

The rate constants for silk yarn soaked in the solution of copper acetate are presented in Table 2. The errors take into account the measurement errors only

Table 1. Concentrations of copper in silk yarn soaked in copper acetate solution

Concentration of copper acetate solution (%)	Concentration of copper (%) in dry fibre
0	0
2	0.31
4	0.65
6	0.99

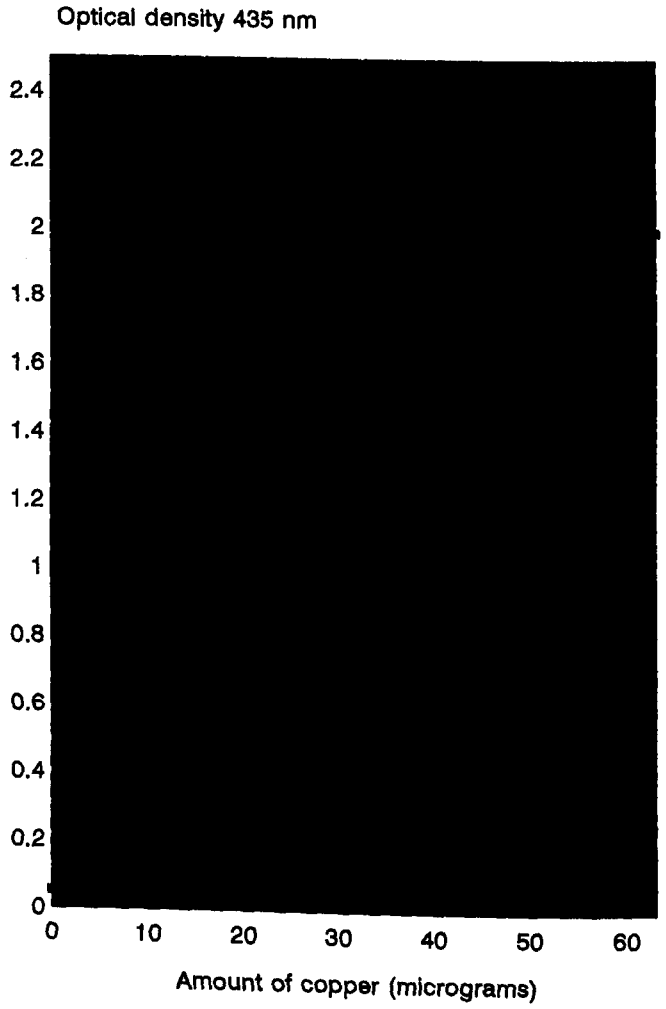


Fig. 2. Calibration curve for determination of copper by zinc dibenzyldithiocarbamate

and assume a linear relationship between ln (tensile strength) and time, as demonstrated in Fig. 1. It was generally observed that there was more scatter in the tensile strength measurements of aged samples. Thus the measurement error increased on ageing. Fig. 3 shows the influence of copper content on the rate of degradation: as the copper content increases the rate increases.

Table 2. Variations in rate constant with varying concentrations of copper present as copper acetate. Ageing temperature 130°C

Concentration of copper %	Time	Mean tensile strength (N)	Standard deviation	ln tensile strength	k (day^{-1})	Standard error of k
0	0	74.1	1.02	4.306		
0	71 h	64.4	1.43	4.165	0.05	0.003
0.31	71 h	44.55	3.17	3.794	0.17	0.007
0.65	71 h	34.09	4.46	3.522	0.26	0.013
0.99	71 h	29.55	3.15	3.363	0.31	0.012

Table 3. Rate constants for deterioration of copper acetate treated and untreated silk at various separations

	T°C	145	130	113	100
	1000/T° absolute	2.392	2.481	2.591	2.681
Treated	k	0.554	0.426	0.037	0.017
	$R\ln k$	−4.90	−7.08	−27.35	−33.81
	SE $R\ln k$	n/a	1.25	0.42	2.93
Untreated	k	0.262	0.110	0.027	0.013
	$R\ln k$	−11.10	−19.19	−29.95	−36.03
	SE $R\ln k$	1.25	1.68	0.42	1.25

Table 4. Experimental activation energies (standard errors in brackets)

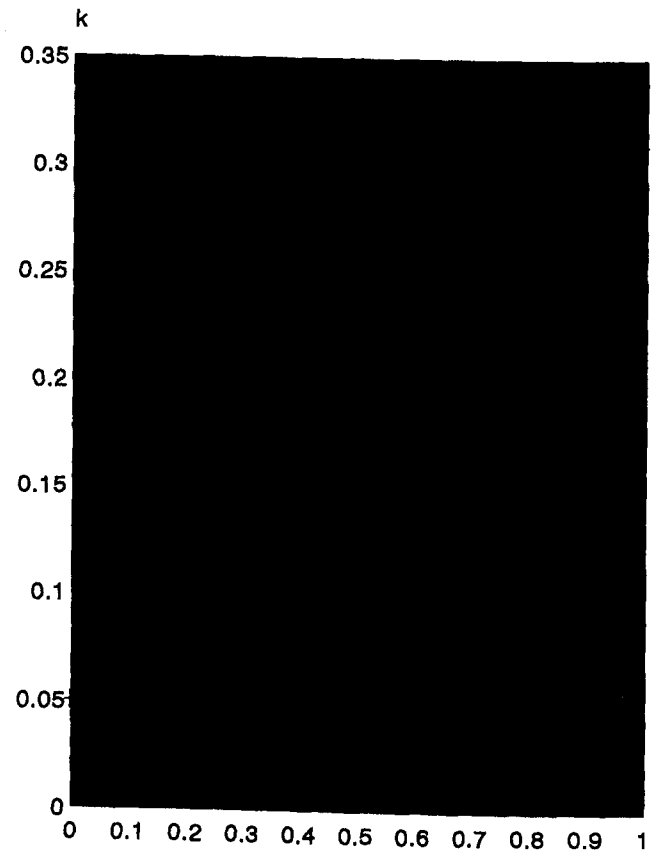
Untreated:	88 (4)	kJ · mol^{-1}
Treated:	109 (21)	kJ · mol^{-1}

Influence of temperature

Table 3 gives the rate constants k and their errors as found from the regressions from treated and untreated silk at 100°C, 113°C, 130°C and 145°C.

Fig. 4 shows the results, with the typical error in $R\ln k$. Separate linear regressions of $R\ln k$ versus $1000/T$ for treated and untreated silk gave slope estimates as in Table 4.

The larger standard error in the activation energy for treated silk reflects the relative lack of fit in the line. It might be predicted that the lines could be parallel as parallel lines are scientifically feasible, and this was tested as a null hypothesis.



(± one sigma errrors based on measurement error of tensile strength)

Fig. 3. Rate constants ($k \cdot day^{-1}$) at various copper concentrations (130°C)

There was no evidence to contradict this hypothesis, on the basis of an approximate *t*-test. The joint estimate of the common slope, ignoring differences in standard errors, is

$$\text{Joint slope:} \qquad 100\ (12) \qquad \text{kJ} \cdot \text{mol}^{-1}$$

The relative lack of fit of the line for treated silk may be explained by inevitable inhomogeneities in the fibre concentration and also the generally greater degree

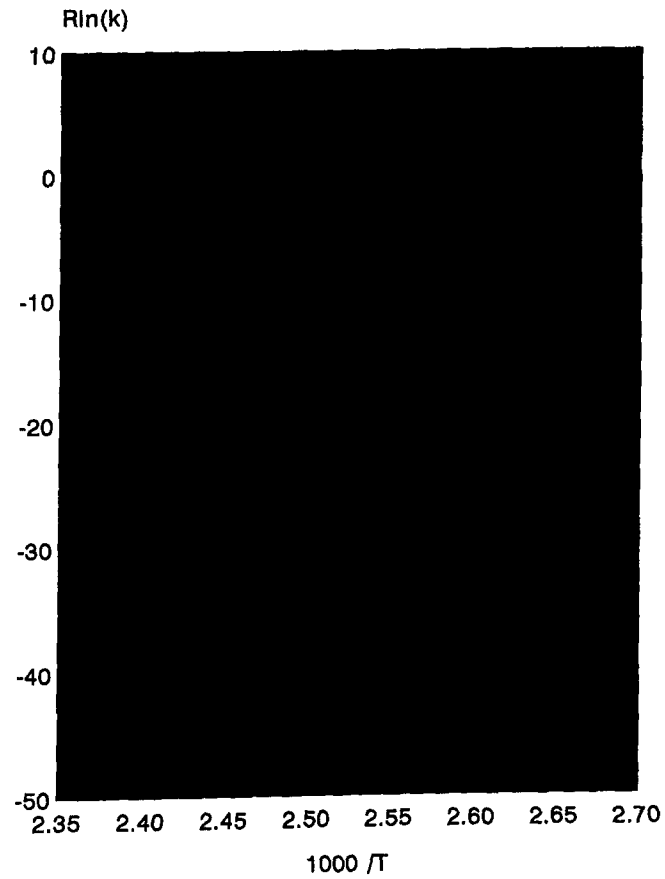


Fig. 4. Activation energy for treated and untreated silk. Temperature T in °A. Activation energy given by slope of lines. Error based on fit.

of degradation in this set, which results in greater scatter in tensile strength measurements.

A rate constant for silk degradation was obtained from the published data of Kuruppillai et al. for 150°C. This is shown superimposed on Fig. 4; although this fits well with the data obtained in this experimental work, it was not used in the calculation of the activation energy.

Effect of stabilizing treatments

The rate constants for various types of treatments were derived in the usual way at 100°C and are shown in Table 5. There were 4 points per regression at times 0, 7, 21 and 42 days.

Table 5. Rate constants for silk treated in various ways

Treatment	k (day^{-1})
% copper	0.012
4% copper	0.031
4% copper+benzotriazole	0.015
4% copper+magnesium bicarbonate	0.013
4% copper+methyl magnesium carbonate	0.024

Table 6. Tensile strength of paper before and after treatment with copper acetate solution; S=tensile strength in newtons. Ageing temperature 100°C

Time (days)	0	6	12	18	24
Untreated ln(S)	3.13	3.07	3.13	3.07	3.1
Treated ln(S)	3.26	3.07	2.84	–	2.5

The typical standard error on k, based on 4 points in each case, was 0.0025. Fig. 5 shows the results. Given the typical error, differences greater than about 0.005 (one tick mark on the vertical scale) are significant.

Comparison of silk ageing with paper ageing

The aim of this section of the work was to compare the accelerating effect of copper acetate on the ageing of a paper with that on silk.

In an attempt to measure the accelerating effect of copper acetate on paper degradation, a statistical analysis of the results for the seventeenth-century paper was attempted. Table 6 shows the results for treated and untreated paper.

The estimates of k by linear regression were 0.001 and 0.032 day^{-1} with errors of 0.0014 and 0.0018, for untreated and treated paper respectively. The results can be seen graphically in Fig. 6. A common estimate of error can be taken as 0.0016.

Approximate 95% confidence limits for k (treated) are $0.032 \pm 2(0.0018)$.

Assuming that the k value for untreated material could go negative, its limits are $0.001 \pm 2(0.0014)$. This is consistent with no change in strength over time.

The treated samples show a faster degradation than the untreated ones. It would have been desirable to know how much faster the copper impregnated samples deteriorated; the ratio of the k estimates is 32 but, ignoring the possibility that the untreated k could be negative, the error on this ratio is approximately 46. The interpretation of this error is problematic, as the distribution of a ratio is not normal (Gaussian), especially when the denominator is near zero as it is here; that is, no conclusion could be reached using these results.

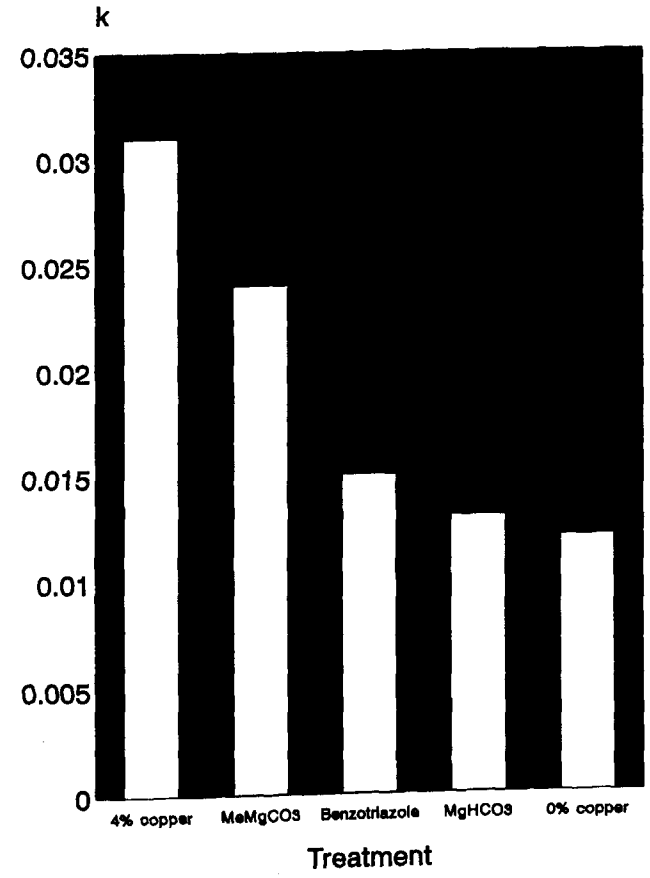


Fig. 5. Rate constants ($k \cdot$day^{-1}) for various treatments (100°C)

DISCUSSION

A kinetic approach has been applied to the study of the effects of verdigris on silk. Normal copper acetate was chosen to represent the verdigris series of compounds. In accelerated ageing conditions, the degradation of silk was accelerated by verdigris in the form of normal copper acetate. The rate of degradation increased with concentration of copper acetate, and on ageing the tensile strength of silk yarn decreased exponentially. An average activation energy of 100 kJ $\cdot$ mol^{-1} was determined for silk with and without a 0.31% copper content. At

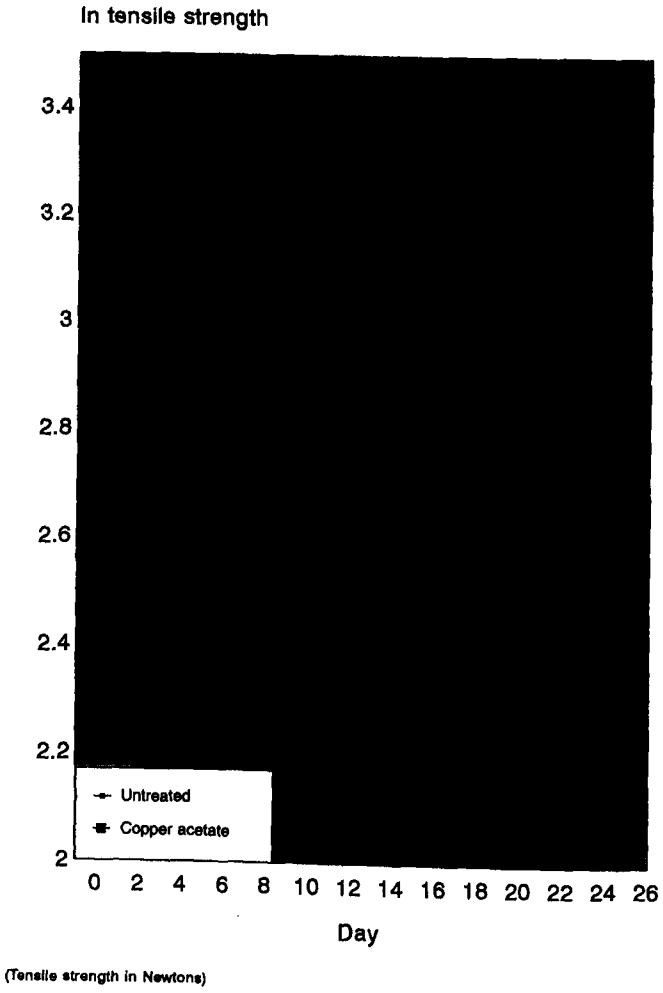


Fig. 6. Aging of seventeenth-century paper (100°C)

all temperatures between 100°C and 145°C the loss of tensile strength was faster in the presence of copper.

Magnesium bicarbonate was shown to be the most effective conservation reagent for attenuating the effects of the verdigris, with benzotriazole coming close behind. With the proven track record and stability of magnesium bicarbonate, it is the preferred choice; the properties of benzotriazole on long-term natural ageing are unknown, and it is probably more hazardous to humans.

Verdigris is apparently not frequently found on silk, as the use of other copper

containing pigments is more popular. The active agent is soluble copper, which is extremely low in concentration in azurite and malachite but high in verdigris. Browning at the back of an area suspected of supporting copper pigments does not necessarily mean that verdigris has been used, as the browning may also be caused by azurite or malachite or a wide range of copper-free chemicals. However, it is indicative of degradation.

Degradation by verdigris is widely known to be a severe problem on paper, but the severity of the problem on silk is more difficult to assess. Examples of severe verdigris damage on silk have not been reported at the British Museum, but other workers have seen examples of severe degradation of silk by verdigris (G. Banik, personal communication, 1992).

Experiments attempting to compare the rates of degradation by copper acetate on silk and paper at 100°C were not successful.

For degradation of silk to be accelerated by verdigris, the verdigris must first gain access to the silk. By the phenomenon of "migration", any soluble component of an applied pigment may travel into adjacent fibres. The verdigris may be suspended in a gum binder, and this may act as a physical barrier between pigment and fibre. Additionally, some silk paintings, and in particular all Japanese paintings, are sized; Japanese artists use an alum/deerskin glue mixture. The gelatine in the glue contains the -S-H groups mentioned by Masri & Friedman[6] as efficient scavengers of transition metals and alum may bind with active sites on the protein. Thus, gelatine may act as a chemically and physically protective layer preventing the passage of copper into the silk. Alum in the size and silk may also influence the degradative effect of the verdigris. However, the study of these phenomena is another research project. Likewise, little is known about the inherent stability of verdigris; samples often have an odour of acetic acid and are thus subject to change on ageing. Partial alteration on ageing to a less damaging compound would lessen the degradative effects of verdigris.

If signs of copper-catalysed degradation on silk are seen, there should be no harm caused to silk or pigment by careful application of magnesium bicarbonate solution. The rate of degradation of silk and hence the severity of the problem in the long term is governed by the type of pigment (solubility), the presence of size on the silk and the method of application (such as whether the pigment is surrounded by binders), and thus, whether the copper ions have physical access to the silk.

CONCLUSION

The rate of degradation of silk by copper acetate (a type of verdigris) increased with compound concentration and temperature. An activation energy has been determined. Magnesium bicarbonate solution is a good inhibitor for the degradation.

ACKNOWLEDGEMENTS

We would like to thank A. Thompson and L. Fleming from the Department of Eastern Pictorial Art section for useful discussion on this project.

SUMMARIES

The Degradation of Silk by Verdigris

Copper acetates are known to degrade paper and silk on ageing. A kinetic study of the rate of degradation of silk has been carried out using silk yarn and normal copper acetate. Tensile testing was used to monitor artificial ageing in a dry oven. The rate of degradation increased with the concentration of copper acetate, and temperature. An activation energy of 100 kJ · mol^{-1} was obtained for silk degradation. Three conservation treatments were used to slow down the rate of degradation; magnesium bicarbonate solution was the most effective.

La dégradation de la soie par le vert-de-gris

Les acétates de cuivre sont connus pour dégrader le papier et la soie au cours du temps. Une étude cinétique de la vitesse de dégradation de la soie a été réalisée en utilisant du fil de soie et un acétate de cuivre courant. La résistance à l'élongation a été utilisée pour contrôler le viecillissement artificiel à sec. La vitesse de dégradation augmente avec la concentration d'acétate de cuivre et la température. Une énergie d'activation de 100 kJ/Mol a été obtenue pour la dégradation de la soie. Trois traitements de restauration ont été appliqués pour ralentir la vitesse de dégradation; la solution de bicarbonate de magnésium a été la plus efficace.

Der Abbau von Seide durch Kupfergrün

Kupferacetat bewirkt bekanntlich über längere Zeit hin eine Schädigung von Papier und von Seide. Es wurde die Kinetik des Abbauvorgangs von Seide untersucht; als Materialien diente Seidengarn und handelsübliches Kupferacetat. Als Kriterium der Festigkeitveränderung durch beschleunigte Alterung (trockene Wärme) diente die Zugfestigkeit. Der Abbaugrad wächst mit steigender Kupferkonzentration und mit steigender Temperatur. Als Aktivierungsenergie des Abbaus von Seide wurden 100 kJ/Mol ermittelt. Drei Methoden zur Verminderung des Abbaus wurden erprobt; Magnesiumbicarbonat erwies sich als die wirkungsvollste.

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