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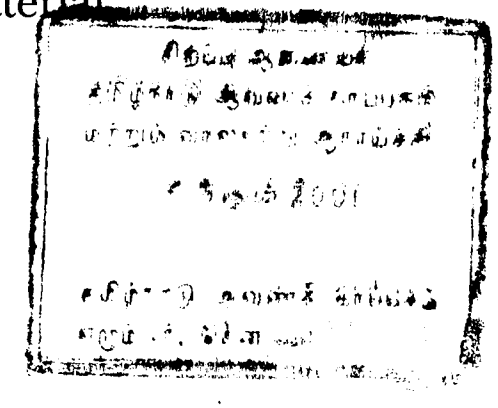

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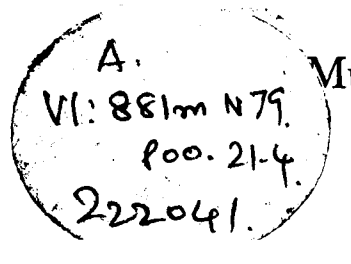

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Migration of Volatile Compounds through Stacked Sheets of Paper during Accelerated Ageing

Part II: Variable Temperature Studies

by A. BÜLOW, P. BÉGIN, H. CARTER & T. BURNS

INTRODUCTION

Acid migration has often been assumed to be the cause of the discolouration of paper that has been in contact with acidic materials[1,2]. More recently, Shahani has proposed that volatile, acidic degradation products are generated during artificial ageing of paper. These compounds accumulate in paper stacks since they are unable to escape into the environment, therefore accelerating the degradation in the centre of a paper stack[3].

Evidence has recently been found for the acid migration through a stack of 30 sheets of commercial alum-rosin sized, fully bleached, kraft paper under conditions of accelerated ageing at 90°C and 69% relative humidity (RH)[4]. However, no conclusions can be drawn from that study as to the impact of the migration of volatile compounds at lower temperatures, where the formation and reaction of degradation products takes place much more slowly. In addition, the relative importance of competing mechanisms during paper degradation may change with lower temperatures[5–7].

The work reported here studied the migration of volatile compounds through paper stacks at three different temperature and humidity conditions, viz. 90°C at 69% RH, 80°C at 65% RH, and 70°C at 61% RH. It was anticipated that the studies at the two lower temperatures will give some indication as to whether or not diffusion of volatile degradation products during artificial ageing takes place under conditions of natural ageing. At the same time, the progress of migration was monitored by removing stacks for testing at four different time intervals.

EXPERIMENTAL

Samples

In order to simulate the paper that is found in books and to allow for significant changes in a relatively short artificial ageing time, an acidic paper was chosen. This paper was made from fully bleached kraft pulp, containing 50% hardwood and 50% softwood pulp. It was alum-rosin sized, and contained 4% clay as a filler.

The samples, arranged in 13 stacks of 50 sheets each, were numbered from the top to the bottom. All sheets were aged. For the actual tests, ten sheets were taken out of each stack (these were sheet nos. 1, 2, 3, 4, 5, 6, 10, 15, 20, and 25). The corresponding sheets of each stack were tested. The experimental setup, using three different conditions and four different intervals, resulted in a total of 130 different samples to be tested, including the control.

The degree of polymerization (DP) was determined using sheet no. 16. This sheet was chosen after all other tests had been carried out, and showed that the rate of degradation essentially did not change in this part of the stacks. Using sheet no. 16 out of each stack resulted in 13 different samples on which to perform the measurements, and allowed for a distinction between the different rates of degradation under the three different ageing conditions.

Accelerated ageing

The stacks, 50 sheets of 8½" x 11" (21.6 cm x 27.9 cm), were placed on glass plates. In order to keep the sheets in place, due to the airflow in the ovens, the stacks were covered with plexiglass frames, about 1" (2,54 cm) wide at each side. This allowed the stacks to be open at the top and to interact with the environment through their centre.

The choice of ageing conditions was based upon experience with experiments recently conducted at the Canadian Conservation Institute. Those studies were performed in order to develop moisture profiles that can be used to determine the temperature and relative humidity combinations that would keep the moisture content of the samples during accelerated ageing the same as they would be during natural ageing at 23° C and 50% RH[8].

According to the results of this study the following ageing conditions were chosen:

- 90°C at 69% RH; the stacks were removed after 5, 9, 16, and 30 days
- 80°C at 65% RH; the stacks were removed after 7, 15, 28, and 50 days
- 70°C at 61% RH; the stacks were removed after 12, 32, 61, and 110 days.

The four stacks used in each ageing condition were always put in the same oven at the same time. The control stack was kept in the dark at 23 ± 1°C and 50 ± 2% RH during the accelerated ageing.

All accelerated ageing was carried out using controlled temperature and humidity chambers manufactured by ESPEC, model ESPEC PRA-3GP. After accelerated ageing, the samples were conditioned at 23°C and 50% RH for at least 24 hours before being tested.

Test methods

After artificial ageing the following test methods were performed: optical properties (including brightness, yellowness, L*a*b*), moisture content, grammage, zero-span tensile strength, pH and the degree of polymerization (DP).

The edges that had been covered by a plexiglass frame during ageing, were trimmed off to ensure that only the centre of each sheet was used for testing. All sheets were cut up in the same way. Fig. 1 shows the distribution of test specimens on a sheet for the different test methods used.

Some of the test methods performed had to be modified with respect to their standard. This was necessary because the amount of sample per specimen could not be adjusted to the amount needed for the tests to be performed, as is normally done. In this project, each sheet of paper was of particular interest in order to examine the effect of the diffusion of volatile products out of a stack. Test methods that had to be modified were the determination of moisture content and pH measurements, respectively. In both cases only half the amount of sample could be used.

Physical properties

- Optical properties were determined according to CPPA standard (E.1)[9] using an ELREPHO 2000 instrument and six replicates per specimen.
- The measurement of grammage was carried out at standard conditions of 23 ± 1° C and 50 ± 2% RH. Due to the particular situation in this project, as mentioned above, grammage could not be weighed in replicates. Instead, every sheet of paper was weighed and measured individually after the edges that had been covered by the plexiglass frames during ageing had been trimmed off. The oven dry grammage was then calculated for each sheet.

Gram-mage (g/m^2)	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span
	Zero-span pH	Zero-span pH	Zero-span pH	Zero-span pH	Zero-span pH	Zero-span pH
	pH Zero-span Optical Properties	pH Zero-span Optical Properties	pH Zero-span Optical Properties	pH Zero-span Optical Properties	pH Zero-span Optical Properties	pH Zero-span Optical Properties
	Zero-span pH	Zero-span pH	Zero-span pH	Zero-span pH	Zero-span pH	Zero-span pH
	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span	Moisture Content Zero-span

Fig. 1: Distribution of test specimens.

- Zero-span tensile tests were carried out in machine direction using 18 replicates per specimen. In order to overcome the tendency of this test to give scattered results, the paper was weighed prior to cutting the strips and the individual weight of every sheet included in the calculation of results. Moisture content was determined according to CPPA standard (G.3)[10] using three replicates per page and 0.5 g per replicate.

Chemical properties

- The determination of pH was carried out in triplicates using the cold extraction method according to CPPA standard (G.25P)[11]. The standard method was modified by using only 0.5 g instead of 1.0 g to carry out the measurements (the amount of water was adjusted accordingly from 70 ml to 35 ml to keep the concentration the same).
- DP measurements were performed in triplicates using cadoxen solvent according to the method described by Kaminska[12].

A scheme showing how the test specimens were cut is given in Fig. 1.

RESULTS AND DISCUSSION

Optical properties

Optical properties as measured by brightness, yellowness, and L*a*b* all showed similar effects. Among these, b* can best be used to demonstrate the changes which occurred during ageing. Brightness, yellowness, L* and a* follow generally the same trends and are therefore not particularly discussed.

There is a significant increase in b* from the top of the stack to the middle, i.e., from page no. 1 to page no. 25 (Fig. 2). It can be seen that interaction between environment and paper sample with respect to optical properties mostly takes place in the first six sheets of a stack. A distinct difference is apparent with respect to all optical properties among the top three sheets (no. 1 to no. 3). However, the next three sheets (no. 4 to no. 6) still exhibit a pronounced increase in b* compared to the control. The increase in b* seems to level off towards the centre of the stack. For all optical properties, no distinct differences can be measured from sheet no. 10 to sheet no. 25. Therefore, sheet no. 15 can be seen as representa-

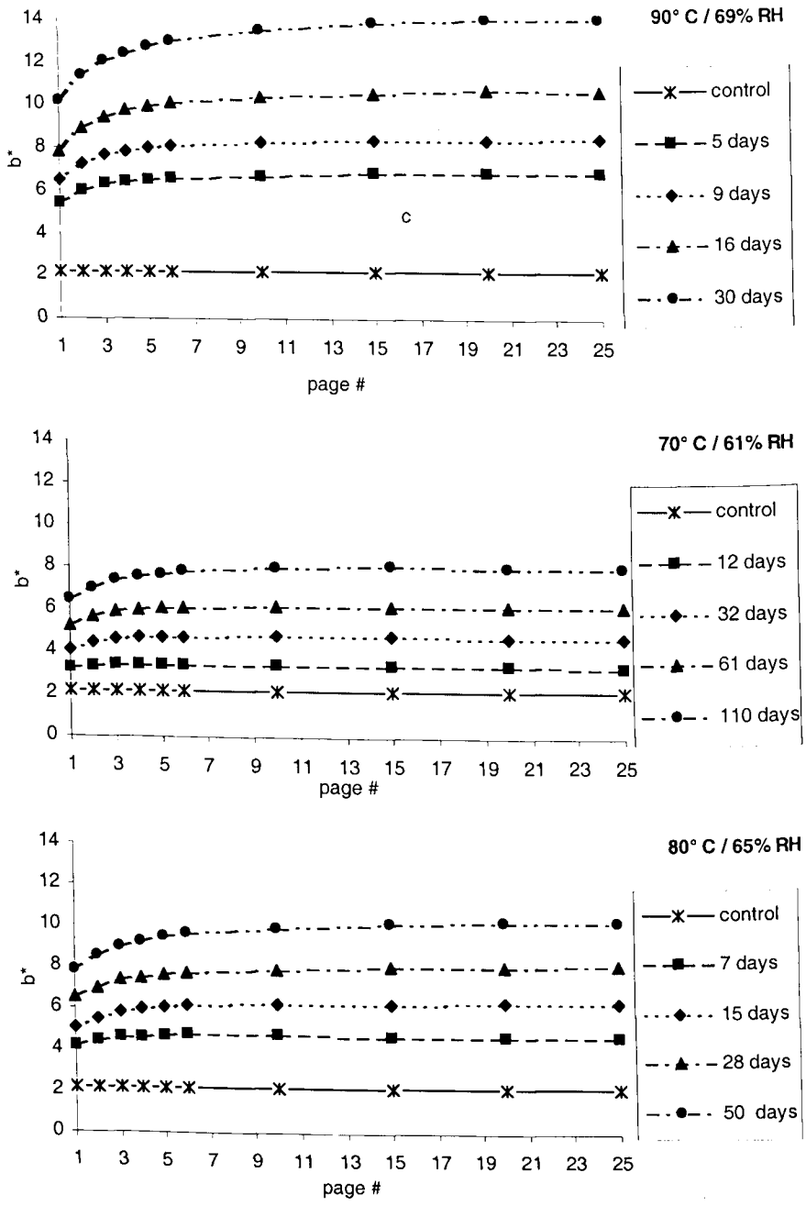

Fig. 2: CIE b* vs. page. NB: the control value represents an average of the ten sheets tested.

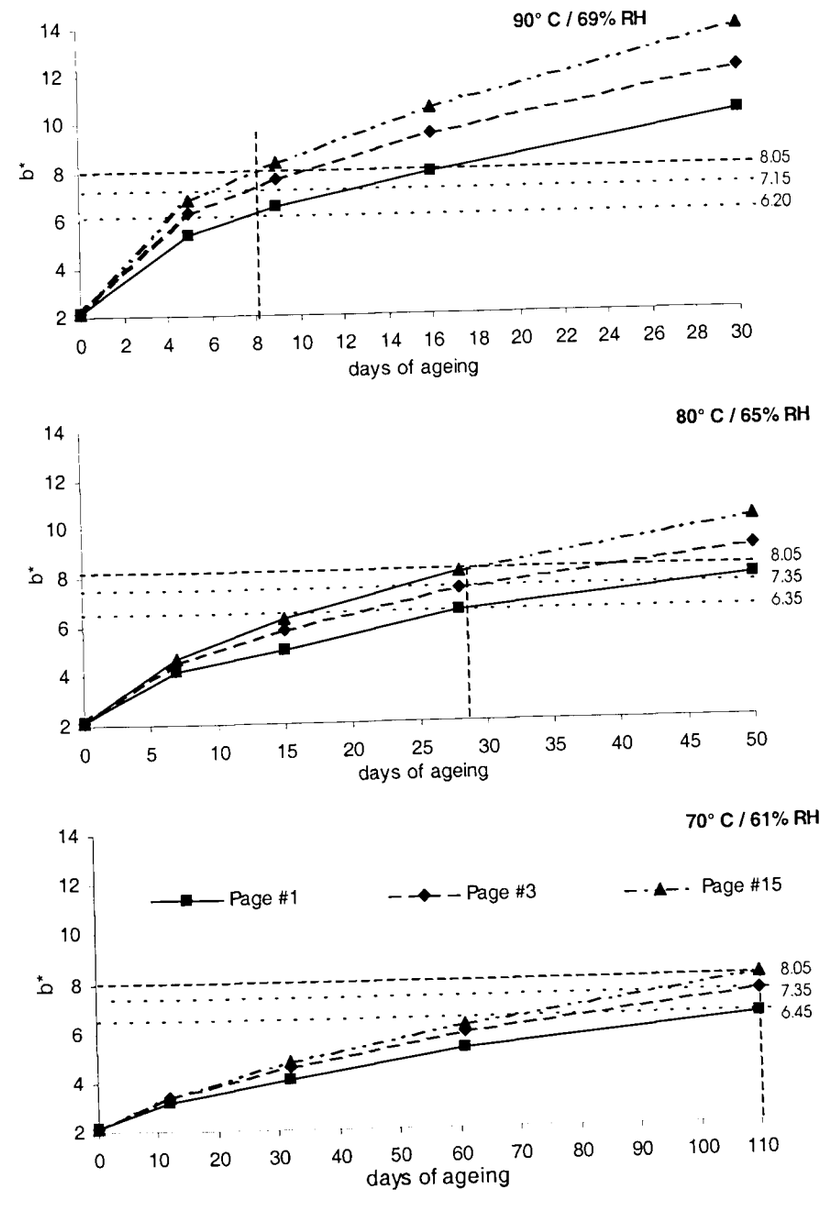

Fig. 3: CIE b* vs ageing time.

tive of sheets from the centre of a stack. This phenomenon can be detected with all three ageing conditions, but is most obvious for the samples aged at the highest temperature, 90°C and 69% RH. In addition, it occurs at an earlier state of ageing.

Very small differences in ageing can be measured for particular sheets at different temperatures. This is further clarified in Fig. 3, again using b* as an example. Since less diffusion takes place in the middle of the stack, an intercept was taken for sheet no. 15 after ageing for 110 days at 70°C (8.05). A second intercept was then taken to measure the differences in the amount of ageing between this sheet and sheets no. 3 and no. 1, respectively. By intercepting the lines that demonstrate ageing at 80°C and 90°C at exactly the same point (8.05, for page no. 15), the differences in ageing at the different temperatures can be determined.

Since chemical reactions are known to proceed more quickly at high temperatures, it is not surprising that the change in optical properties was greater after ageing at 90°C than ageing at 80°C and 70°C. This indicates a faster degradation rate at 90°C than at lower temperatures.

The significant change of initial optical properties through the top six sheets and the gradual leveling off through the sheets below, seems to confirm earlier studies, indicating that volatile products, occurring in paper, accelerate cellulose degradation[3,13,14]. These products are able to escape from the top of a paper stack, whereas they remain trapped towards the centre of the stack, thereby accelerating the ageing of paper in the middle of the stack.

The fact that measurable differences between the top sheet and sheets no. 3 and no. 15, respectively, are slightly smaller at lower temperatures than at higher temperatures, suggests that diffusion might not play as significant a role at room temperature as has previously been thought. However, since not all optical properties followed this trend (brightness, for example, is an exception), and are generally very small, no conclusions can be drawn from these properties alone.

pH

Since acidity is the most significant factor that affects paper stability, measuring pH has been more commonly used for assessing paper degradation than optical properties. In this study, the pH shows generally the same trend as the optical properties but, while optical properties are only able to distinguish clearly between the top three sheets, pH demonstrates a clear difference up to the sixth sheet (Fig. 4). However, unlike optical properties, small differences in pH can still

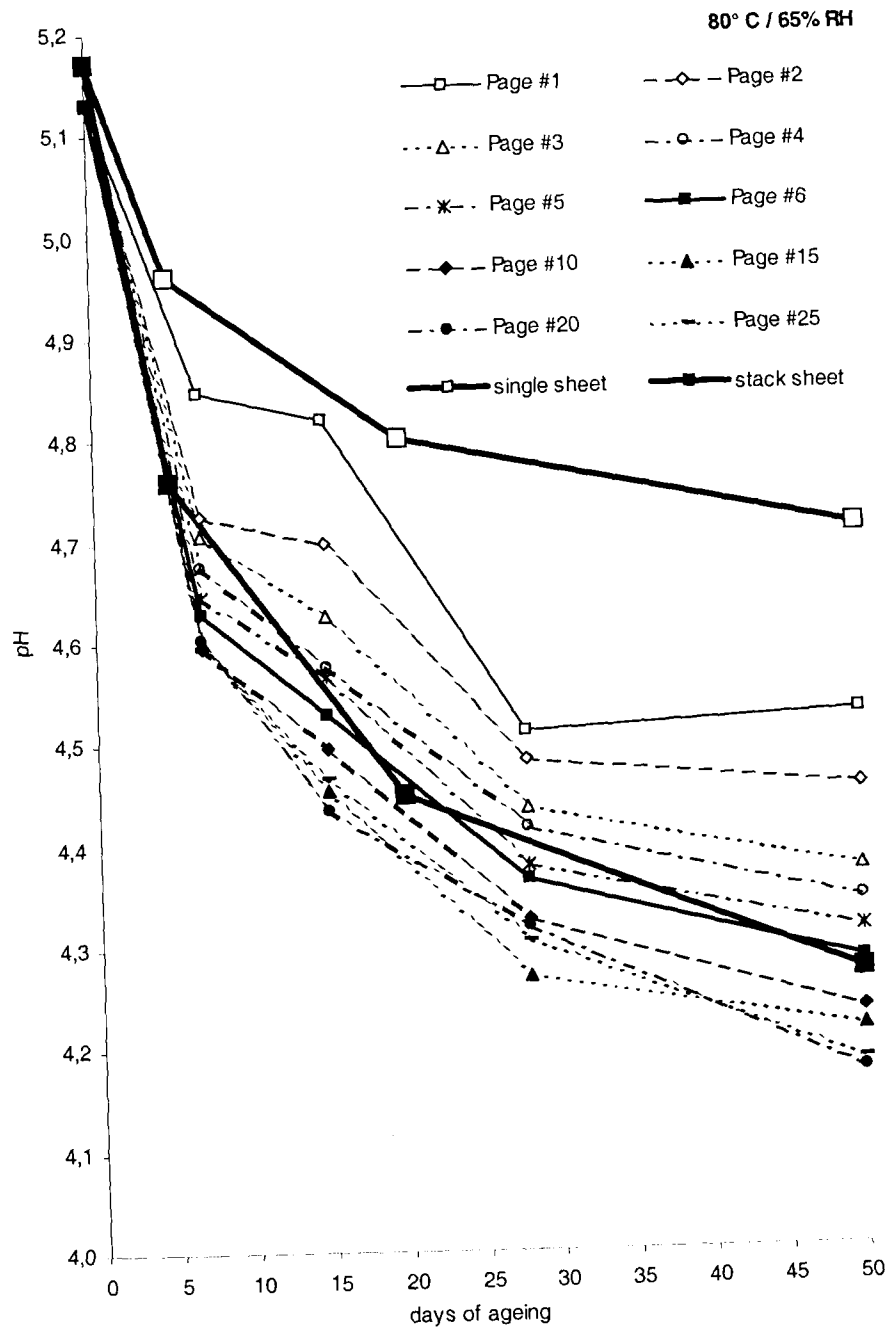

Fig. 4: pH vs ageing time at 80°C / 65% RH.

be observed between sheets no. 6 and no. 15. Below the sheet no. 15, the acidity level stays the same within the experimental error. In addition, the determination of pH not only reveals an increase in acidity for a paper sheet in a particular stack, but also suggests that some of the volatile products trapped inside a stack are acidic. As with the optical properties, the change in pH increases as the ageing temperature is increased.

The difference in pH at different temperatures measured between the top sheet and sheets no. 3 and no. 15, respectively, is more obvious than for the optical properties. The lower the ageing temperature, the smaller is the difference in pH between the top sheet and a sheet from the middle of the stack. Thus, the pH indicates that, the higher the ageing temperature, the more pronounced is the stack effect, i.e. the more a particular sheet will be influenced by its arrangement as part of a stack.

This fact can be further clarified by comparing the results of this study with pH measurements on the same paper used in another study currently being carried out at the Canadian Conservation Institute[8]. This study compares the difference in ageing between paper aged as single sheets and paper arranged as a stack, after ageing at 80°C and 65% RH. Direct comparison reveals a marked difference in pH between a sheet, aged individually by hanging it on clamps to avoid contact with adjacent sheets, and a sheet that has been part of a stack, even if open on top. The sheet aged as a single sheet is considerably less degraded than the top sheet of a stack (Fig. 4). Therefore, the diffusion of volatile products from a stack influences every sheet in the stack, even the top sheet that was able to interact, at least partially, with the environment in the ageing chamber.

As can be expected, the stack aged samples from the above-mentioned study gave similar results to the samples from the middle of a stack in this study at ageing conditions of 80°C and 65% RH (Fig. 4). In both cases, measurements were performed on sheets that had been aged in the centre of a stack.

Zero-span tensile strength

Although every single sheet used for zero-span tensile strength had been weighed prior to analysis, this test gave comparatively widely scattered results, as is typical. Therefore, no clear conclusions can be drawn with respect to possible diffusion through the stack. In addition, breaking length, as measured by zero-span tensile strength, is most sensitive for DP's below 700 to 800, i.e. it demonstrates distinct changes only after the sample is considerably degraded[15]. Obviously, the artificial ageing at 70°C and 80°C, respectively, did not cause enough changes in the given

time to be clearly identified with this test. However, zero-span tensile strength shows an increased rate of degradation with increased temperature in the ageing chamber and follows in this respect the same trend as the other properties discussed (Fig. 5).

DP

The degree of polymerization (DP), as determined on one sheet from the centre of each stack (no. 16), i.e. one sheet had been measured at every ageing condition and every interval, including the control stack, confirms phenomena previously seen with other properties such as optical properties, pH and zero-span tensile strength.

Since the degree of polymerization is a more sensitive indicator of cellulose degradation than the mechanical properties, DP values are used to determine the rate of degradation of cellulose (degradation rate constants)[16]. Fig. 6 shows a significant difference in the rate of degradation between the different accelerated ageing conditions. Degradation rates are higher at elevated temperatures than at lower temperatures.

Since only one sheet per stack was tested, no conclusions can be drawn from the DP data as to the diffusion rate throughout the stacks at the different ageing temperatures employed. However, since both physical and chemical tests can be used to determine the rate of deterioration, different studies in the past tried to correlate data obtained with zero-span tensile strength as a measure of fibre strength, and those obtained from viscosity measurements as a mean of cellulose degradation[15–18].

In fact, recent experiments by Zou et al.[19] and Gurnagul[20] do reveal a relationship between the fibre strength as measured by zero-span tensile strength and the degree of polymerization, since the average chain length of the cellulose molecules has a significant impact on the fibre strength as it ages. Therefore, extensive depolymerization of cellulose can produce significant losses in fibre strength. Further experiments by Zou et al.[16] confirm that the loss of fibre strength for a particular paper is uniquely determined by the extent of cellulose degradation.

It has been found that viscosimetric determinations are more sensitive during the initial stage of ageing but as the degradation proceeds tensile measurements become more sensitive[15]. However, a linear relationship between fibre strength and DP can be found by plotting zero-span tensile strength against the number of broken cellulose bonds (n), which is calculated as:

$$N = \frac{DP_0}{DP_t} - 1$$

where DP0 is the initial degree of polymerization, and DPt is the degree of polymerization at time t[21]. This relationship is shown in Fig. 7. As can be seen from this graph, there is a good correlation between zero-span tensile strength and the number of broken bonds for the paper examined.

Although the experiment did show a correlation between breaking length and the number of broken bonds, it is questionable whether the degree of polymerization can be inferred from zero-span tensile strength. There are two main reasons. The loss of mechanical properties is a consequence, but not a direct indication, of chemical degradation of cellulose[16]. Furthermore, zero-span tensile strength, as a measure of fibre strength, is less precise than the determination of the degree of polymerization. However, in an experimental setup such as the one in this study, where only one paper is examined after exposure to various accelerated ageing conditions, a baseline could be determined on one sample, correlating degree of polymerization and zero-span tensile strength. From this, DP values for every other sample in the experiment could be estimated using zero-span tensile strength data.

Conclusions

This project examined the ageing behaviour of acidic, fully bleached kraft paper. The paper was aged in stacks, which were open on top, at three different ageing conditions using controlled elevated temperatures and relative humidity. The results showed clearly that volatile products are able to escape from the top of the stack, whereas they remain trapped towards the centre, thereby accelerating the ageing of papers in the middle of the stack. This was found to be particularly true for the first six sheets of a stack, aged at 70° C / 61% RH, 80° C / 65% RH, and 90° C / 69% RH. Furthermore, a measurable difference between the sheets is apparent at an early stage of ageing.

The test methods employed in this project detected different states of deterioration under different ageing conditions, mainly among the top six sheets. Below those, the study proved this paper to age similarly to papers aged in closed stacks. However, compared to papers aged as single sheets, the top sheets here showed a marked difference, indicating a significant stack effect during artificial ageing, i.e. the diffusion of volatile products through the top influences every sheet of the stack.

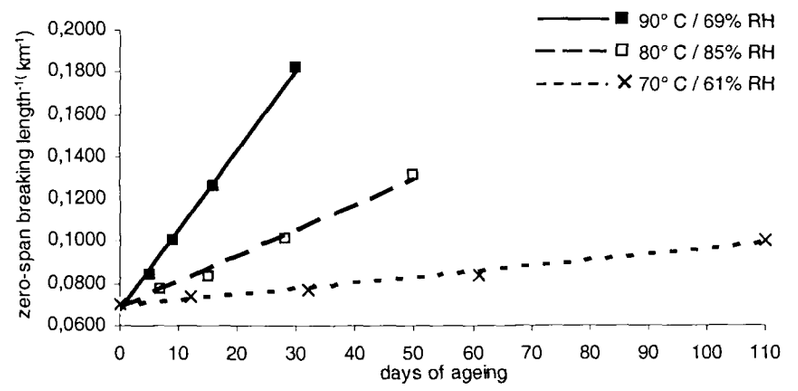

Fig. 5: Rate of degradation (Zero-span breaking length; page #15.)

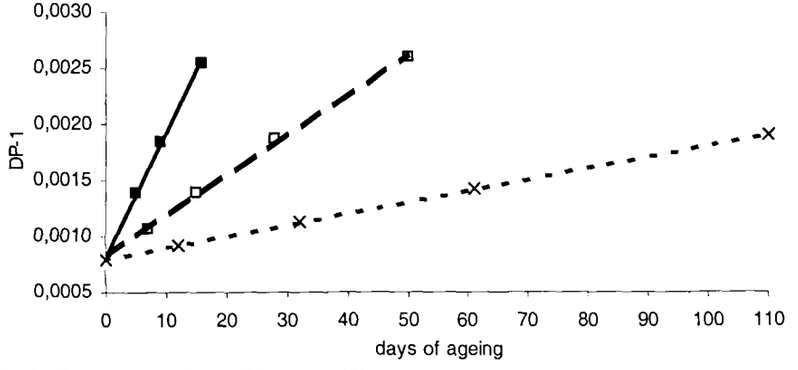

Fig. 6: Rate of degradation (DP; page #16).

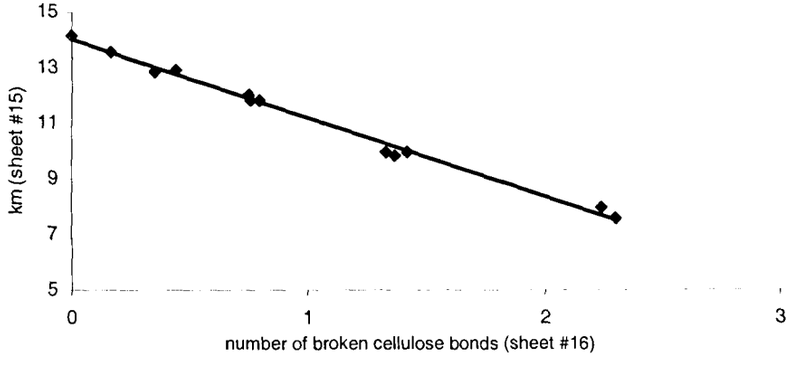

Fig. 7: Zero-span vs number of broken bonds.

In addition, the experiment indicated that mechanisms seen at high temperatures are not as pronounced at lower temperatures, therefore suggesting that the diffusion effect seen at high temperature ageing may only play a minor role in natural ageing.

Furthermore, this project investigated the correlation between the degree of polymerization and zero-span tensile strength as a measure of fibre strength in order to find a simplified method for the determination of fibre degradation by means of a physical testing method. The results revealed a good correlation between breaking length and degree of polymerization. For experiments such as this, where only one paper was used at different ageing conditions and a good baseline has been determined for the degree of polymerization versus zero-span tensile strength, it is possible to estimate the degree of polymerization for all samples. However, it should be kept in mind that, due to the lack of significant change in zero-span tensile strength until a critical DP level (700–800) has been reached, this method can only give estimates of cellulose degradation.

Future research should involve the determination of the degree of polymerization in a similar experimental setup for every sheet of a stack to clarify whether or not differences seen between sheets at different ageing conditions are significant. The study should also include paper aged as single sheets in order to determine how much the top sheet of a stack is influenced by the diffusion of volatile products from the centre of the stack. Further research is also desirable regarding the nature of these volatile compounds. The research should be directed towards determining whether those products are inherent in paper or represent actual degradation products evolving from natural or artificial ageing.

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SUMMARIES

Migration of Volatile Compounds through Stacked Sheets of Paper during Accelerated Ageing. Part II: Variable Temperature Studies.

In order to investigate the effects of diffusion during paper ageing an alum-rosin sized, fully bleached, kraft paper was aged in stacks, at three different conditions, and four different intervals. The stacks were open at the top to allow diffusion of volatile products to take place. Tests, including grammage, moisture content, brightness, yellowness, L*a*b*, zero-span tensile strength, pH and the degree of polymerization show less change in paper properties at the top of the stack than in the centre. This indicates a diffusion effect where volatile compounds escape from the paper at the top of the stack, but remain trapped towards the centre, where more severe degradation occurs. More work is required to determine if this diffusion effect is the same at ambient conditions as it is at the elevated temperatures used in this study.

Migration de composés volatiles dans une pile de papier au cours du vieillissement accéléré. Partie II : Etudes à différentes températures de vieillissement.

Afin de vérifier si au cours du vieillissement les composés volatiles se diffusaient dans la pile de papier on a procédé au vieillissement accéléré de piles de papier complètement blanchi fait à base de cellulose et collé à la résine d'alun dans trois conditions différentes et à quatre intervalles différents. Les piles de papier n'avaient pas de couvercle en haut pour permettre aux substances volatiles de s'échapper. Des mesures ont été faites sur le grammage, le pourcentage d'humidité, la blancheur, le jaunissement, les composantes trichromatiques selon le système CIE-L*a*b*, la résistance à la traction zéro, le pH et le degré de polymérisation. Ces mesures ont démontré que les propriétés des feuilles de papier situées en haut de la pile avaient moins changé que celles des feuilles situées au centre. Ceci indique qu'une diffusion des substances volatiles a lieu et que certaines s'échappent par le haut dans l'atmosphère environnante alors que d'autres se concentrent vers l'intérieur de la pile et y continuent leur travail de dégradation du papier. Des analyses complémentaires sont nécessaires pour pouvoir déterminer si l'effet de diffusion reste le même dans des conditons normales de température ambiante que lors de températures plus élevées.

Die Wanderung von flüchtigen Bestandteilen durch Papierstapel bei der beschleunigten Altzerung. Teil II: Untersuchung zu verschiedenen Alterungstemperaturen.

Um festzustellen, ob die flüchtigen Bestandteile bei der Alterung in einem Papierstapel wandern und ihn durchdringen, wurde ein alaungefällt harzgeleimtes Papier aus gebleichtem Sulfatzellstoff in Stapeln bei drei verschiedenen Bedingungen für jeweils vier verschiedene Zeiträume beschleunigt gealtert. Die Stapel waren oben ohne Abdeckung, so daß die flüchtigen Bestandteile austreten konnten. Gemessen wurden Flächengewicht, Feuchtegehalt, Weißgrad, Vergilbung, die Farbwerte nach dem CIE-L*a*b*-System, Nullbruchkraft, pH und Polymerisationsgrad. Es zeigte sich, daß die Blätter oben im Stapel eine geringere Veränderung dieser Werte erfuhren als die im Innern. Dies ist ein Anzeichen dafür, daß die flüchtigen Bestandteile im Stapel wandern und an seiner Oberfläche in die umgebende Luft entweichen. Im Innern bewirken sie einen ver-

stärkten Abbau des Papiers. Weitere Untersuchungen müssen zeigen, ob dieser bei erhöhten Temperaturen beobachtete Effekt auch bei Raumtemperatur stattfindet.

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Anna Bülow
De Montfort University
Faculty of Applied Sciences
Department of Chemistry
The Gateway
Leicester LE1 9BH
U.K.

Paul Bégin
Canadian Conservation Institute
1030 Innes Road
Ottawa, Ontario, Canada
K1A 0M5

Henry Carter
Augustana University College
4901 46 Avenue
Camrose, Alberta, Canada
T4V 2R3

Thea Burns
Queen's University
Art Conservation Program
Kingston, Ontario, Canada
K7L 3N6

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Iron-Gall Ink Corrosion: A Compound-Effect Study

by MARGA A.P.C. DE FEBER, JOHN B.G.A. HAVERMANS & PETER DEFIZE

INTRODUCTION

For about 2000 years, since the Romans, iron-gall inks have been used reaching a peak in popularity during the late Middle Ages. It was a popular ink for documentation, e.g., the Dutch *Vereenigde Oostindische Compagnie* (VOC) archives, and for ink drawings, e.g., by Rembrandt and van Gogh.

However, now serious problems are occurring: the iron-gall ink literally eats its way through the paper, which eventually results in loss. At present, this phenomenon, called iron-gall ink corrosion, is not yet fully understood and gives rise to many questions. The origin of the destructive mechanism by iron-gall inks is a result of a complex overlapping of different processes. The complex composition of the inks and the environmental and storage conditions, among other things, play an important role in this context[1]. Historical iron-gall inks consist of various compounds, however basic ingredients are iron(II)sulphate and gallnut extracts. These extracts contain gallotannins which, together with iron(III)ions, form the actual ink complex. Iron(III)ions are formed by air oxidation of iron(II)ions. Gum Arabic was also frequently added in order to stabilise the ink particles and to achieve a better adhesion to the paper. According to the literature, the molecular ratio of iron(II)ions and gallic acid in the ink complex should be equal to 1. This means that in order to obtain a stable ink, the same ratio should be applied when composing the ink[2].

However, comparison of historical ink recipes shows that most inks contained a surplus of iron(II)sulphate. Neevel[2] calculated the molar ratios of iron(II)sulphate and tannin in over a hundred 15th to 19th century historical recipes collected by various researchers[3,4]. This analysis shows that nearly all inks contained more iron than was needed for the formation of the complex. The surplus of iron(II) ions is not completely oxidised and will therefore remain in the paper. Even after centuries, these ions can still be present. From the currently known mechanisms acting in the iron-gall ink corrosion process, we know that the oxidative degradation of cellulose is catalysed by iron(II)ions: the so-called Fenton-reaction. In this reaction, very reactive hydroxyl radicals are formed. Formation of these radicals is seen as one of the most important causes of the oxidative degradation of cellulose[5,6]. Besides the contribution of the iron(II) towards the accelerated deterioration, however, the roles of both other main compounds remain unknown. Therefore, our research aims to determine what contribution each component of iron-gall inks make to iron-gall ink corrosion. The research was carried out using the design of experiments (DOE) technique looking at the effects of varying concentrations of the main components of iron-gall ink.

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EXPERIMENTAL SET UP

Paper materials

For this project papers originating from the EC STEP CT90-0100 project[7] were used These papers were made specially for this project and therefore production process, composition and ageing behaviour are well defined. The papers used were made of bleached-sulphite, softwood cellulose (>99%) and do not contain sizing or fillers, which are known to influence the reactions between inks and carrier material[1]. The paper chosen was also free of lignin since it is known from the literature that lignin might function as an anti-oxidant. Lignin reacts with the hydroxyl radicals formed in the Fenton reaction, and therefore can break the oxidative degradation process. This was confirmed by experimental work of Berkhout[8].

Inks

According to the literature, the most frequent molar ratio between iron(II) and tannin equals 5.5[2]. Therefore a reference ink was composed using the three main components. The ink composition and chemical manufacturers are listed as follows. $FeSO_4 \cdot 7H_2O$ iron(II)sulphate (pro analyse, Brocacef (The Netherlands), 0.15 mol/l, hydrolysable tannic acid (pro analyse, Fluka Chemie, Germany), 0.027 mol/l) and gum Arabic (Verfmolen de Kat, Zaandam, The Netherlands), 31.4 g/l in distilled water. The gum Arabic was identified by means of infrared spectroscopy. Here the specific carbohydrate compounds were identified. Varying the amounts of the three main components led to the subsequent manufacture of different inks. For each component a *high* and *low* level were chosen by doubling and dividing in half the concentration of the component in the refer-

ence ink. In total 8 (= 2^3) different inks can be composed in this way, these are presented in Table 1. The reference ink is ink 9.

Furthermore two additional inks were composed with molar ratios iron(II): annic acid of 1 and smaller (ink 10 and 11 respectively). This was done in order to check the theory that a surplus of iron(II)ions is mainly responsible for the iron-gall ink decay process. For statistical purposes also a "centre point" ink was composed with concentrations exactly between the high and low level of each component (ink 12).

Ageing

The different inks were applied to the paper materials by means of a Hewlett Packard 7475A plotter according to the pattern in Fig. 1.

After application of the ink, all materials were subjected to accelerated ageing using a climate of 90 °C and 50% relative humidity. As a reference blank paper sheets were also tested. Samples were taken before and after 3 after 3, 6, and 12 days. After a reconditioning period of at least 24 hours (at 23 °C and 50% RH), the tensile strength of the samples was measured according to the ISO standard 1974[9]. We assume that the decrease in tensile strength can be considered as a measure of paper degradation by iron-gall ink corrosion. Interpretation of the results was made using applied statistics. The software package chosen for this purpose was Design-Ease for Windows[10].

RESULTS AND DISCUSSION

Experiments

In Fig. 2 the experimental results are presented for 4 applied inks. The x-axis shows the ageing time, while the tensile strength in N/m is given on the y-axis. From this Fig. it can be seen that the decay process develops by an exponential process. High regression coefficients (> 0.95) were obtained by fitting exponential curves through the measured values.

We see that the decrease in tensile strength increases when this molar ratio increases. This is in accordance with the assumption that the molar ratio iron(II)-tannic acid influences the iron-gall ink corrosion process. However, from Fig. 2 it is also obvious that, even with a molar ratio of 1, the decay process is still occurring (although to a lesser extent). This can be explained, for example, by the acidity of the ink (pH about 4).

Table 1: Composition of the tested inks.

Ink	Fe(II)SO4	Tannic acid	Gum Arabic	Ink	Fe(II)SO4	Tannic acid	Gum Arabic
1	low	low	low	5	high	low	High
2	low	low	high	6	high	low	Low
3	low	high	high	7	high	high	Low
4	low	high	high	8	high	high	High

Reference (ink 9): $Fe(II)SO_4$ 0.15 mol/l; Tannic acid: 0.027 mol/l; Arabic gum 34.4 g/l

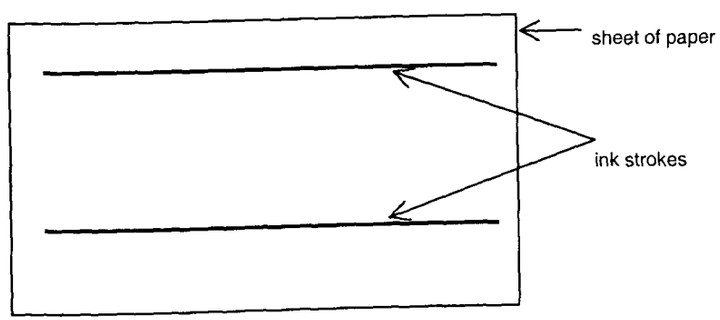

Fig. 1: Ink pattern applied in iron-gall ink corrosion experiments.

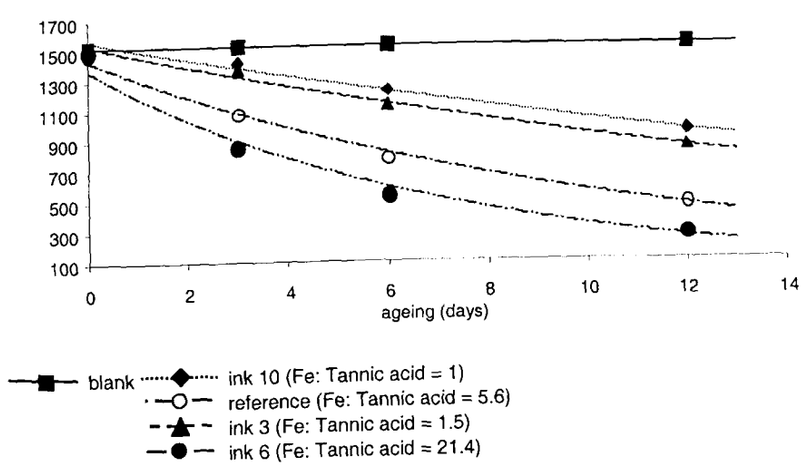

Fig. 2: An example of the obtained results of the iron-gall ink DOE-experiments: the measured tensile strength in N/m is given on the y-axis and the ageing time in days is given on the x-axis.

In Fig. 3 the decrease in tensile strength is presented as a function of the molar ratio iron(II)-tannic acid.

Statistics

All experimental results were evaluated using Design-Ease for Windows in order to determine the separate influences of the three main components[10]. The results obtained are summarised in Table 2. No significant effects could be determined before ageing, which is logical since at this time the decay process has not yet started.

From the results, we see that iron(II)sulphate dominates in the iron-gall ink corrosion process, and that the tensile strength will decrease when the iron(II)sulphate concentration increases. The effects of tannic acid and gum Arabic are opposite and therefore less dominating. Thus when their concentration increases, the tensile strength will also increase.

As 12 different ink compositions were investigated, it was also possible to examine so-called "interaction" effects between the used components (e.g. the supposed interaction between iron(II) and tannic acid). However, based on our results these interactions could not be determined statistically possibly due to the standard error found in the tensile measures. However, this does *not* mean that they do not exist. It only indicates that we were just not able to show that they do exist. Further research using other analytical methods might give a more certain answer on this question.

Figs. 4 A–C summarise the results of the statistical interpretation. They show the decrease in tensile strength as a consequence of the effect of each main component. To determine the overall tensile strength decrease, the Figs. can be combined (dependent on the level (high/low) of the component).

CONCLUSIONS

Based on the results obtained, the following conclusions can be drawn:

- All three main components do have an influence on the iron-gall ink corrosion process. This effect can be seen after a period of 3 days accelerated ageing.
- Iron(II)sulphate is the main cause of the iron-gall ink corrosion process.
- The higher the concentration of iron(II)sulphate in the ink, the more iron-gall ink corrosion will take place.

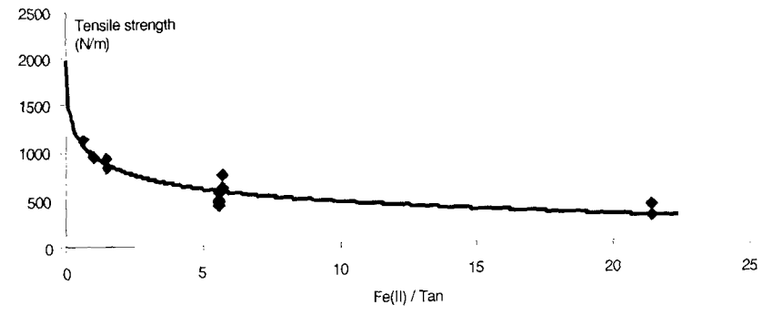

Fig. 3: Tensile strength as a function of molar ratio iron(II) : tannic acid.
Note: The quality of the logarithmic plot was demonstrated by its correlation coefficient, $R^2 = 0.8727$.

Table 2: Measured effects of the three main components on tensile strength (based on 12 inks)

	3 days			6 days			12 days		
	Low	High	Δ	Low	High	Δ	Low	High	Δ
Fe(II)SO4	1325	965	360	1043	681	362	755	378	377
Tannic acid	1070	1219	149	757	966	209	445	688	243
Gum Arabic	1065	1225	160	776	948	172	507	626	119

- The effects of tannic acid and gum Arabic are opposite, thus slowing down the deterioration.
- The above means that the "worst-case ink" is composed by mixing a high level of iron(II)sulphate and low levels of tannic acid and gum Arabic (ink 6). This conclusion is affirmed by the experiments.
- No "interaction effects" could be determined by the performed experiments. However it was shown that iron-gall ink corrosion increases when the molar ration iron(II)-tannic acid increases.

ACKNOWLEDGEMENT

We would like to take the opportunity of thanking the Dutch Ministry of Economic Affairs, the Dutch State Archives, the Boymans Van Beuningen Museum, Hoekloos b.v., Shell Research and Technology Centre, Twin Holland Filtration b.v., and Weiss Enet b.v. for supporting this research. Without the funding of these organisations this project would not have been possible.

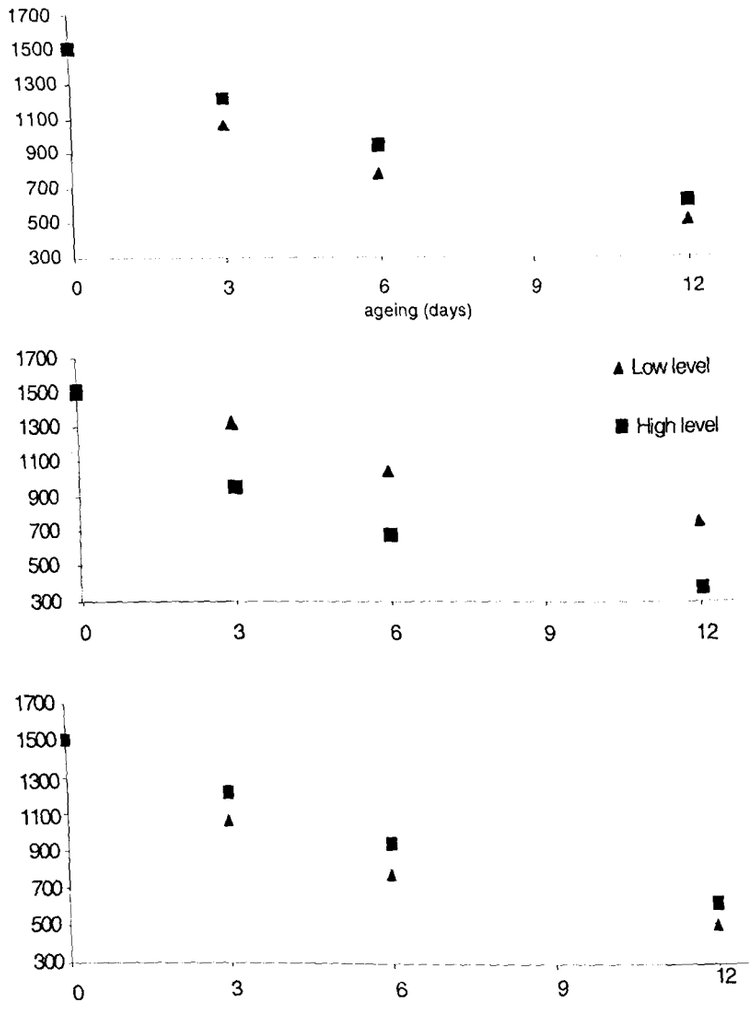

Fig. 4: The Tensile strength in N/m vs. ageing time in days: Effect of the concentration level of iron(II)sulphate on the decrease in tensile strength after 12 days of ageing at 90 °C and 50% RH.
A (upper graph): high level 0.3 mol/l, low level 0.07 mol/l FeSO4. B (middle graph): high level 0.05 mol/l, low level 0.014 mol/l tannic acid. C (lower graph): high level 62.8 9/l, low level 15.7 g/l gum Arabic.

SUMMARIES

Iron-Gall Ink Corrosion: A Compound-Effect Study

By means of design of experiments (DOE) the role of varying concentrations of the main components in iron-gall ink were investigated. The main components in the inks used were iron(II)sulphate, tannic acid and gum Arabic. In total 12 different ink compositions were made and plotted as a line on bleached softwood sulphite paper. By applying accelerated ageing and measuring the tensile strength, the contribution of each component towards the accelerated ageing of paper was calculated. It was concluded that all three main components do have an influence on the iron-gall ink corrosion process. This effect can be seen after a period of 3 days accelerated ageing at 90°C and 50% relative humidity. The presence of iron(II)sulphate is dominant in the iron-gall ink corrosion process while tannic acid and gum Arabic are opposing, thus slowing down the deterioration.

Corrosion de l'encre gallique ferrée : Une étude sur la fonction des différents composés de l'encre

Des analyses ont été faites d'après la méthode DOE (design of experiments) afin de déterminer le rôle joué par les différentes concentrations des éléments essentiels entrant dans la composition de l'encre gallique ferrée. Ces éléments essentiels sont le sulfate(II) de fer, l'acide tannique et la gomme arabique. 12 encres de concentrations différentes ont été préparées et répandues par ligne sur du papier blanchi fait à base de pâte au sulfite. Ensuite des mesures ont été faites pour déterminer dans quelles proportions les éléments cités ont contribué à la modification de la résistance à la traction après le vieillissement accéléré. Il s'est révélé que tous les trois contribuent aux processus de dégradation sous la forme de tache de rouille, ce qui apparaît déjà après 3 jours de vieillissement à une température de 90°C et un taux d'humidité relative de 50 %. Le sulfate de fer accélère le processus de la rouillure de l'encre alors que l'acide tannique et la gomme arabique le freinent.

Tintenfraß: Eine Studie zur Funktion der verschiedenen Komponenten von Eisengallustinte

Es wurde die Bedeutung verschiedener Konzentrationen der wesentlichen Komponenten von Eisengallustinte, nämlich Eisen(II)sulfat, Tannin und Gummi Arabicum, nach der DOE-Methode (design of experiments) untersucht. 12 in diesen ihren Konzentrationen verschiedene Tinten wurden als Linie auf Papier aus gebleichtem Sulfitzellstoff aufgetragen. Dann wurde gemessen, in welchem Ausmaß die genannten Komponenten nach beschleunigter Alterung zur Veränderung der Bruchkraft beitragen. Es zeigte sich, daß alle drei zu den Abbauvorgängen beitragen, die als "Tintenfraß" in Erscheinung treten, was bereits nach dreitägiger Alterung bei 90° C und 50% rF deutlich wird. Das Eisensulfat befördert den Tintenfraß, während Tannin und Gummi Arabicum ihn verlangsamen.

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Marga A.P.C. de Feber
John B.G.A. Havermans *
TNO Industrial Technology
Paper Production Technology
PO Box 6031
2600 JA Delft
The Netherlands
Phone +31.15.2696762 fax +31.15.2696511
e-mail j.havermans@ind.tno.nl

Peter R. Defize
TNO Institute of Applied Physics
Applied Statistics
PO Box 155
2600 AD Delft
The Netherlands
Phone +31.15.2692136

* Author to whom the correspondence should addressed

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Application of Seven Borane Complexes in Paper Conservation

by MARINA BICCHIERI, FRANCESCA MARIA SEMENTILLI & ARMIDA SODO

Introduction

The care of cultural heritage has an essential contribution to society for both cultural and business reasons.

The role of scientists is very important in all the fields connected with protection, restoration and use of cultural heritage.

For these reasons the Italian CNR set up a special project, divided into five sub-projects, covering all fields related to the safeguard of cultural heritage.

The scientific approach to paper conservation concentrates on cellulose and the study of cellulose degradation, in order to choose the best conservation path.

It is well known that all the degradation agents exert a synergetic action: the combined action of two different degrading compounds being greater than the sum of the two single agents.

A lot of work has been carried out to combat acidity: aqueous and non-aqueous solutions, spray compounds and mass-deacidification are in fact now available. In contrast, only a few products can be used to counter oxidation.

Oxidation is a sly process, leading to the loss of paper strength, to its yellowing (if conjugated double bonds are formed in the cellulose chain) and to the increase of acidity in the paper (if carboxyl groups are formed). The obvious procedure to hinder oxidation is the reduction of the oxidised groups. Unfortunately, only a few compounds can be used on paper, without damage to the fibre structure and the inks.

During reduction, hydrogen evolves and, if the reaction is too fast (that is a lot of hydrogen is produced in a very little time), the fibre wall could be broken. This effect has been observed and confirmed by conservators when they have used sodium borohydride as a reducing agent. Furthermore, if the pH of solutions chosen is too high, alkaline hydrolysis, or peeling, or β-alkoxy elimination could

* CNR = Consiglio Nazionale delle Ricerche (National Research Council)

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occur, leading to the breaking of the cellulose chain. To minimise these negative effects mild, "slow" and not very alkaline reducing agents should be chosen.

In the last few years borane *tert*-butylamine complex (TBAB) has been used in the I.C.P.L. laboratories of Rome, as a mild reagent in reducing carbonyl groups in oxidised paper[1-6]. However, we would like to offer conservators a greater choice of products, which they could apply in different solvents for different conservation needs. For this reason we decided, within the CNR Special Project "Cultural Heritage", to set up an investigation into different reducing products for paper conservation and to test the possibility of simultaneous non-aqueous deacidification and reduction.

EXPERIMENTAL

Materials

- Whatman n°1 chromatography paper (pure cotton cellulose paper);
- potassium metaperiodate (KIO_4) 0.015M water solution at pH=5.0 by addition of 0.1M hydrochloric acid;
- borane ammonia complex (AB);
- borane N,N-diisopropylethylamine complex (DIPEAB);
- borane dimethylamine complex (DMAB);
- borane morpholine complex (MB);
- borane *tert*-butylamine complex (TBAB);
- borane triethylamine complex (TEAB);
- borane trimethylamine complex (TMAB).

Technical and safety data of the studied borane complexes are reported in the Appendix. Aqueous and non-aqueous solutions were all prepared at 0.2M concentration. Borane complexes were also characterised by Raman spectroscopy[7].

Preparation of samples

Three sets of samples were prepared:

- untreated Whatman n°1 chromatography paper;
- oxidised Whatman n°1 chromatography paper;
- oxidised-reduced Whatman n°1 chromatography paper. Reduction treatments for this set of samples were carried out two days after oxidation.

Table 1: Solubility and pH values for aqueous solutions of reducing agent.

borane complex	solubility in water	pH
ammonia (AB)	very soluble in cold water	9.08
N,N-diisopropylethylamine (DIPEAB)	liquid compound, air sensitive, slightly miscible with water (emulsion is obtained)	10.37
dimethylamine (DMAB)	soluble in cold water	9.05
morpholine (MB)	very soluble in cold water	8.80
tert-butylamine (TBAB)	soluble after slight warming	9.10
triethylamine (TEAB)	liquid compound slightly miscible with water (emulsion is obtained)	10.00
trimethylamine (TMAB)	soluble only after warming. By cooling a gel begins to be formed	8.32

Table 2: Solubility of borane complexes in organic solvents.

solvent complex:	AB	DIPEAB*	DMAB	MB	TBAB	TEAB*	TMAB
n-hexane	6	1	6	6	6	6	5
petroleum ether	6	1	6	6	6	6	5
toluene	6	1	5	4	3	1	3
diethyl ether	6	1	6	6	3	6	5
chloroform	5	1	5	5	5	1	1
ethylene chloride	5	1	5	5	5	1	1
methylene chloride	5	1	5	6	5	1	1
1,1,1, trichloro ethane	5	1	5	5	5	1	1
ethyl alcohol	1	2	5	7	1	1	7

1 very soluble
2 very soluble, but partially decomposes
3 soluble
4 soluble by warming
5 slightly soluble
6 insoluble
7 decomposes
* liquid/liquid solutions

Samples were oxidised by immersion in potassium metaperiodate (KIO_4) 0.015M for 15 minutes, followed by 2 immersions in distilled water for 5 minutes. Reduction was carried out by immersion in the prepared solutions for 60 minutes. The papers were then washed twice for 5 minutes in the same solvent used to make up the solution of the borane compound. Untreated papers were used as a reference sample; oxidised papers simulated an ancient document and the reduction of oxidised papers were performed to test the effectiveness of the reducing treatment.

Table 1 reports the solubility and the pH of each aqueous solution of the reducing agent. Table 2 contains the solubility of the reducing agent in different solvents. The solubility tests were carried out to find non-aqueous applications of the reducing treatment. Table 3 and Figs. 1 and 2 report the carbonyl content of

Table 3: Aqueous reduction treatments of unaged samples.

borane complex	water content (%)	carbonyl content (mmoles per g100 paper)	reduction effectiveness (%)
none (untreated paper)	4.95	0.50 ± 0.03	-
none (oxidised paper)	7.62	4.43 ± 0.74	-
ammonia (AB)	4.82	0.61 ± 0.12	86.2
N,N-diisopropylethylamine (DIPEAB)	8.22	0.61 ± 0.07	86.2
dimethylamine (DMAB)	8.15	0.98 ± 0.10	77.9
morpholine (MB)	5.07	1.31 ± 0.11	70.4
tert-butylamine (TBAB)	9.86	0.51 ± 0.08	88.5
triethylamine (TEAB)	8.89	1.45 ± 0.15	67.3
trimethylamine (TMAB)	6.35	1.49 ± 0.09	66.4

the papers treated with the seven tested reducing agents in aqueous solution and the effectiveness of the treatments. All values were corrected by the water content of paper. From solubility data and effectiveness of reducing reaction in water, we chose to test, for non-aqueous applications the following borane complexes: ammonia, N,N-diisopropylethylamine, *tert*-butylamine, triethylamine and trimethylamine. N,N-diisopropylethylamine borane complex was soluble in all the solvents considered in this work, but, due to the residual odour it left on the paper, is not a favoured option. However, for completeness we decided to test its properties anyway with a few solvents (ethanol, diethylether and n-hexane).

All compounds were tested in ethanol. The other solvents were chosen as a function of their toxicity: if possible the less non-polar solvent was employed. Organic solutions of reducing agent were prepared at the same 0.2M concentration as that of aqueous treatments. Results are reported in Table 4. In Fig. 3 the effectiveness of all non-aqueous treatments are shown.

The paper samples (oxidised and oxidised-reduced) treated with aqueous solutions and the untreated, used as a reference, were artificially aged for 14 and 28 days at 80°C 65% RH. Tables 5 and 6 report the chromaticity co-ordinates in the L*a*b* space and the carbonyl content as a function of the ageing period respectively. The effectiveness of aqueous reduction treatments, as a function of the ageing period, is plotted in Fig. 4.

Conclusions

All the tested reducing agents gave very good results when used in aqueous solutions (Table 3).

Table 4: Reduction treatments of unaged samples.

borane complex	carbonyl content (mmoles per g100 paper)	reduction effectiveness (%)
	Ethanol	
none (oxidised paper)	4.43 ± 0.74	-
AB	1.02 ± 0.15	77.0
DIPEAB	2.94 ± 0.22	33.6
TBAB	1.41 ± 0.12	68.2
TEAB	3.34 ± 0.33	24.6
	diethylether	
none (oxidised paper)	4.43 ± 0.74	-
DIPEAB	4.10 ± 0.33	7.5
TBAB	3.09 ± 0.25	30.2
	toluene	
none (oxidised paper)	4.43 ± 0.74	-
TBAB	1.80 ± 0.09	59.4
TEAB	3.21 ± 0.29	27.6
	n-hexane	
none (oxidised paper)	4.43 ± 0.74	-
DIPEAB	4.35 ± 0.41	1.8
	Chloroform	
none (oxidised paper)	2.05 ± 0.07	-
TEAB*	1.56 ± 0.25	23.9
TMAB	1.10 ± 0.05	46.3
	ethylene chloride	
none (oxidised paper)	2.05 ± 0.07	-
TEAB**	1.76 ± 0.32	14.1
TMAB	1.87 ± 0.17	8.9
	methylene chloride	
none (oxidised paper)	2.05 ± 0.07	-
TEAB	1.90 ± 0.02	7.3
TMAB	1.81 ± 0.07	11.7
	1,1,1 trichloro ethane	
none (oxidised paper)	2.05 ± 0.07	-
TEAB	2.04 ± 0.01	0.5
TMAB	1.92 ± 0.04	6.3

* The reduction treatments are inhomogeneous, leading to two distribution of carbonyl (respectively: 1.40 ± 0.02 and 1.73 ± 0.03 mmoles per 100 g of paper)

** The reduction treatments are inhomogeneous, leading to two distribution of carbonyl (respectively: 1.95 ± 0.04 and 1.46 ± 0.02 mmoles per 100 g of paper)

In organic solvents only AB and TBAB, the former in ethanol the latter in ethanol and in toluene, are able to exert their reducing power. The other reducing agents, except for TMAB in chloroform, are not active (Table 4).

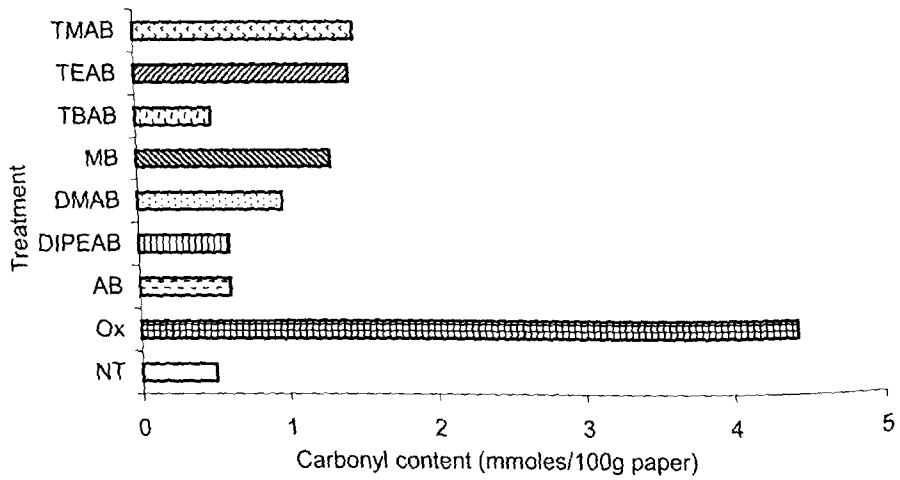

Fig. 1: Carbonyl content after aqueous reduction treatments

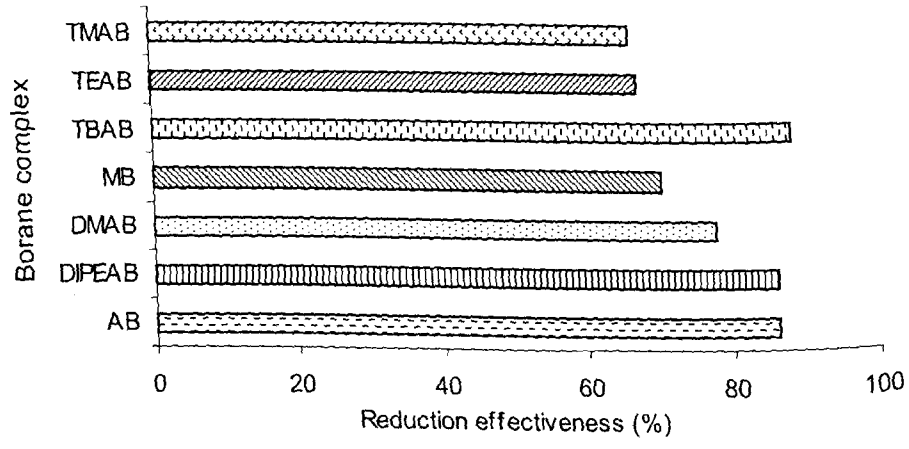

Fig. 2: Effectiveness of aqueous reduction treatments

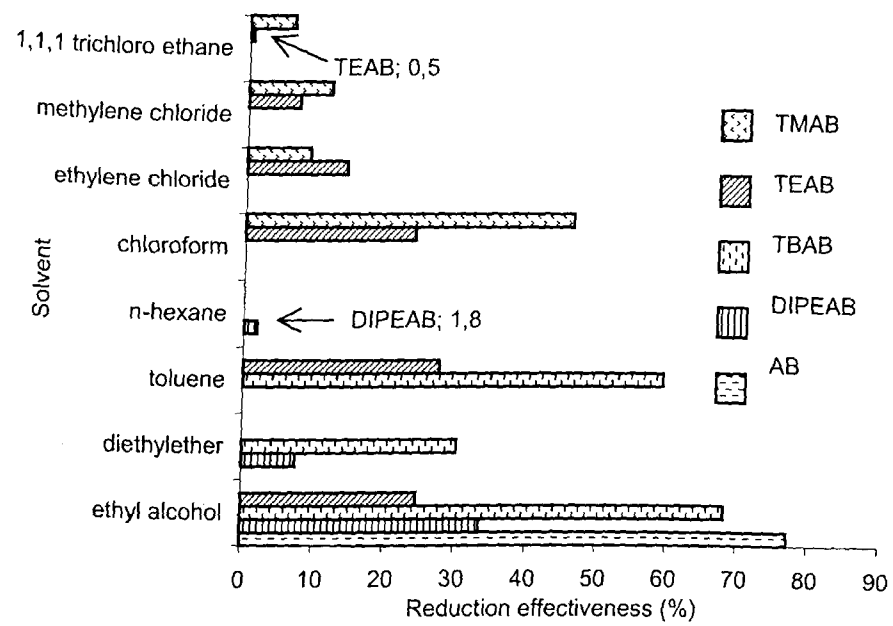

Fig. 3: Effectiveness of non-aqueous reduction treatments

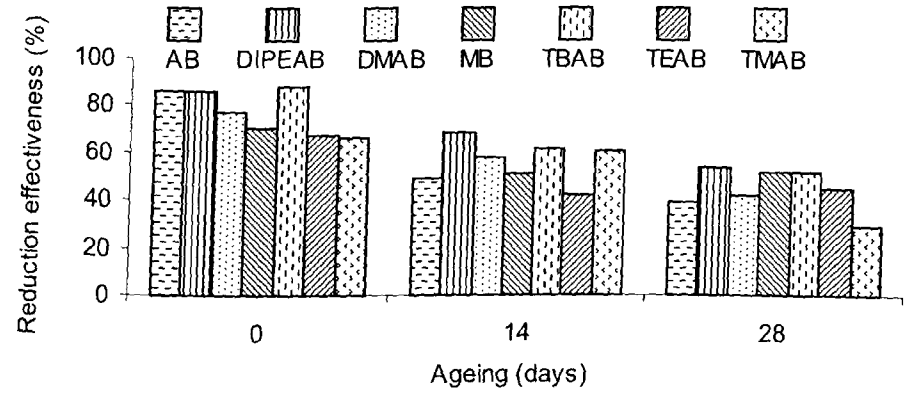

Fig. 4: Effectiveness of aqueous reduction treatments as a function of the ageing period.

Table 5: Chromaticity co-ordinates as a function of the ageing period.

borane complex		0 days	14 days	Δ 14-0	28 days	Δ 28-0
none (untreated samples)	L*	95.70	95.46	-0.24	94.77	-0.93
	a*	-0.08	-0.27	-0.19	+0.34	+0.42
	b*	+0.16	+1.16	+1.00	+4.09	+3.90
none (oxidised samples)	L*	95.71	93.50	-2.21	93.51	-2.20
	a*	-0.08	+0.05	+0.13	-0.32	-0.24
	b*	+0.16	+5.29	+5.13	+6.74	+6.60
ammonia (AB)	L*	95.75	95.74	-0.01	95.20	-0.55
	a*	-0.08	-0.14	-0.06	-0.02	+0.06
	b*	+0.16	+1.41	+1.25	+2.76	+2.60
N,N-diisopropylethylamine (DIPEAB)	L*	95.71	95.49	-0.22	94.92	-0.79
	a*	-0.08	-0.32	-0.24	-0.09	-0.01
	b*	+0.16	+2.80	+2.64	+4.05	+3.90
dimethylamine (DMAB)	L*	95.70	95.33	-0.37	93.74	-2.00
	a*	-0.08	-0.20	-0.12	+0.06	+0.14
	b*	+0.16	+2.86	+2.70	+4.38	+4.20
morpholine (MB)	L*	95.75	95.22	-0.53	94.07	-1.70
	a*	-0.08	-0.17	-0.09	+0.09	+0.17
	b*	+0.16	+3.13	+2.97	+4.69	+4.50
tert-butylamine (TBAB)	L*	95.75	95.62	-0.13	94.56	-1.20
	a*	-0.08	-0.13	-0.05	-0.06	+0.02
	b*	+0.16	+1.92	+1.76	+2.98	+2.80
triethylamine (TEAB)	L*	95.72	94.36	-1.36	93.18	-2.50
	a*	-0.08	-0.19	-0.11	+0.18	+0.26
	b*	+0.16	+4.76	+4.60	+5.93	+5.80
trimethylamine (TMAB)	L*	95.75	94.09	-1.66	92.46	-3.30
	a*	-0.08	-0.14	-0.06	+0.44	+0.52
	b*	+0.16	+5.08	+4.92	+7.25	+7.10

pH values of the aqueous solutions of all the reducing agents studied are high enough to alkalinise the paper, without inducing alkaline degradation (Table 1).

The aqueous reduction of oxidised papers, followed by ageing (simulating the ageing of a restored ancient paper) offers a good protection with regard to the formation of oxidised groups, when compared to the oxidised unreduced papers. Obviously, borane compounds are not able to hinder the further intrinsic degradation of the paper, but the initial low amount of carbonyl groups prevents the fast increase of oxidised functions.

From carbonyl content data we can see that the treatment of oxidised papers with reducing agents has an effectiveness of 66% up to 88% before the ageing and an effectiveness of 30 up to 52% after 28 ageing days (Table 6). Furthermore, the samples treated thus are found to be thermally more stable[5,8].

Table 6: Aqueous reduction treatments of aged samples.

borane complex	carbonyl content (mmoles per g100 paper)		reduction effectiveness (%)	
	14 days ageing	28 days ageing	14 days ageing	28 days ageing
none (oxidised paper)	7.48 ± 0.31	9.17 ± 0.48	-	-
AB	3.80 ± 0.13	5.56 ± 0.25	49.2	39.4
DIPEAB	2.35 ± 0.10	4.21 ± 0.30	68.6	54.1
DMAB	3.14 ± 0.20	5.34 ± 0.36	58.0	41.8
MB	3.69 ± 0.28	4.44 ± 0.41	50.7	51.6
TBAB	2.89 ± 0.16	4.43 ± 0.37	61.4	51.7
TEAB	4.30 ± 0.25	5.04 ± 0.39	42.5	45.0
TMAB	2.96 ± 0.19	6.50 ± 0.43	60.4	29.1

Concerning the optical properties, it is possible to see from Table 5 data that the best behaviour is shown from papers treated with borane-ammonia complex (AB) and borane *tert*-butylamine complex (TBAB). The yellowing of the papers treated with borane dimethylamine complex (DMAB) and borane N,N-diisopropylethylamine complex (DIPEAB) is faint: it is observable only instrumentally and not visually. We remember that the yellowing effect is especially measured by the increase of the b* co-ordinate, the decrease of the luminosity (L* co-ordinate) being less important for originally white papers.

All experimental data point out, in conclusion, that treatments using reducing agents with all the studied borane compounds in water protect the paper against ageing and oxidation. The best results were obtained for AB, TBAB and DIPEAB. The latter, unfortunately, leaves an unpleasant residual odour on the treated papers. AB and TBAB can also be used in organic solutions, i.e. they can be used on water soluble graphic media. They were in fact employed in the restoration of De Nittis graphic works, performed in collaboration with the Istituto Nazionale per la Grafica[9,10], in a simultaneous treatment of alcoholic deacidification and reduction of some unbounded books of the Liebig's *Annalen* belonging to the Department of Chemistry, University of Rome "La Sapienza"[11] and in the treatment of three De Chirico lithographs.

ACKNOWLEDGEMENT

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SUMMARIES

Application of Seven Borane Complexes in Paper Conservation

Seven borane complexes were tested for aqueous and non-aqueous conservation treatments of paper. All the reducing agents gave very good results when used in aqueous solutions with an effectiveness of 66 ÷ 88% before ageing and 30 ÷ 52% after 28 ageing days.

The best results were obtained from borane ammonia complex (AB), borane *tert*-butylamine complex (TBAB) and borane N,N-diisopropylethylamine complex (DIPEAB). The latter, unfortunately, leaves an unpleasant residual odour on the treated papers. AB and TBAB can also be used in organic solutions, enabling the treatment of graphic media soluble in water.

Utilisation de sept différents complexes de borane dans la conservation du papier

Sept différents complexes de borane ont été testés pour savoir si leur utilisation était valable dans les traitements aqueux et non aqueux de conservation du papier. Tous les agents réducteurs ont donné de très bons résultats lorsqu'ils étaient utilisés dans des solutions aqueuses avec un taux d'efficacité de 66 ÷ 88 % avant vieillissement et de 30 ÷ 52 % après 28 jours de vieillissement.

Les meilleurs résultats ont été obtenus avec l'ammonium de borane (AB), le tert-butylamine de borane (TBAB) et le complexe de borane N, N-diisopropyléthylamine (DIPEAB). Ce dernier agent réducteur laisse cependant une odeur résiduelle désagréable sur les papiers traités. Les complexes AB et TBAB peuvent également être utilisés dans des solutions organiques lorsqu'il convient d'éviter un traitement aqueux pour un support graphique soluble à l'eau.

Zur Anwendung von sieben verschiedenen Boran-Komplexen in der Papierrestaurierung

Sieben Boran-Komplexe wurden auf ihre Anwendbarkeit in wäßrigen und nichtwäßrigen Verfahren der Papierrestaurierung hin untersucht. In ersterer zeigten alle sehr gute Ergebnisse, d.h. einen Wirkungsgrad von 66 ÷ 88% vor und von 30 ÷ 52% nach einer 28tägigen beschleunigten Alterung.

Die besten Ergebnisse wurden erzielt mit dem Boran-Ammonium- (AB), dem Boran-*tert*-Butylamin- (TBAB) und dem Boran-N,N-Diisopropylethylamin-Komplex (DIPEAB). Dieses letztgenannte Reduktionsmittel hinterläßt allerdings im Papier einen unangenehmen Geruch. AB und TBAB können auch in organischen Lösemitteln angewandt werden, wenn bei einem empfindlichen graphischen Blatt eine wäßrige Behandlung zu vermeiden ist.

APPENDIX: TECHNICAL AND SAFETY DATA OF THE STUDIED COMPLEXES

Borane ammonia complex Cas Number: 13774-81-7

- **Hazards identification:** Explosive; heating may cause an explosion; avoid contact with acid; keep away from heat.
- **Physical and chemical properties**: White powder with flakes; hygroscopic; store in a cool dry place.
- **Incompatibilities**: Strong oxidising agents; acids. Protect from moisture.
- **Toxicological information** (caution: substance not yet fully tested): May be harmful by inhalation, ingestion, or skin absorption; may cause eye irritation; may cause skin irritation.
- **EC risks and safety classes:**
  - R 5 (heating may cause an explosion)
  - S 15 (keep away from heat)
  - S 26 (in case of contact with eyes, rinse immediately with plenty of water and seek medical advice)
  - S 27 (take off immediately all contaminated clothing)
  - S 36/37/39 (wear suitable protective clothing, gloves and eye/face protection).

Borane n,n-diisopropyllethylamine complex Cas Number: 88996-23-0

- **Hazards identification:** Flammable; corrosive; causes burns; keep away from sources of ignition – no smoking; in case of contact with eyes, rinse immediately with plenty of water and seek medical advice; take off immediately all contaminated clothing; wear suitable protective clothing, gloves and eye/face protection. Combustible, moisture sensitive.
- **Physical and chemical properties**: Yellow liquid, moisture sensitive. Keep away from heat and open flame; melting point: 15°C to 17°C; flashpoint 39°C specific gravity: 0.822.
- **Incompatibilities**: Acids oxidising agents; heavy metal salts; oxygen. May decompose on exposure to moist air or water.
- **Toxicological information** (caution: substance not yet fully tested): Harmful if swallowed, inhaled, or absorbed through skin; causes burns; material is ex-

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tremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes and skin.

- **EC risks and safety classes:**
  - Flammable; corrosive
  - R 34 (causes burns)
  - S 16 (keep away from sources of ignition – no smoking)
  - S 26 (in case of contact with eyes, rinse immediately with plenty of water and seek medical advice)
  - S 27 (take off immediately all contaminated clothing)
  - S 36/37/39 (wear suitable protective clothing, gloves and eye/face protection).

Borane dimethylamine complex Cas Number: 74-94-2

- **Hazards identification:** Flammable; toxic; toxic by inhalation, in contact with skin and if swallowed; causes burns; keep away from sources of ignition – no smoking.
- **Physical and chemical properties**: Stable white crystals; melting point: 35°C to 36°C.
- **Incompatibilities**: Acids; oxidising agents; heavy metal salts; oxygen.
- **Toxicological information:** Harmful if swallowed, inhaled, or absorbed through skin; causes burns; material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes and skin. Toxicological properties have not been thoroughly investigated.
- EC risks and safety classes:
  - Flammable; toxic
  - R 23/24/25 (toxic by inhalation, in contact with skin and if swallowed)
  - R 34 (causes burns)
  - S 16 (keep away from sources of ignition – no smoking)
  - S 45 (in case of accident or if you feel unwell, seek medical advice immediately)
  - S 26 (in case of contact with eyes, rinse immediately with plenty of water and seek medical advice)
  - S 36/37/39 (wear suitable protective clothing, gloves and eye/face protection).

Borane-morpholine complex Cas Number 4856-95-5

- **Hazards identification:** Corrosive; causes burns.; in case of contact with eyes, rinse immediately with plenty of water and seek medical advice; after contact with skin, wash immediately with plenty of water; take off immediately all contaminated clothing; wear suitable protective clothing, gloves and eye/face protection.
- **Physical and chemical properties**: White crystalline chunks moisture sensitive; melting point: 97°C to 99°C.
- **Incompatibilities**: Acids; acid chlorides; acid anhydrides; alcohols; may decompose on exposure to moist air or water.
- **Toxicological information:** Harmful if swallowed, inhaled, or absorbed through skin; causes burns; material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes and skin.
- EC risks and safety classes:
  - corrosive
  - R 34 (causes burns)
  - S 26 (in case of contact with eyes, rinse immediately with plenty of water and seek medical advice)
  - S 28 (after contact with skin, wash immediately with plenty of water)
  - S 27 (take off immediately all contaminated clothing)
  - S 36/37/39 (wear suitable protective clothing, gloves and eye/face protection).

Borane tert-butylamine complex Cas number: 7337-45-3

- **Hazards identification:** Harmful; harmful by inhalation, in contact with skin and if swallowed; irritating to eyes, respiratory system and skin; in case of contact with eyes, rinse immediately with plenty of water and seek medical advice; wear suitable gloves and eye/face protection.
- **Physical and chemical properties**: White crystalline flakes; melting point: 96°C to 97°C.
- **Incompatibilities**: Strong oxidising agents; strong acids.
- **Toxicological information:** May be harmful by inhalation, ingestion, or skin absorption; causes eye and skin irritation; material is irritating to mucous membranes and upper respiratory tract.

- EC risks and safety classes:
  - Harmful
  - R 20/21/22 (harmful by inhalation, in contact with skin and if swallowed)
  - R 36/37/38 (irritating to eyes, respiratory system and skin)
  - S 26 (in case of contact with eyes, rinse immediately with plenty of water and seek medical advice)
  - S 37/39 (wear suitable gloves and eye/face protection).

Borane triethylamine complex Cas Number: 1722-26-5

- **Hazards identification:** Highly flammable; corrosive; causes burns; harmful by inhalation, in contact with skin and if swallowed; keep away from sources of ignition – no smoking; in case of contact with eyes, rinse immediately with plenty of water and seek medical advice; take off immediately all contaminated clothing; take precautionary measures against static discharges. Wear suitable protective clothing, gloves and eye/face protection.
- **Physical and chemical properties**: Colourless liquid; boiling point: 97°C/ 12mm; melting point: 4°C to 2°C; flashpoint -7°C; specific gravity 0.783.
- **Incompatibilities**: Acids; oxidising agents; heavy metal salts; oxygen. may decompose on exposure to moist air or water.
- **Toxicological information:** Harmful if swallowed, inhaled, or absorbed through skin; causes burns; material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes and skin.
- **EC risks and safety classes:**
  - Highly flammable
  - Corrosive
  - R 34 (causes burns)
  - R 20/21/22 (harmful by inhalation, in contact with skin and if swallowed)
  - S 16 (keep away from sources of ignition – no smoking)
  - S 26 (in case of contact with eyes, rinse immediately with plenty of water and seek medical advice)
  - S 27 (take off immediately all contaminated clothing)
  - S 33 (take precautionary measures against static discharges)
  - S 36/37/39 (wear suitable protective clothing, gloves and eye/face protection).

Borane trimethylamine complex Cas Number: 75-22-9

- **Hazards identification:** Harmful; harmful by inhalation, in contact with skin and if swallowed; irritating to eyes, respiratory system and skin; in case of contact with eyes, rinse immediately with plenty of water and seek medical advice; wear suitable protective clothing; avoid contact with acid.
- **Physical and chemical properties**: White powder; melting point: 93°C to 95°C.
- **Incompatibilities**: Acids; acid chlorides; acid anhydrides; oxidising agents; alcohols.
- **Toxicological information**: Harmful if swallowed, inhaled, or absorbed through skin; causes eye and skin irritation; material is irritating to mucous membranes and upper respiratory tract.
- EC risks and safety classes:
  - Harmful
  - Corrosive
  - R 20/21/22 (harmful by inhalation, in contact with skin and if swallowed)
  - R 36/37/38 (irritating to eyes, respiratory system and skin)
  - S 26 (in case of contact with eyes, rinse immediately with plenty of water and seek medical advice)
  - S 36 (wear suitable protective clothing).

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Marina Bicchieri
Laboratory of Chemistry
Istituto Centrale per la Patologia del Libro
Via Milano 76, I-00184 Roma, Italy
Tel: +390648291217; Fax: +39064814968
e-mail: icplch@tin.it

Francesca Maria Sementilli
Laboratory of chemistry, with ICPL grant
Istituto Centrale Patologia del Libro
Via Milano 76, I-00184 Roma, Italy
Tel: +390648291217; Fax: +39064814968
e-mail: icplch@tin.it

Armida Sodo
Dipartimento di Fisica, Università di Roma Tre,
Unità di Ricerca dell'INFM, with INFM grant
Via della Vasca Navale 84, I-00146 Roma, Italy
Tel: 0655177229; Fax 065579303;
E-mail: sodo@fis.uniroma3.it

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The Natural Ageing of Paper After Exposure to Daylight

by VLADIMÍR BUKOVSKÝ

Introduction

Nowadays there is a good deal of information about the influence of light on the ageing of groundwood papers[1, 2, 3]. Light induced oxidation degradation reactions are typical reactions of lignin, characteristically manifest as the yellowing of paper, producing a large amount of low molecular degradation products, a significant increase of acidity and intensely reduced strength during 30 days of daylight ageing, even with significantly reduced UV[4]. Groundwood paper can reach this state during exhibitions, whilst being used for study , during restoration, etc., that is in any environment where there are no strict exposure time limits. The negative influence of light on groundwood paper is, in this situation, even more dangerous than its acid degradation[5]. However, the deacidification of historic groundwood papers is one of the most crucial steps to their rescue and is a process which can significantly contribute to the prevention of the degradation of modern papers, particularly for their long-term storage in archives[6]. It is, however, a misinterpretation that deacidified groundwood papers can be exhibited in uncontrolled light without any risk[4]. If magnesium (Mg) is introduced into the paper during deacidification, the course of light induced oxidation reactions is significantly limited by the bond of Mg to fenolic OH- groups, which play an important role during the initiation of oxidation degradation reactions on the molecule of lignin[7]. On the other hand, the alkaline environment created by the deacidification process, which in the case of solvent soluble magnesium organic compounds is very high, has a negative influence on the stability of the lignin molecule and therefore on the mechanical properties of groundwood papers[8]. The aim of this work is to find out to what extent other oxidation reactions on lignin will be taking place, (cellulose is not significantly changed by oxidation after deacidification), when paper has already been exposed to daylight for a relatively long time with a significantly reduced UV component.

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Characteristics of mechanical pulps, such as yellowing,[9] apparent after short exposure to UV radiation and more commonly visible light, are reduced to the value they had before that exposure, when the paper is subsequently put into the dark. We wanted to find out whether light induced oxidation processes on lignin, combined with considerable deterioration of paper, have an influence on further oxidation occurring in the dark. Since deacidification of groundwood papers is one of the crucial steps in prolonging their lifetime[10], we were interested to see whether the influence of Mg on light induced oxidation would be modified in any way during subsequent natural ageing of papers.

MATERIALS AND METHOD

Paper samples: To judge the influence of light induced oxidation on the course of oxidation we used two different modern and three historic newsprint papers with a lignin content of between 15 % and 21,3 %[3,4].

1. Newsprint made in Štetí 1996, Czech Republic
2. Newsprint made in Větrní 1996, Czech Republic
3. Newsprint from Slovakia 1953
4. Newsprint from Croatia 1942
5. Newsprint from Hungary 1882

Samples were deacidified (D-samples) in a 4 % methanol solution of methyl methoxymagnesium carbonate (MMMC) to create an alkaline reserve of between 2,1 and 6,1 % w/w in the papers[4]. Control samples (C-samples) were soaked only in pure methanol. Both groups of treated newsprint papers were aged by daylight passing through 2 panes of window glass for 165 days in the following intervals:

- I : 15 days
- II: 32 days
- III: 48 days
- IV: 77 days
- V: 119 days
- VI: 156 days.

These are the same intervals as used in our previous work[4]. After irradiation the paper was stored for 12 months in a dark deposit at room climate. The course

Table 1. Annual increase of carbonyls (mmol/100g paper) in newsprint papers, C-samples and D-samples.

Paper	Treatment	1997	1st year 1998	2nd year 1999	3rd year 2000
1	Control	3,2	5,5	7,7	7,8
	deacidified	3,0	4,9	6,9	6,8
2	Control	3,6	4,7	5,7	6,6
	deacidified	3,1	4,6	5,1	4,7
3	Control	5,1	8,5	11,8	–
	deacidified	5,0	7,7	10,4	–
4	Control	6,6	8,7	11,1	10,3
	deacidified	6,3	8,4	10,3	7,8
5	Control	7,3	8,5	10,0	9,2
	deacidified	7,2	8,3	8,8	9,5

of oxidation was evaluated by means of determining the carbonyls in the paper[11]. By using previous analyses and measured values of carbonyls in non-irradiated newsprints we tried to find a long-term natural course of oxidation of the observed papers stored at room climate without the presence of light.

RESULTS AND DISCUSSION

Ageing of newsprint

The results collected over 3 years enable us to estimate the natural ageing of selected groundwood papers; cf. Table 1.

Initially, the carbonyl content in the modern newsprint paper from the manufacturer is quite low: 3,2 mmol/100 g in paper 1, 3,6 mmol/100 g in paper 2. The carbonyl content increases during the next two years, and we assume that within three years it achieves an equilibrium, which is 2,4 times higher in a low quality paper (paper 1) and 1,8 times higher in a better quality paper (paper 2). This increase refers to the oxidative degradation process occurring in such a paper under the conditions of normal use in the reading room and of storage at room climate. As soon as an equilibrium is achieved, this process is slowed down.

Further oxidation, after this initial equilibrium, can be observed in the historic newsprint papers. The carbonyl content changes relatively slowly during storage

(paper 5). Comparing the values of the carbonyl content of historic newsprint it can be assumed that, during storage at room climate, the carbonyl forming oxidation process will be slowed down even further with ongoing time. A deviation from a stable state, however, can easily happen, initiated, for example, by exposure to daylight. In deacidified papers the course of oxidation is not significantly different. Mg introduced into the paper by deacidification with MMMC has only a limited influence on oxidation.

Amount of carbonyls

The length of irradiation significantly influences the oxidation of paper as made evident by the production of carbonyls (Fig. 1). After approximately 40 days in all papers, a certain maximum level of carbonyls is reached, and the presence of Mg in the paper has a significant inhibiting influence on the course of light induced oxidation[4].

The next course of oxidation occuring under room climate is expressed by the amount of carbonyls present during 12 months of storing. The relative change is shown in Fig. 2.

The course of ageing of both observed modern newsprint paper samples (samples no. 1 and 2) is similar.

Natural ageing of paper after irradiation

Groundwood papers after 30–50 days of direct irradiation by daylight significantly yellow; they are more acid and they lose their strength very quickly[4]. This process is a result of very intense light induced degradation reactions of radical character hitting mainly lignin. A certain balance in carbonyl content (a maximum level) is reached after a relatively short irradiation (Fig. 1).

Consequently we were interested to see whether the connection between the short irradiation of groundwood papers and the very intensively occuring changes in the structure of lignin, become obvious in the lifetime of these papers after their subsequent storage in room climate conditions (Fig. 1 and 2), where, in dark rooms and in the presence of oxygen, autooxidation degradation reactions both in lignin and cellulose occur as part of natural ageing (Tab. 1).

The speed of this process is, however, very slow compared to the speed of light induced oxidation reactions. After 12 months of storage we found that in modern newsprint papers (samples 1 and 2) that have been irradiated for only a relatively short time (up to approximately 50 days) the degradation reactions

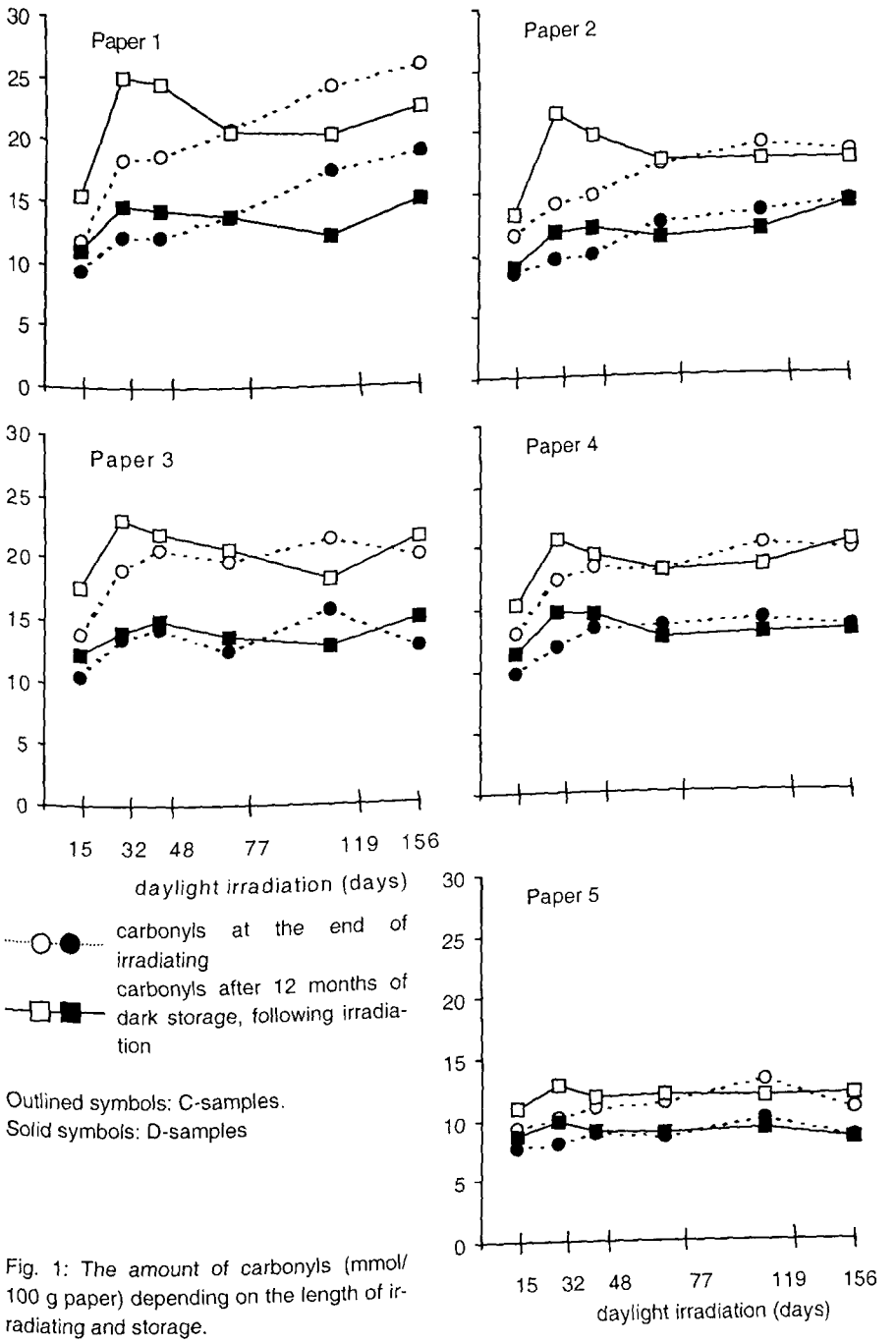
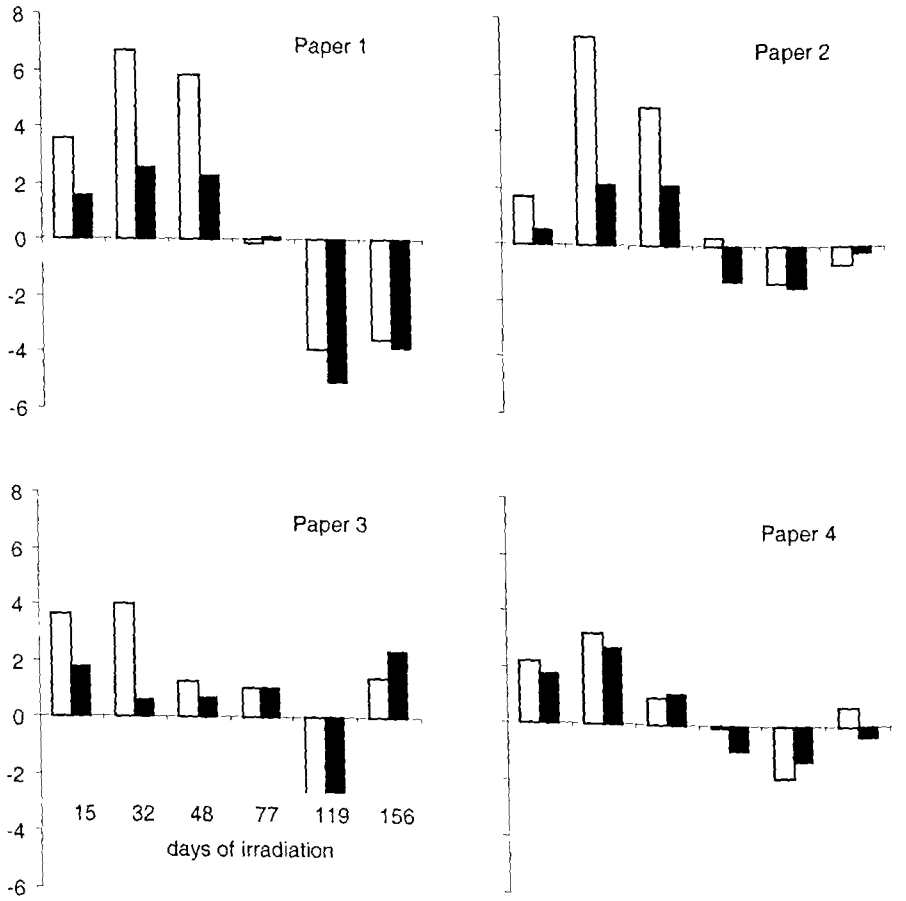


Fig. 1: The amount of carbonyls (mmol/100 g paper) depending on the length of irradiating and storage.



Outlined columns: C-samples.
Solid columns: D-samples

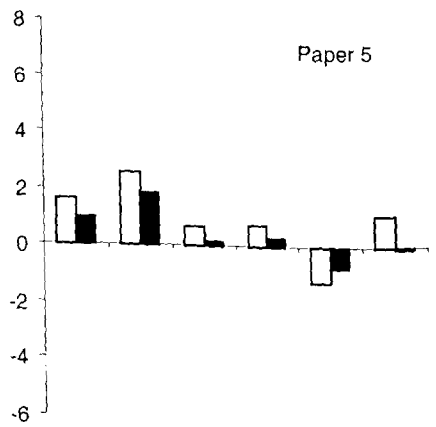


Fig. 2: Change of carbonyl content (mmol/100 g paper) of irradiated paper as a result of 12 months dark storage.

during 12 months of dark storage occur at a significantly more rapid rate than the rate of natural ageing without previous daylight irridiation. This means that besides the slow autooxidation reactions in paper, degradation processes induced by light, even when exposure has been for a short time, occur or continue in the dark.

In papers where a balance was reached, i.e. a certain maximum oxidation level during light induced oxidation, the amount of carbonyls did not change, even during long-term storage. In some cases (sample 1) the amount of carbonyls even gradually decreases during which time oxidation and degradation processes continue; the carbonyls are changed into other degradation products and a new balance, with lower carbonyl content, is slowly reached. A similar influence of daylight irradiation, with a consequent influence on the course of oxidative degradation reactions during long-term storage, was also observed in historic groundwood papers (samples 3, 4 and 5). The intensity of changes was reduced with increasing deterioration. The more the paper deteriorated the less the intensity of the changes. Deacidification of groundwood papers with agents containing Mg significantly inhibits light induced oxidating degradation of cellulose and lignin. Inhibition influence is shown even during the long-term storage of papers irradiated by daylight. This fact confirms that reactions continuing in the dark during the storage of irradiated papers are initiated by light; they may have some similar characteristics as light induced oxidation degradation reactions.

CONCLUSIONS

- Irradiation of groundwood paper is a significant degradation factor comparable to the acidic degradation of this type of paper.
- Short-term irradiation significantly degrades groundwood paper.
- Short-term irradiation of groundwood paper initiates oxidation degradation reactions; they are continued during subsequent dark storage at room climate.
- Groundwood paper should not be placed in an environment without guaranteed controlled light conditions (exhibitions, study rooms, etc.).
- Deacidification of paper with Mg containing agents significantly inhibits light induced oxidation of groundwood paper, i.e. those that are initiated by irradiation previous to storage in the dark at room climate.
- It might be questioned whether this inhibition effect is also true for other oxidation processes in the paper.

SUMMARIES

Natural Ageing of Paper After Daylight Irradiation

Sunlight, even after harmful UV has been filtered out, significantly degrades groundwood paper. The greatest changes in paper occur after approximately 30 days of irradiating. Short-term irradiation of paper initiates light induced oxidation reactions, which continue even after paper is stored in the dark. Mg in paper significantly inhibits light induced oxidation during direct irradiation of the paper and eliminates the influence of irradiation on the intensity of light induced oxidation degradation reactions, which are a characteristic of the natural ageing of paper.

Vieillissement naturel du papier qui a été exposé à l'irradiation de la lumière du jour.

La lumière solaire, même après filtrage de la plus grande partie des rayons ultra-violets, dégrade considérablement le papier journal. Cette dégradation du papier atteint son maximum après environ 30 jours d'irradiation. Même une irradiation de courte durée suffit pour déclencher des réactions d'oxydation induites par la lumière qui se poursuivent encore après que le papier ait été déposé dans un endroit obscur. La présence de magnésium dans le papier inhibe considérablement cet effet d'oxydation induite par la lumière lors d'une irradiation directe du papier et élimine même l'influence de l'irradiation sur l'intensité des réactions de dégradation par oxydation induite par la lumière, réactions qui contribuent en partie au vieillissement naturel du papier.

Natürliches Altern von Papier, das einer Bestrahlung mit Tageslicht ausgesetzt war

Sonnenlicht bewirkt auch nach dem Herausfiltern des UV-Anteils einen beträchtlichen Abbau von Zeitungspapier. Dieser Abbau erreicht ein Maximum nach 30 Bestrahlungstagen. Bereits kurzzeitige Bestrahlung setzt Reaktionen einer lichtinduzierten Oxidation in Gang, welche sich dann bei nachfolgender Lagerung des Papiers im Dunkeln fortsetzen. Ist Magnesium im Papier vorhanden, wird diese lichtinduzierte Oxidation während einer Bestrahlung in nennenswertem Ausmaß vermindert, und die von Licht hervorgerufene Einleitung von abbauenden Oxidationsvorgängen, die einen Teil des natürlichen Alterns von Papier ausmachen, wird eliminiert.

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Vladimír Bukovský
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Physicomechanical Properties of Paper Treated With Polymers

by ABD-ALLA M. A. NADA, SAMIR KAMEL & MOHAMED EL-SAKHAWY

INTRODUCTION

Polymers are used in paper technology in many ways. Bleached pulps, e.g., especially those bleached with hydrogen peroxide, tend to lose brightness by yellowing on exposure to light or heat. Therefore, stability against yellowing has become a major problem. Even more, the presence of lignin containing fibers e.g. of mechanical pulp, implies a great sensitivity to light[1-2]. Some polymers, e.g. polyethylene glycol and butyl hydroxy toluene, are used to stabilize lignin containing paper towards light and heat induced yellowing[3]. Moreover, the polymer can be used as a wet-end additive for filler retention and to improve draining[4-5]. Thermoplastics are apt to strengthen paper by coating, and also aqueous dispersion or lattices have been used in this way[6-8]. Modified natural polymer, e.g. cationic starch, can be added in the paper making process to increase the mechanical properties and improve machine runnability[9]. Mechanical properties of paper sheets can also be improved by modifying the interfiber bonding; one of the relevant methods being to add carboxymethyl cellulose and synthetic resins to the pulp[10-12]. Modification of the pulp by acetylation or grafting can have the same effect[13-15]. Recently the use of parylene monomer and its polymerisation *in situ* has been considered for paper strengthening in conservation[16], again in paper conservation, some copolymers can be used to improve the resistance of old papers from brittleness[17].

The aim of this study is to improve the physicomechanical properties and stability of the brightness of paper sheets on ageing by using polymer solution. The effect of two kinds of polymer solutions at different concentrations, on the mechanical properties of paper made of mechanical and chemical kraft pulp are investigated. A mixture of the two polymer solutions in different ratios, i.e. polyethylene glycol and polyvinyl alcohol, is used. The effect of ageing at different temperatures on the mechanical properties, on sizing effect and brightness are investigated.

Table 1: Treatments

no.	kind of polymer	amount (g)	water (g=ml)	dipping time (sec)
1	polyethylene glycol (PEG); molecular weight 4000	10	90	30
2	polyethylene glycol (PEG); molecular weight 4000	15	85	30
3	polyethylene glycol (PEG); molecular weight 4000	20	80	30
4	polyvinyl alcohol (PVA: *Vinarol*™* DV)	1	99	30
5	polyvinyl alcohol (PVA: *Vinarol*™* DV)	3	97	30
6	polyvinyl alcohol (PVA: *Vinarol*™* DV)	5	95	30
7	PEG 2.5 g + PVA 1,25 g	3.75	100	30
8	PEG 2.3 g + PVA 0,6 g	2.9	100	30

* product of Hoechst (Germany)

EXPERIMENTAL

Three different kinds of paper were used for the experiment:

- A: Bleached mechanical pulp, delivered from Al-Ahram Newspaper Printer Organization, Cairo.
- B: Unbleached kraft bagasse pulp, delivered from Edfo Paper Mill (Upper Egypt).
- C: Kraft bagasse pulp bleached with alkaline hydrogen peroxide, prepared from pulp of 40°SR, beaten according to the Swedish Standard Method (SCA).

The sheets were weighed and then treated as given in Table 1.

The paper sheets were dried and weighed to calculate the retained polymer (g/m^2).

Some of the treated sheets were aged at different temperatures (130–150° C) for one hour.

The following properties were determined according to the relevant Tappi Standards:

- Grammage, i.e. weight of 1 m^2, after heating at 105° C for 3 hours
  Breaking length (km), i.e. tensile strength [p] x 1000 x 1000 / grammage [g] / 15 [mm] = tensile strength [p] x 66667 / grammage [g]
- Tear factor, i.e. tear strength [mN] x 16 (pendulum factor) x 100 / number of testes sheets / grammage
- Burst factor = Burst strength x 1000 / grammage

Brightness was determined using Hunter Lab. MD25 Optical Sensor.

Table 2. Retained polymer (g/m²)

Paper	Treatment:	1	2	3	4	5	6	7	8
A: Mechanical pulp		4	5.2	6.1	0.9	2.2	4.0	4.2	5.1
B: Unbleached bagasse		4.1	–	6.0	0.8	2.3	4.3	5.3	5.2
C: Bleached bagasse		4.9	–	6.8	1.0	--	5.1	5.6	6.1

RESULTS AND DISCUSSION

Polymer retention

From Table 2 it can be seen that the mechanical pulp paper sheet retains less polymer after having been dipped into the solution for 30 sec. than those made of bagasse, and in particular less than the bleached bagasse. This can be attributed to the fact that mechanical pulp fibers have a smaller surface area than the cooked fibers; consequently the amount of polymer that is retained at the surface is lower. Moreover, the retained polymer on the unbleached bagasse paper sheets is lower than that on those made of bleached bagasse sheets. This may be explained by the presence of lignin in unbleached sheets. The hardness resulting from lignin increases the adhesion between cellulose and hemicellulose molecules in the fiber with the consequence that the polymer solution cannot penetrate into the fiber of unbleached bagasse pulp. On the other hand, the bleached kraft bagasse paper sheet has nearly no lignin; the fiber is soft and has a larger surface area, which promotes the penetration of the polymer solution.

From Table 1 it can also be seen that the amount of retained polyethylene glycol is higher than that of polyvinyl alcohol. This is due to the larger molecules of PVA, which results in a solution with a higher viscosity, even if the concentration is lower than that of polyethylene glycol. The larger the molecules the less they can penetrate into the fiber. Increased concentration of the polymer solution results in increased retention in the paper sheets.

Mechanical properties

Mechanical properties of the differently treated samples of paper sheets are given in Table 3. It can be seen that bagasse paper sheets have greater mechanical strength than mechanical pulp paper sheets, which is generally the case with cooked pulps. Chemical cooking produces soft fiber that is homogeneously distributed during the sheet forming process. This results in increased interfiber

Table 3. Mechanical properties of different kinds of paper sheets

Paper	Breaking length (km)	Tear factor	Burst factor
A: Mechanical pulp	2.8	26.8	11.2
B: Unbleached bagasse	4.3	40.9	32.0
C: Bleached bagasse	3.9	52.1	30.0

bonding and consequently in a greater mechanical strength of the paper sheets. The fiber of semicooked mechanical pulp is less soft and can produce less interfiber bonding in the paper sheets. Looking at the two bagasse pulps it can be seen that the breaking length of the unbleached paper sheets is higher than that of the bleached pulp. This is due to the degradation of the cellulose chains, which occurs during the bleaching process. In contrast, the tear factor of the bleached bagasse sheets is higher than that of unbleached sheets. This can be attributed to the increase of the interfiber bonding between the fibers of bleached bagasse sheets, which is more soft and elastic than unbleached bagasse fiber.

Properties of the treated sheets: mechanical properties

Treatment with polyethylene glycol

As can be seen from Table 4, treating the paper sheets with polyethylene glycol solution generally decreases the mechanical strength. This can be attributed to the waxy property of polyethylene glycol that brings about a lubricating effect of the fibers resulting in decreased cross-linking and interfiber bonding. With the

Table 4 : Percentage change of mechanical properties of the sheets treated with polyethylene glycol solution.

	Breaking length			Tear factor			Burst factor		
Paper:	A	B	C	A	B	C	A	B	C
Untreated	100	100	100	100	100	100	100	100	100
Treatment 1 vs Untreated	-7,4	-9,3	-7,9	-16,1	-4,9	-5,8	-14,0	-3,1	-1,0
Treatment 2 vs Untreated	-11,1	-14,0	-18,4	-21,7	-11,0	-11,3	-22,4	-9,4	-3,3
Treatment 2 vs Treatment 1	-4,0	-5,1	-11,4	-6,7	-6,4	-5,9	-9,8	-6,5	-2,4
Treatment 3 vs Untreated	-14,8	-16,3	-21,1	-19,1	-14,4	-15,2	-5,6	-10,9	-6,7
Treatment 3 vs Treatment 1	-8,0	-7,7	-14,3	-3,6	-10,0	-10,0	9,8	-8,1	-5,7
Treatment 3 vs Treatment 2	-4,2	-2,7	-3,2	3,3	-3,8	-4,3	21,7	-1,7	-3,4

two bagasse pulps the percentage decrease of breaking length is higher than the percentage decrease of tear and burst factors: breaking length is greatly affected by the interfiber bonding. Doubling the concentration of PEG does not necessarily mean doubling the loss of mechanical strength, for example, mechanical pulp paper (Paper A) soaked in 20% PEG solution (Treatment 3) has suffered the smallest burst loss: 5.6% compared to a 14% loss with the 10% solution.

Treatment with polyvinyl alcohol

Treatment of paper sheets by dipping in polyvinyl alcohol solution increases the mechanical properties of paper sheets (Table 5), and the higher the concentration, the higher the strength increase. This is due to the increase of the cross-linking and interfiber bonding. There is only one exception. By soaking the mechanical pulp paper (Paper A) in 1% PVA solution (Treatment 4) the tear factor was increased by 16.1%, by soaking in 3% solution (Treatment 5) the tear factor was increased by only 12.7%, and by soaking in 5% solution (Treatment 6) it even decreased by 2.2%. With the other strength properties – breaking length and burst factor – the mechanical pulp paper is the one that shows the highest increase rates. An explanation for these phenomena might be the increase of interfiber bonding via bondings between fiber and polymer. If the polymer content of the solution is increased by more than 3% (Treatment 6), tear and burst factors of the kraft pulps are slightly further increased (Treatment 6 vs Treatment 5), even if the retained polymer is decreased (Table 2). This can be attributed to the fact that the interfiber bonding has reached a maximum at a certain amount of retained polymer, and this maximum results from a 3% polymer solution.

Generally, mechanical properties are highly affected by a treatment with polyvinyl alcohol solution, and the results vary with the kind of paper as well as with

Table 5: Percentage change of mechanical properties of the sheets treated with polyvinyl alcohol.

	Breaking length			Tear factor			Burst factor		
Paper:	A	B	C	A	B	C	A	B	C
Untreated	100	100	100	100	100	100	100	100	100
Treatment 4 vs Untreated	25,9	0,0	10,5	16,1	4,9	1,7	52,3	4,7	10,0
Treatment 5 vs Untreated	59,3	11,6	26,3	12,7	14,9	16,9	69,2	10,0	16,3
Treatment 5 vs Treatment 4	26,5	11,6	14,3	-2,9	9,6	14,9	11,0	5,1	5,8
Treatment 6 vs Untreated	85,2	11,6	31,6	-2,2	19,3	21,9	107,5	13,1	19,7
Treatment 6 vs Treatment 4	47,1	11,6	19,0	-15,8	13,8	19,8	36,2	8,1	8,8
Treatment 6 vs Treatment 5	16,3	0,0	4,2	-13,3	3,8	4,3	22,7	2,8	2,9

Table 6: Brightness (%) of the paper sheets.

Treatment	Paper A	C	Treatment	Paper A	C
control	60,8	69,7	control	60,8	69,7
Treatment 1 (10% PEG)	60,9	70,0	Treatment 4 (1% PVA)	59,9	69,8
Treatment 2 /15% PEG)	60,9	70,1	Treatment 5 (3% PVA)	59,1	69,2
Treatment 3 (20%) PEG)	61,2	70,4	Treatment 6 (5% PVA)	58,9	68,9

the concentration of polymer solutions (Table 5). The percentage increase of the mechanical properties of bleached mechanical paper sheets is higher than that in case of the bagasse sheets. This is due to the low initial mechanical properties of the mechanical pulp paper, which is highly affected by a treatment with the polymer causing an increase in cross-linking and interfiber bonding. In the same way the mechanical properties of bleached bagasse sheets (Paper C) improve more after being treated with polyvinyl alcohol solution than do the same properties of the unbleached bagasse sheets (Paper B). Also the amount of retained polymer is higher in the bleached bagasse sheets than in the unbleached ones. The interfiber bonding and cross bonding between the fibers, however, is higher in the bleached sheets. The presence of lignin (ca. 6 %) in the unbleached fiber has a decreasing effect on the bonding between fiber and polymer.

Brightness

The brightness of the bleached mechanical and bagasse sheets treated with polyethylene glycol is slightly increased (0.1–0.7 %, while it is reduced by a somewhat greater amount (0.1–19%) by treatment with polyvinyl alcohol solution. (Table 6). The higher the concentration, the greater the amount of change in both cases.

Ageing

Ageing of untreated bleached mechanical pulp (A) and bleached bagasse (C) paper sheet at different temperatures (130–150°C) for one hour caused deterioration in the mechanical properties and a decrease of the brightness (Table 7). This is due to the increased degradation of the cellulosic fibers and oxidative formation of C=O double bonds, which are the reason for the yellowing of the treated sheets[18]. Loss in the mechanical properties and brightness was increased with higher temperatures. It is interesting to note that the properties of the sheets treated with polyethylene glycol are less affected by ageing than those treated with PVA

Table 7: Properties after ageing

	Paper A		aged at		Paper C		aged at	
	Unaged	130°C	140°C	150°C	Unaged	130°C	140°C	150°C
Breaking length (km)								
untreated	2,7	2,7	2,5	2,1	3,8	-	3,7	-
Treatment 1 (10% PEG)	2,4	-	2,4	-	2,4	-	2,5	-
Treatment 5 (3% PVA)	4,3	-	3,9	-	4,8	-	4,3	-
Tear factor								
untreated	26,7	28,1	17,2	13,5	52,0	-	48,7	-
Treatment 1 (10% PEG)	22,4	-	15,2	-	43,8	-	41,8	-
Treatment 5 (3% PVA)	30,1	-	16,4	-	60,8	-	54,3	-
Burst factor								
untreated	10,7	11,1	12,1	11,2	30,0	-	28,1	-
Treatment 1 (10% PEG)	8,3	-	11,0	-	16,0	-	15,4	-
Treatment 5 (3% PVA)	18,1	-	10,8	-	34,9	-	31,3	-
Brightness (%)								
untreated	60,8	59,4	56,1	55,4	69,7	-	66,3	-
Treatment 1 (10% PEG)	60,9	-	58,8	-	70,0	-	68,5	-
Treatment 5 (3% PVA)	60,3	-	55,8	-	69,5	-	66,9	-

and even less than the untreated sheets (Fig. 1). Treating sheets with polyethylene glycol can preserve papers against yellowing over time. The stabilizing effect of polyethylene glycol for brightness is more pronounced with mechanical paper sheets. The protective mechanism of polyethylene glycol on paper towards light and ageing is unknown; the polymer is thought to act as an antioxidant[19].

Mixture of PEG and PVA

In order to combine the positive effect of the two tested polymers, a mixture of both was used.

Table 8 shows the properties of the bleached mechanical pulp and bagasse paper sheets treated with a mixture of the two polymers (Treatment 7 and Treatment 8; cf. Table 1) before and after one hour of accelerated ageing at 140°C. It becomes clear that the mechanical properties are improved. Slightly reducing the share of PEG (2.5 → 2.3 g) and halving the amount of PVA (1.25 → 0.6 g) results in reduced mechanical strength (with the exception of the tear factor of paper A), but in slightly increased brightness. Also, the ageing stability is improved by treating the sheets with the mixture of the two polymers (Fig. 3), as well as that of the mechanical properties and of brightness (Fig. 2).

Table 8: Properties of unaged and aged sheets treated with mixtures of PEG and PAV.

		Paper A		Paper C	
		Unaged	aged at 140°C	Unaged	aged at 140°C
untreated	Breaking length (km)	2,7	2,5	3,8	3,7
Treatment 7 (PEG 2,5g + PVA 1,25 g)		3,9	4,1	4,3	5,4
Treatment 8 (PEG 2,3g + PVA 0,6 g)		3,2	3,5	3,9	4,1
untreated	Tear factor	26,7	17,2	52,0	48,7
Treatment 7 (PEG 2,5g + PVA 1,25 g)		28,4	24,4	54,2	60,4
Treatment 8 (PEG 2,3g + PVA 0,6 g)		29,5	25,1	52,4	58,2
untreated	Burst factor	10,7	12,1	30,0	28,1
Treatment 7 (PEG 2,5g + PVA 1,25 g)		12,5	15,5	35,0	36,4
Treatment 8 (PEG 2,3g + PVA 0,6 g)		11,0	13,2	33,3	35,2
untreated	Brightness (%)	60,8	56,1	69,7	66,3
Treatment 7 (PEG 2,5g + PVA 1,25 g)		61,2	58,2	71,0	69,4
Treatment 8 (PEG 2,3g + PVA 0,6 g)		61,8	58,1	71,4	70,0

Conclusion

- Paper sheets treated with polyethylene glycol solution have lower mechanical properties than untreated sheets, but their brightness and the ageing stability of both mechanical properties and brightness are improved.
- Paper sheets treated with polyvinyl alcohol solution have greater mechanical properties than untreated sheets, but their brightness is less stable on ageing than that of sheets treated with polyethylene glycol.
- Paper sheets treated with a mixture of the two polymers improves not only the mechanical properties, but also the stability of the brightness on ageing.

Summaries

Physicomechanical Properties of Paper Treated With Polymers

Bleached mechanical pulp and kraft bagasse paper sheets bleached with alkaline hydrogen peroxide were treated with polyethylene glycol and polyvinyl alcohol. Mechanical properties of the treated sheets with polyethylene glycol deteriorated but improved by treating them with polyvinyl alcohol. The deterioration and improvement in the mechanical properties increase by

increasing the concentration of the polymer solution. Improvement in the mechanical pulp sheets had a higher percentage increase than the bagasse sheets. Brightness of the sheets treated with polyethylene glycol was more stable when aged than untreated sheets and those treated with polyvinyl alcohol. Sheets treated sheets with a mixture of polyethylene glycol and polyvinyl alcohol improved not only the mechanical properties but also the stability of the brightness of the treated sheets on ageing.

Propriétés physiques et mécaniques du papier traité avec des polymères

Des feuilles de papier, fait à base de pâte mécanique et de pâte à la soude de bagasse, blanchies au péroxyde d'hydrogène en milieu alcalin ont été traitées au polyéthylèneglycol et au polyalcool de vinyle. Le polyéthylèneglycol a détérioré les propriétés mécaniques des feuilles traitées, par contre le polyalcool de vinyle les a améliorées. Cet effet de détérioration ou d'amélioration des propriétés mécaniques croît en fonction de l'augmentation du taux de concentration de la solution polymère. Le taux d'amélioration obtenu était supérieur pour les feuilles de papier à base de pâte mécanique que pour celles à base de bagasse. La blancheur des feuilles traitées au polyéthylèneglycol supportait mieux le vieillissement que les feuilles non traitées ou celles traitées au polyalcool de vinyle. Le traitement effectué avec un mélange de ces deux solutions polymères (polyéthylèneglycol et polyalcool de vinyle) améliorait non seulement les propriétés mécaniques des feuilles mais aussi la stabilité de leur blancheur au cours du vieillissement.

Physikalische und mechanische Eigenschaften von polymerbehandeltem Papier

Probeblätter aus Holzstoff und Natronzellstoff von Bagasse. im alkalischen Medium gebleicht mit Wasserstoffperoxid. wurden mit Polyäthylenglykol mit Polyvinylalkohol behandelt. Die Behandlung mit Polyäthylenglykol verschlechterte,. die mit Polyvinylalkohol verbesserte die mechanischen Eigenschaften, beides verstärkt mit steigender Konzentration der Polymerlösung. Die prozentuale Steigerung war bei den Blättern aus Holzstoff höher als bei denen aus Bagasse-Zellstoff.. Die Helligkeit der mit Polyäthylenglykol behandelten Blätter veränderte sich bei beschleunigter Alterung weniger als die Helligkeit der unbehandelten und der mit Polyvinylalkohol behandelten Blätter. Eine Mischung der beiden Polymerlösungen verbesserte nicht nur die mechanische Festigkeit, sondern auch die Alterungsstabilität der Helligkeit.

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Abd-Alla M. A. Nada.
Samir Kamel & Mohamed El-Sakhawy
Cellulose & Paper Dept.
National Research Centre.
Dokki
Cairo
Egypt

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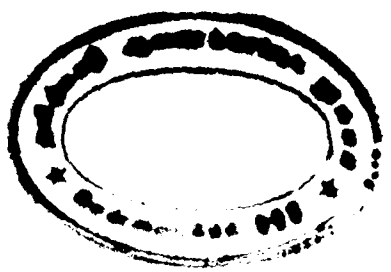
Obituary

Fausta Gallo, the Grand Old Lady of paper conservation research, passed away on the 5th of August 2000.

Fausta Gallo was born on the 6th of November 1931 in Rome. She was the daughter of Alfonso Gallo, founder of the Istituto Centrale per la Patologia del Libro, the first institute to be exclusively dedicated to paper conservation research world-wide and in the beginning concentrated on fighting biological decay of library materials. Fausta Gallo studied Natural Sciences at the University "La Sapienza" in Rome and graduated in 1953 with a degree thesis on paper-infesting insects. She was assistant Professor at the chair of Zoology at the same University for some years. From 1952 she worked as a researcher and consultant at the Istituto Centrale per la Patologia del Libro, where later, in 1957, she became head of the Biology Laboratory. She acted as director and co-ordinator of many interventive conservation programmes in Italian libraries affected by biodeterioration. The most demanding of these was her involvement in Florence after the flood of November 4, 1966 for which she received recognition from the Education Ministry. She took part in many National and International Conferences and taught courses at Italian and foreign institutions. Her dedication to the subject is obvious from the literal legacy she leaves behind: more than 80 published works on various aspects of biology as applied to library materials many of which have been translated into English, French, German and Japanese.



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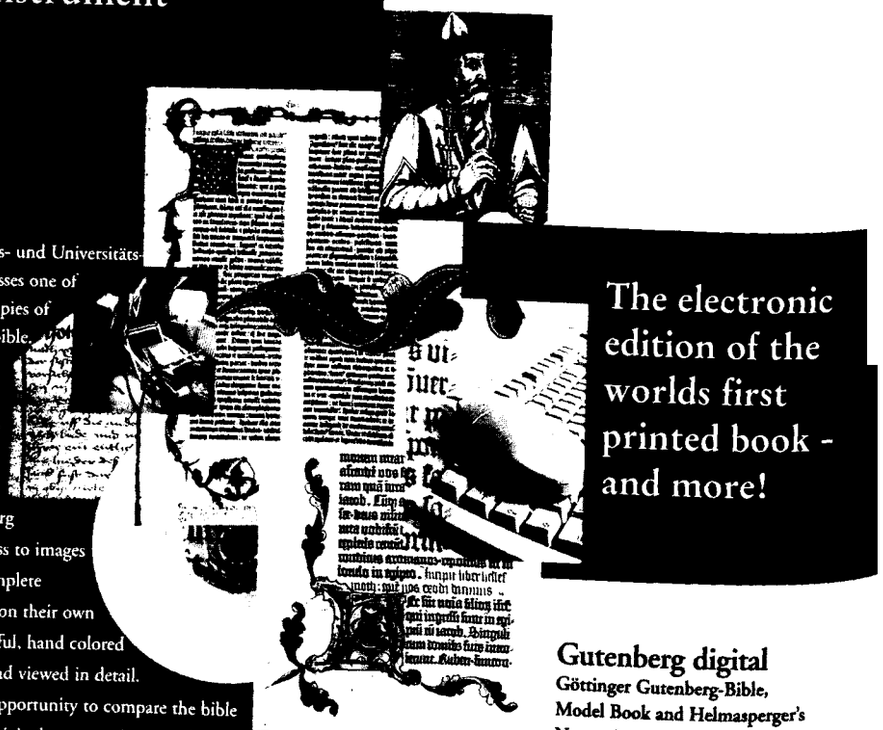

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