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The Effect of Ageing, on Paper Irradiated by Laser as a Conservation Technique

by JAMES CAVERHILL, JUDITH STANLEY, BRIAN SINGER & IAN LATIMER

INTRODUCTION

For a particular conservation treatment to be considered ethically permissible, it should not cause immediate, or long term degradation of the work of art. Previous reports by the authors[1] have shown that the Nd:YAG laser operating at 1.06 µm can remove ball-point pen ink from paper in a controlled fashion, causing less visible damage than contemporary methods of mechanical ink removal. The main advantage being that laser treatment is considerably more localized. However, we were worried that intense use of the laser on paper may cause physical or chemical damage. Tests (using constant rate of elongation equipment at the Paper Science Department, UMIST) on laser treated paper have shown that there is no reduction in tensile strength of the paper up to the fluence level required to remove the ink. Above this level, however, there is a tendency for the paper to tear at laser treated sites, when put under tension[2,3].

The Nd:YAG laser has the effect of heating its target, therefore there is a possibility of thermal degradation. The thermal degradation of paper has been well documented[4–6], and describes the formation of free radicals, carbonyl, carboxyl, and hydroperoxide groups. Peroxide activity was tested for by means of the Russell effect[7–9], and results inferred that there may be oxidation reactions taking place at the paper surface as a result of laser treatment[3]. The production of carbonyl and carboxyl groups on cellulose is largely responsible for the discoloration and yellowing of paper[10–13]. No such discoloration was witnessed on the laser treated *Roma* paper, however it is a good quality 100% cotton paper and under normal conditions one would not expect to see immediate colour changes. We were keen to establish whether oxidation had occurred and also whether the *Roma* samples would discolour on ageing.

Artificial accelerated ageing is one way of simulating the effects of long periods of natural ageing, but it is impossible to say exactly how long without

knowing the activation energies of all the reactions which are likely to take place[14–17]. There is no accepted set of standard accelerated ageing conditions therefore workers in this field are obliged to choose techniques and conditions they feel most adequately serve their purpose[18–26]. This paper reports the results of investigations into the change in colour, and strength, of artificially aged Q-switched Nd:YAG laser treated *Roma* 100% rag cotton paper. The measurement of the laser beam parameters used throughout this report have been described previously[1], but to summarize; the laser was focused on the surface of the paper samples using a 10 cm convex lens, giving a spot size of 0.14 mm. $\pm$ 2 x 10^{-3}. The pulse rise time was typically between 70 and 150 ns, and the repetition rate 10 Hz. The peak power was not measured, but would be between 1 and 2 x 10^5 W per pulse, depending on the pulse duration and the flashlamp voltage. The profile measured horizontally and vertically through the beam showed a 'top hat' shaped beam (within 10%), and therefore the energy distribution was assumed to be uniform throughout the spot.

Part 1: Artificial ageing tests

Experimental

Striking artificial ageing results can be achieved very quickly using extreme conditions, however these are unlikely to represent natural ageing with much accuracy. We wished to simulate as closely as possible the natural ageing of Nd:YAG laser treated *Roma* paper. In natural ageing circumstances the paper would be exposed to ultra-violet radiation[27] and degraded as a result of acid catalyzed hydrolysis[28]. Paper samples were prepared and placed in:

i) a light box delivering 800,000 Lux with a UV component of 180 mWcm^{-2} (northern temperate daylight), and

ii) a humid oven maintained continuously at 90°C, and 50% RH. All samples were artificially aged at the Paper Science Department, UMIST.

Samples of *Roma* paper were fixed to a moving stage and the laser brought to focus by measurement. For each sample the laser was made to pass 20 times back and forth over the paper surface. Each run was 10 mm. long with a spacing of 0.5 mm. between runs, in this way a square of paper 10 x 10 mm. was irradiated. Paper samples were laser treated over the fluence range 3–32 Jcm^{-2}, where 29 Jcm^{-2} was found to be the threshold below which ink removal was not complete[1], and 32 Jcm^{-2} was found to be the threshold above which visible damage occurred. Four sets of samples were made at each fluence level. Two of the four

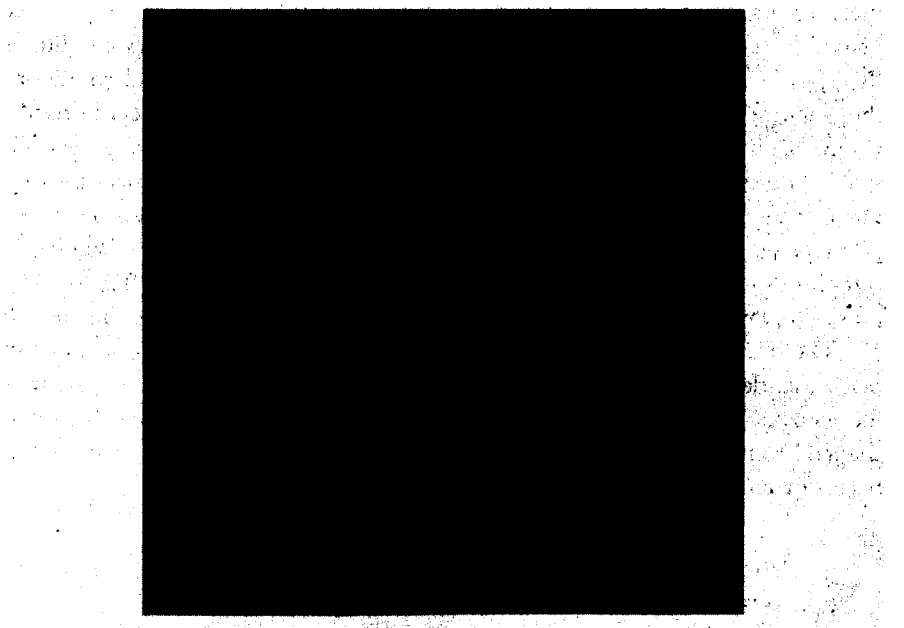

Fig. 1: Appearance of *Roma* cotton paper, Nd:YAG laser treated using a fluence of 32 Jcm^{-2}, and aged for one month in a humid oven, at 90° C and 50% R.H.

sets were light aged (48 hours and 120 hours respectively), and the remaining two sets were humid aged (1 week and 1 month respectively).

Results

The results of light ageing are equivocal as there was no discernible difference in appearance between the laser treated regions and the untreated areas. This does not mean that the laser has no effect on the paper samples, merely that any chemical change that does occur is not prone to discoloration on exposure to UV light.

Humid oven ageing yielded far more interesting results, where there was considerable red/brown discoloration to paper samples laser treated with a fluence of 32 Jcm^{-2} (Fig. 1). Even after one day of humid ageing the site of laser treatment at 32 Jcm^{-2} was noticeable. It is clear from these results that the Nd:YAG laser treatment of the paper samples is having some chemical effect. Close examination of the paper surface before and after laser treatment, suggests that the laser

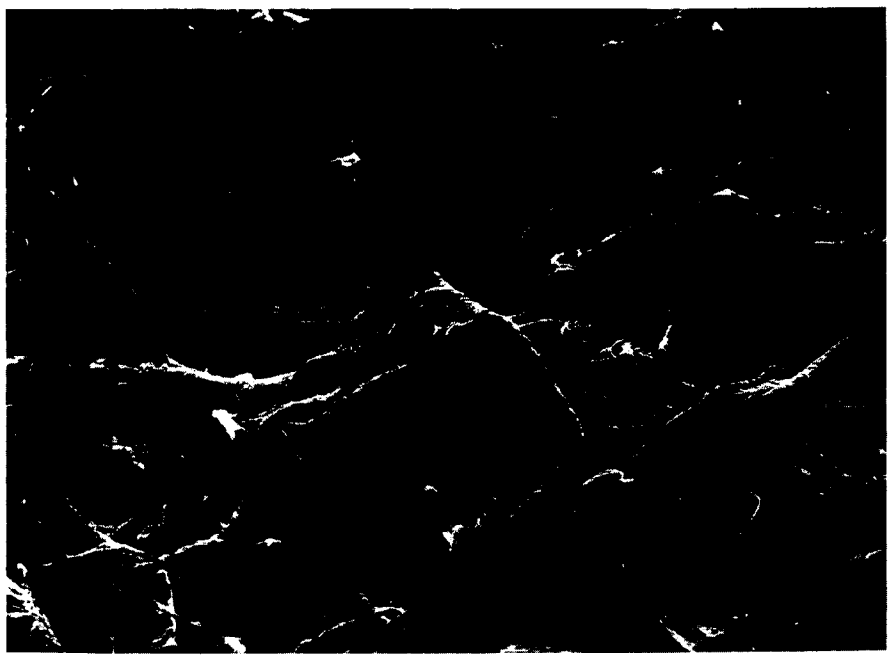

Fig. 2: SEM photograph (x400) of the surface of *Roma* cotton paper before Nd:YAG laser treatment, showing the gelatin size coating the paper fibres.

is removing the size from the surface of the paper fibres (Fig. 2 & 3). The presence of size on the surface of the paper fibres may have a significant effect on the absorption of energy by the fibres, and therefore on the heating effect of the laser pulses. We decided to carry out a series of simple tests to compare the chemical changes in laser treated *Roma* paper, with those of *Roma* with the size removed.

Part 2: Comparison of the chemical effect of laser treatment on standard sized and size removed *Roma* paper

Stain tests with Ponceau S showed the size to be gelatin, a protein, therefore some sheets of *Roma* paper were immersed in a bath of protease enzymes to effect its removal[29].

Test samples were compared as follows:

i) Russell effect experiments to determine presence of peroxide activity

ii) methylene blue test to determine presence of carboxyl groups

Fig. 3: SEM photograph (x400) of the surface of *Roma* cotton paper after Nd:YAG laser treatment using a fluence of 32 Jcm^{-2}, showing the removal of the gelatin size from the paper fibres.

iii) diffuse reflectance FTIR spectroscopy

iv) observation of colour change after humid ageing.

EXPERIMENTAL

Russell effect experiments to determine the presence of peroxide activity

Increasing the temperature accelerates the degradation of cellulose resulting in the formation of peroxides as one of the degradation products. Monitoring the abundance of peroxides can be used as a crude indicator of temperature change, therefore the presence of peroxides was tested for by means of the Russell effect[7–9]. If degraded organic material is placed in contact with a specially sensitized film, the peroxides released from the material can affect the film, creating a dark image of the oxidised region.

Samples of sized and size-removed *Roma* paper were laser treated over the fluence range described in Part 1 (3–32 Jcm^{-2}). Samples were fixed side by side on

the moving stage and the laser brought to focus by measurement. The laser was made to follow six lines (three on each sample) 14 mm. long and 10 mm. apart, for each fluence level. In this way we ensured that each sample received the same treatment. To achieve maximum contrast the paper samples were kept in the dark for several weeks before laser treatment and the Russell effect tests commenced immediately after laser treatment. Repeat tests for the Russell effect were carried out using the same samples two weeks after the original tests.

Film for the Russell effect tests was prepared using Kodak LPF4 film immersed in 0.005 M ammonium hydroxide solution for two minutes, washed in a 0.5% solution of Kodak Photoflo, and allowed to dry in a light-tight box. The process was carried out in a darkroom with OA safelight illumination. It is preferable to sensitize the film on the day of the test as it has a tendency to fog after a few days, even if kept in the dark. The Russell images were created by placing the paper samples face up on a sheet of glass (to cut out background oxidation activity) in a large lidded box. The film was placed over the paper samples. To ensure good contact another sheet of glass was placed over the film. The film was developed using Ilford ID11 stock solution and fixed with Kodak Unifix 1:5.

Methylene blue test to determine presence of carboxyl groups

Methylene blue is an indicator used for determining the amount of carboxyl groups in cellulose[30–33]. The concentration of absorbed methylene blue can be measured spectrophotometrically, but in addition the dye is an excellent tool for indicating the presence of carboxyl groups. Samples of laser treated *Roma* (standard sized and size removed) were prepared as described in Part 1 to create an irradiated square 1 cm^2 in area. Samples were prepared using a fluence of 32 Jcm^{-2}. They were immersed for 2 minutes in a 0.1 % solution of methylene blue, and rinsed in several changes of water for 3 hours. Samples of the standard sized and size removed paper were abraded with a scalpel and tested as above to confirm that physical disruption of the surface would not confuse results.

Diffuse reflectance FTIR spectroscopy

Since they were introduced in the 1980's Fourier Transform infrared (FTIR) instruments have become widely used for the analysis of chemical change in both paper and cotton textiles[34–38]. Diffuse reflectance FTIR spectroscopy has been widely used for paper analysis since it requires little sample preparation and produces relatively distortion free spectra of the surface. Diffuse reflectance FTIR

spectra for the 4000–600 cm^{-1} region were taken of laser treated *Roma* paper (standard sized and size removed), using a Perkin Elmer Paragon 1000. We anticipated a very subtle change in the laser treated regions of the paper samples, and therefore decided to record the difference between spectra rather than the spectra themselves. Three spectra were interpreted:

(i) standard sized *Roma* paper using a background of size removed *Roma* paper.

(ii) laser treated standard sized *Roma* paper using a background of standard sized *Roma* paper.

(iii) laser treated size removed *Roma* paper using a background of size removed *Roma* paper.

Heat degradation of cellulose is known to lead to the formation of carbonyl and carboxyl groups, therefore we studied the spectra of the laser treated samples specifically for changes in the abundance of either functional group. The brown discoloration resulting from ageing laser treated paper suggested the creation of conjugated systems, which tend to shift the peaks to lower wavenumbers. This possibility was included in the interpretation of the spectra. We also anticipated absorption peaks characteristic of amide groups due to the gelatin size.

The regions of the spectra we were interested in are as follows[40,41]:

a) aldehydes
   (i) strong C=O stretching, 1740–1720 cm^{-1}
   (ii) moderate C-H stretch doublet, 2900–2820 and 2775–2700 cm^{-1}
   (iii) C=O stretching shifted by conjugation, 1705–1680 cm^{-1}

b) ketones
   (i) strong C=O stretching, 1725–1705 cm^{-1}
   (ii) C=O stretching shifted by conjugation, 1685–1665 cm^{-1}

c) acids
   (i) strong C=O stretching, 1725–1700 cm^{-1}
   (ii) broad complex band due to O-H stretching, 3000–2500 cm^{-1}
   (iii) carboxylate anion stretching, 1610–1550 and 1400–1300 cm^{-1}

d) amides
   (i) C=O stretching, 1690–1650 cm^{-1}
   (ii) N-H stretching, 3320–3140 cm^{-1}
   (iii) N-H bending, 1550–1510 cm^{-1}

e) carbon skeleton
   (i) C=C stretching shifted by conjugation, 1680–1610 cm^{-1}

Observation of colour change in humid aged laser treated cotton paper

Samples of *Roma* paper were prepared as described in Part 1 to create an irradiated square 10 x 10 mm. in area. All paper samples were laser treated at a fluence of 32 Jcm^{-2}, placed in a humid oven (90°C, and 50% RH), and aged from between one day to one month. The reflectance spectrum (400–700 nm) of each laser treated sample was recorded and compared with untreated paper aged for the same period. Spectra were recorded using a Hitachi U3000 spectrophotometer.

RESULTS

Russell effect experiments to determine presence of peroxide activity

We achieved completely different results for the two paper samples under test. The Russell image from the standard sized *Roma* paper sample, created immediately after laser treatment, clearly shows a series of white lines where the laser has passed (Fig. 4a). The Russell image from the size removed *Roma* paper sample, clearly shows the expected result, a series of black lines where the laser has passed (Fig. 4b). Repeat tests two weeks later show a series of black lines for the standard sized paper sample (Fig. 4c), and no discernible lines for the size removed sample (Fig. 4d). The tests were repeated with newly created samples and although the intensity of white and dark lines varied, the general outcome was the same (Table 1).

A quick glance at the Russell images shows there to be considerably more background peroxide activity associated with the standard sized *Roma* samples, than their size removed equivalents, and perhaps this is crucial to interpreting the Russell photographs. The laser treatment of standard sized paper was accompanied by sparking and loud cracking which suggests vaporization of the size, and the SEM photographs (Fig. 2 & 3) tend to support this claim. Therefore the abundance of peroxides emitted from size, in the locality of the laser treated regions may be greatly reduced immediately after treatment, and thus appear as white lines or regions of relative inactivity on the Russell photographs. However in the case of the size removed samples, laser energy is absorbed directly by the cellulose, but without the sparking. The size removed paper is not vaporized, merely heated inducing auto-oxidation and the production of peroxides. Geuskens et al.[42] claim thermally induced auto-oxidation is "autocatalytic and from a certain stage, hydroperoxides are decomposed more quickly than they are formed", and therefore the concentration of peroxides must go through a maximum. Thermal deterioration studies have shown that at lower tempera-

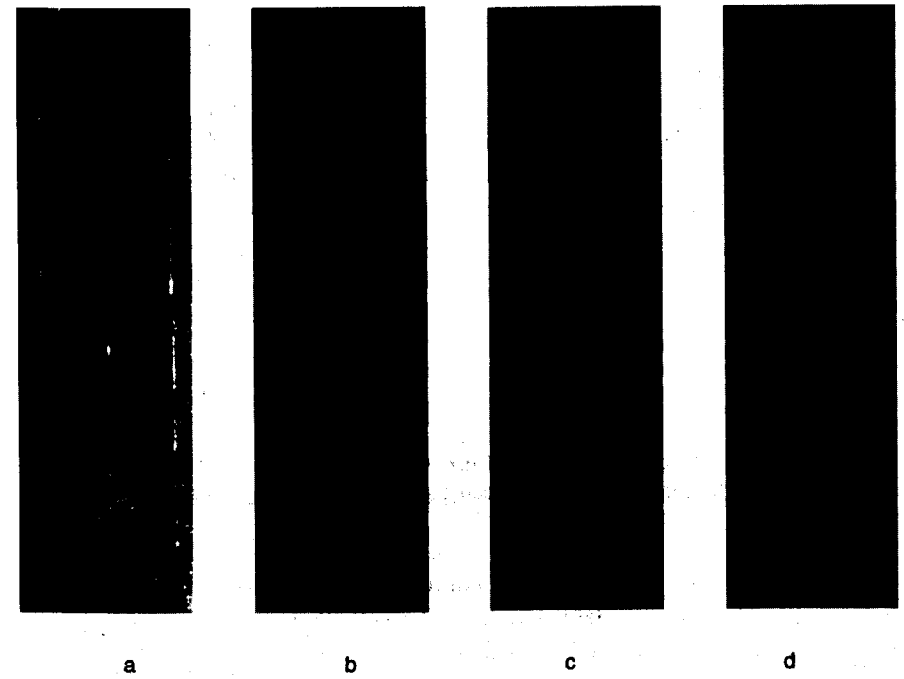

Fig. 4: The Russell effect image taken from *Roma* cotton paper; a and b: immediately after Nd:YAG laser treatment, using a fluence range of 3 –32 Jcm^{-2}, standard sized (a) and size removed (b) ; c and d: two weeks after treatment, standard sized and size removed

Table 1. The appearance of the Russell images of standard sized, and size removed *Roma* cotton paper, Nd:YAG laser treated using a fluence range of 3–32 Jcm^{-2}, recorded immediately, and two weeks after treatment.

Fluence/ $Jcm^{-2} \pm 0.8 Jcm^{-2}$	standard sized	size removed	standard sized + 2 weeks	size removed + 2 weeks
32	white lines	black lines	black lines	no lines
29	white lines	black lines	black lines	no lines
26	white lines	black lines	black lines	no lines
23	white lines	black lines	black lines	no lines
19	white lines	black lines	no lines	no lines
16	white lines	no lines	no lines	no lines
13	white lines	no lines	no lines	no lines
10	no lines	no lines	no lines	no lines
7	no lines	no lines	no lines	no lines
3	no lines	no lines	no lines	no lines

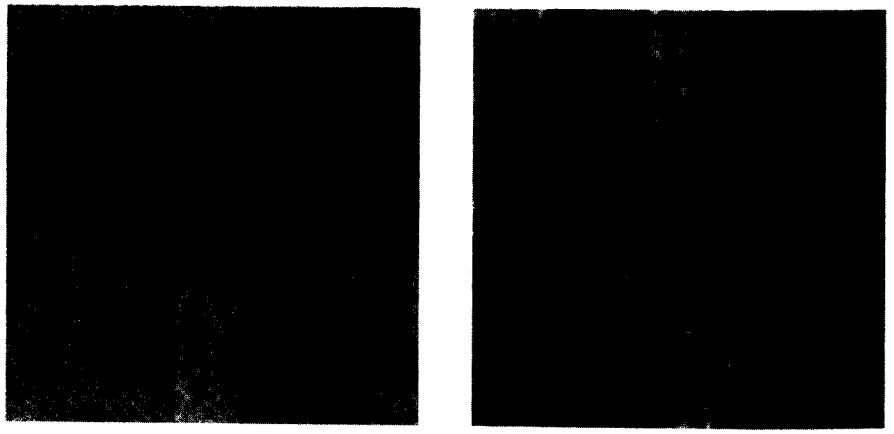

Fig. 5: Appearance of *Roma* cotton paper, Nd:YAG laser treated using a fluence of 32 Jcm^{-2}, and stained with 0.01% methylene blue solution. Left: size removed; right: standard sized.

tures, the time it takes to reach the maximum in hydroperoxide concentration is increased[43]. This may explain why after 2 weeks there are black lines clearly visible on the standard sized Russell image, whereas no lines on the size removed equivalent. The heat transferred to the cellulose of the standard sample from the vaporization of the size may be less than that transferred direct to the cellulose of the size removed sample. Thus more time is required to build up the peroxide concentration to a maximum i.e. 2 weeks, by which time the auto-oxidation reaction of the size removed sample has terminated.

Methylene blue test to determine presence of carboxyl groups

The most obvious result from the methylene blue tests was that the standard sized paper absorbed more blue than the size removed paper, showing that a considerable amount of acidity had been removed during the enzyme treatment. There was an obvious deepening in the shade of blue for the laser treated size removed sample (Fig. 5 left), which was not evident in the case of the standard sized paper. This suggests that laser treatment of size removed *Roma* paper is more likely to lead to production of carboxylic groups than similar treatment of standard sized *Roma*. However, using fluences above 32 Jcm^{-2}, on the standard sized paper did give rise to a local darkening (Fig. 5 right). Scalpel abrasions did give rise to a slight local darkening which suggests the uptake of methylene blue may be affected by the surface texture of the paper.

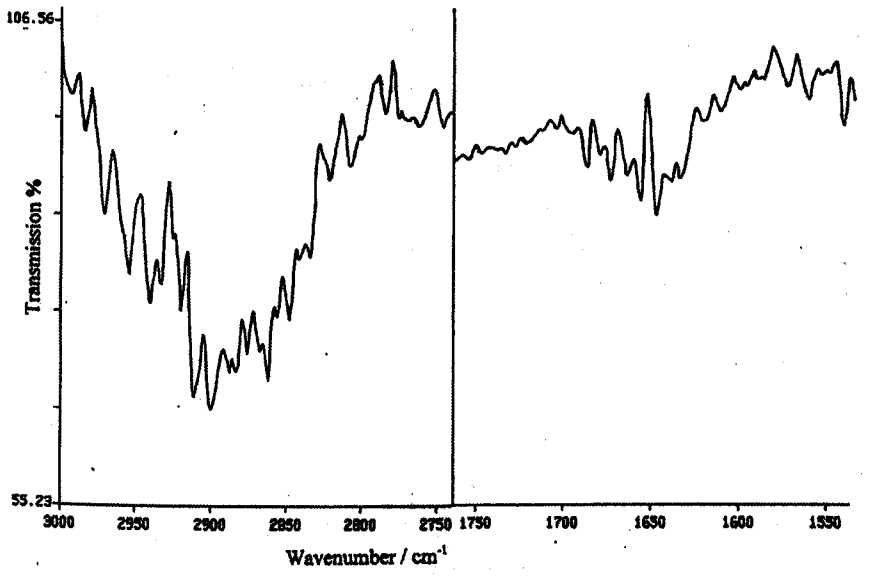

Fig. 6: Diffuse reflectance FTIR spectrum showing the difference between the reflectance spectra of standard sized *Roma* cotton paper and those of the same paper after laser treatment.

Diffuse reflectance FTIR spectroscopy

The spectra showed little difference between the sized and size removed paper except for two strong absorption peaks at 1680–1650 cm^{-1} and 1558–1541 cm^{-1}. These peaks can be attributed to the C=O stretching, and N-H bending of the amide groups present in the gelatin size.

The spectra showed some difference between the laser treated and untreated regions of the paper, with a strong broad band at 3000–2800 cm^{-1} and several peaks 1690–1650 cm^{-1} (Fig. 6). The peaks in the 1690–1650 cm^{-1} region suggest the presence of conjugated C=O, and C=C groups. The lack of any peaks in the 2800–2700 cm^{-1} infers that aldehydes are not present. The O-H stretching between 3000–2800 cm^{-1} may be due to carboxylic groups, though we must take into account the possibility of there being extra water associated with the laser treated region due to the ablation of the size. It appears that laser treatment of standard sized *Roma* paper produces conjugated ketones and carboxyls, although it must be stressed that the peaks recorded are barely discernible from the background noise, and further research should be carried out to verify this result.

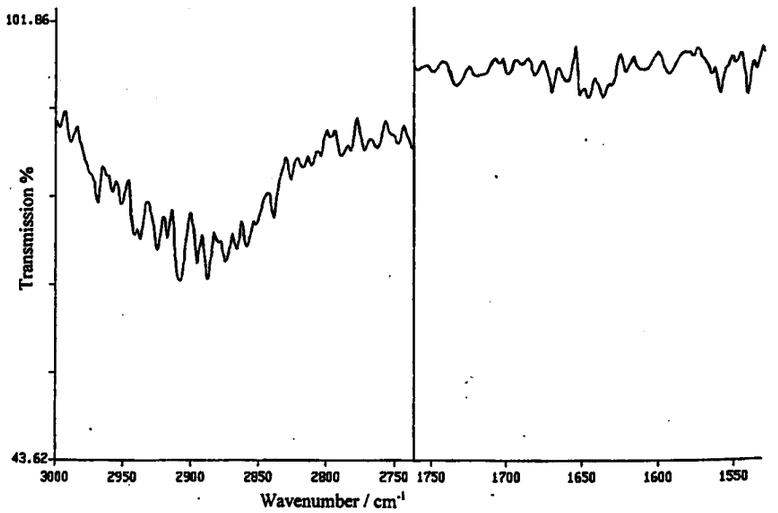

Fig. 7: Diffuse reflectance FTIR spectrum showing the difference between the reflectance spectra of size removed *Roma* cotton paper and those of the same paper after laser treatment.

The spectra showed only a very slight difference between the laser treated and untreated, size removed paper. There was a strong absorption band at 3000–2800 cm^{-1} but much less pronounced than for the standard sized sample, and practically no peaks in the 1690–1650 cm^{-1} region (Fig. 7). This suggests that laser treatment of size removed *Roma* causes significantly less oxidation than treatment of the sized equivalent.

Observation of colour change in humid aged laser treated cotton paper

There were markedly different results for the standard sized and size removed humid aged laser treated *Roma* samples.

Standard sized paper; localized red/brown discoloration of the laser treated area was noticeable after one day of humid ageing, and became progressively more obvious as ageing was increased (Fig. 8). This points to an increasing tendency to absorb the blue component of the spectrum, thus giving the sample a redder appearance on ageing.

Size removed paper; the laser treated regions of the samples were only marginally darker than their untreated equivalents, even after one month of humid

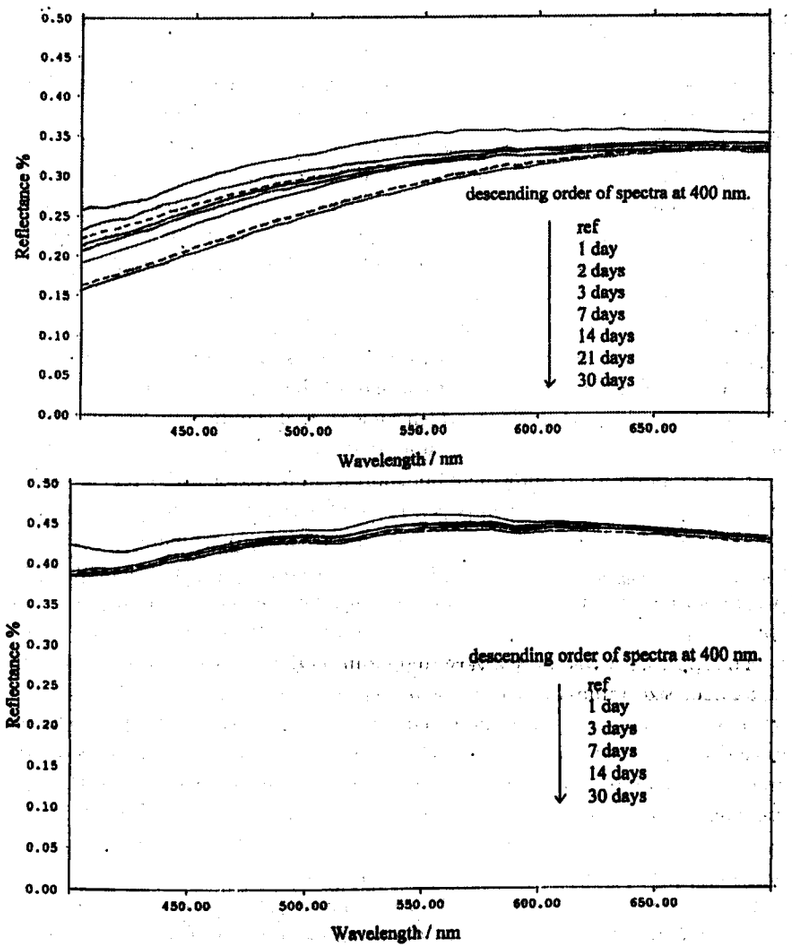

Fig. 8 and 9: Visible light reflectance spectra of standard sized (Fig. 8: above) and of size removed (Fig. 9: below) laser treated *Roma* cotton paper. The spectra of Fig. 8 show the gradual decrease in reflectance of blue light by the laser treated areas, as the exposure to artificial ageing is lengthened. The spectra of Fig. 9 show the almost negligible change in light reflectance of the laser treated areas, even after exposure to one month of artificial ageing.

ageing (Fig. 9). There is an almost imperceptible change in the spectrum of size removed, laser treated *Roma* over the ageing period.

Discussion

The discoloration of *Roma* cotton paper, as a result of humid ageing, clearly shows that laser treatment does have a long term chemical and physical effect (Fig. 1), even though there is no visible sign of severe damage immediately after treatment. However, with the size removed, there is practically no local discoloration of humid aged, laser treated paper. This suggests that the interaction between the laser and the size is responsible for the discoloration of the paper on ageing. The SEM photographs (Fig. 2 and 3) show that the size at the paper surface is removed by laser treatment. The sparking and loud cracking which accompanied laser treatment of the standard sized paper is characteristic of high energy absorption, therefore it is reasonable to assume some heat is conducted into the surrounding fibres. Laser treatment of the size removed paper did not give rise to sparking or cracking, which suggests that significantly less energy was absorbed. These assumptions are supported by results from the Russell effect tests, which point to an immediate but short lived peroxide activity as a result of laser treatment of size removed paper. It took 2 weeks to register peroxide activity after laser treatment of the standard sized paper, presumably because the peroxides were produced via the relatively slow conduction of heat into the paper, rather than the fast pulse interaction with the size. There was also a greater abundance of peroxides produced as a result of laser treatment to standard sized paper. Peroxide action on cellulose results in oxidation of the primary and secondary alcohol groups to carbonyl and carboxyl groups. The methylene blue test gave a positive result for increased carboxylic groups for size removed laser treated *Roma* paper, but barely registered an increase in carboxyls for the sized equivalent. Diffuse reflectance FTIR spectroscopy showed that there was a local increase in the abundance of conjugated ketones and possibly carboxylic groups as a result of laser treatment to standard sized paper, however it appears little oxidation takes place if the size has been removed.

In summary, laser treatment of size removed *Roma* paper causes a barely measurable amount of oxidation to the cellulose resulting in the production of carboxylic groups, and no discernible discoloration on ageing. Laser treatment of standard sized *Roma* paper causes a small, yet measurable amount of oxidation to the cellulose resulting mainly in the production of conjugated ketones, and considerable discoloration on ageing. Given that the increase in ketones and possibly carboxyls is so small for laser treated sized paper, it is surprising that the discoloration is so marked after moderate humid ageing. It may be that with the size removed, the paper is more prone to hydrolysis, however it is possible that the locally produced ketones are the root cause. Ranby[44] and more recently Whitmore and Bogaard[45], have investigated the "weak links" in polysaccharide

chains due to the creation of modified groups. Ranby suggests that oxidation at certain sites in cellulose chains creates a region that is more prone to hydrolytic attack than usual thus creating a "weak link". Whitmore and Bogaard conclude that it is possible "the degradation of a paper is determined not only by its acid content or cellulose DP but also by its content of such modified weak links, which essentially create a cellulose that may, at least for a time, tend to degrade more rapidly."

Conclusion

The research reported here was aimed at answering the question of whether the use of a Q-switched Nd:YAG laser for paper conservation techniques e.g. ink removal from paper, would create long term damage to the paper fibres. In the short term it appears that the laser causes less visible effect than other mechanical means of cleaning[3]. However after one day in moderate accelerated ageing conditions, the areas on the paper samples treated using the laser had noticeably darkened. This suggests that the laser is causing some oxidation to the cellulose or size, an assumption supported by chemical analysis. Clearly this represents an unsatisfactory outcome for a prospective conservation technique, however the results of laser treatment on the same paper with the gelatin size removed are much more favourable. There is no discernible discoloration on ageing, and only a slight increase in the abundance of carboxyl groups. Unfortunately papers used as artist's supports will almost certainly contain a size, and are thus likely to be adversely affected by laser treatments. However, the heating effect of the Nd:YAG laser is most marked for long pulse durations for example those used in this research 70–150 ns. rise time. It is possible to operate the laser with a pulse rise time of 15 ns. which would significantly lower the heating effect and therefore be less likely to result in discoloration on ageing. Research on this subject is already underway and the results will be reported in due time.

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SUMMARIES

The effect of ageing, on paper irradiated by laser as a conservation technique

Previous studies of ink removal by Q-switched Nd:YAG laser suggest that there is little physical damage to the paper fibres. However, laser removal of ink necessarily has a heating effect on the paper surface. This study examines the possibility that there may be oxidation of the cellulose as a result of laser treatment. The effect of humid ageing on Nd:YAG laser treated cotton paper was investigated, and considerable discoloration was witnessed. Laser treated paper samples were tested for oxidation of functional groups using the Russell effect test, the methylene blue test and Fourier Transform infra-red (FTIR) spectroscopy. The Russell effect test strongly inferred peroxide activity and the likelihood of oxidation of the cellulose. The methylene blue test suggested an increased abundance of carboxylic groups after laser treatment. FTIR spectra of laser treated paper showed an increased presence of conjugated ketones and carboxyls, but gave little solid evidence of oxidation as the absorption peaks attributed to oxidized cellulose are barely discernible from the background noise. These results suggest that the oxidation of paper, by Q-switched Nd:YAG laser, is slight but may be enough to cause localized discoloration at some time in the future.

L'effet du vieillissement sur du papier ayant subi une irradiation au laser comme technique de conservation

Des études antérieures réalisées pour enlever l'encre au moyen d'un laser déclenché au néodyne (Nd:YAG = Néodyne: grenat d'yttrium- aluminium) permettent de supposer que cette procédure ne détériore que très peu les fibres du papier. Cependant ce traitement au laser provoque inévitablement un effet d'échauffement de la surface du papier. Cette étude a pour objet d'examiner si le traitement au laser a entraîné une oxydation de la cellulose. On a étudié l'effet d'un vieillissement humide sur du papier chiffon traité au laser Nd:YAG et on a pu constater une décoloration considérable. Des échantillons de papier traités au laser ont été soumis au test de l'effet Russell, à la méthode du bleu de méthylène et à la spectroscopie infrarouge de transformation de Fourier (FTIR) afin de déterminer si une oxydation des groupes fonctionnels avait eu lieu. Les résultats du test de Russell penchaient largement dans le sens d'une activité peroxyde et d'une oxydation probable de la cellulose. Le test au bleu de méthylène permettait de supposer que le traitement au laser avait entraîné un fort accroissement des groupes carboxyles. La spectroscopie infrarouge de transformation de Fourier (FTIR) du papier traité au laser a mis en évidence que des groupes conjugués cétoniques et carboxyles avaient augmenté, mais on ne pouvait pas absolument en conclure que des processus d'oxydation avaient eu lieu car il était presque impossible de discerner les bandes d'absorption de la cellulose oxydée du bruit de fond. Ces résultats permettent de supposer que l'oxydation, que subit le papier traité au laser mentionné plus haut, bien que minime, puisse éventuellement être assez forte pour apparaître dans un avenir lointain sous forme de décoloration localisée.

Die Wirkung einer Alterung auf Papier, das aus konservatorischen Gründen mit Laser bestrahlt wurde

Frühere Untersuchungen zur Entfernung von Schrift mit Hilfe von *Q-switched Nd:YAG*(= Neodym:Yttrium-Aluminium-Granat)-Laser ließen vermuten, daß diese Behandlung die Fasern des

Papiers nur geringfügig schädigt. Die Laserbehandlung hat jedoch unvermeidlich ein Erhitzen der Papieroberfläche zur Folge. Die hier vorgelegte Studie prüft die Möglichkeit, ob die Cellulose als Folge der Laserbehandlung oxidativ geschädigt wird. Es wurde die Wirkung einer Feuchtalterung auf Hadernpapier untersucht, das mit Nd:YAG Laser behandelt worden war, und es zeigte sich eine Farbveränderung in nennenswertem Ausmaß. Laserbehandelte Papierproben wurden mit Hilfe des Russel-Effekts, der Methylenblau-Methode und Fourier-Transformations-Infrarot-Spectroskopie (FTIR) daraufhin untersucht, ob eine Oxidation der funktionellen Gruppen stattgefunden hat. Der Russel-Test ergab mit Nachdruck Anzeichen für eine Peroxid-Aktivität und damit für eine stattgehabte Oxidation der Cellulose. Die Methylenblau-Methode ließ auf eine starke Zunahme von Carboxylgruppen schließen. Die FTIR-Spektren des laserbehandelten Papiers zeigten eine Zunahme von konjugierten Keto- und Carboxylgruppen, aus denen aber nicht mit Sicherheit auf Oxidationsvorgänge geschlossen werden kann, da die Adsorptionsbanden der oxidierten Cellulose kaum vom Hintergrundrauschen zu unterscheiden sind. Diese Ergebnisse lassen vermuten, daß die Oxidation, die Papier durch eine Behandlung mit dem genannten Laser erfährt, zwar gering ist, jedoch möglicherweise stark genug, um in fernerer Zukunft als lokale Verfärbung in Erscheinung zu treten.

REFERENCES

1. Caverhill, J., I. Latimer & B. Singer: *An investigation into the use of a laser for the removal of modern inks from paper.* The Conservator 20 (1996): 65–77.
2. *Tensile breaking properties of paper and paperboard (using constant rate of elongation apparatus).* Tappi T494om–88 (1988).
3. Caverhill, J., B. Singer & L. Latimer: *An investigation into the use of lasers in paper conservation.* Institute of Paper Conservation Conference, London, April 1997. Published 1998: 284–290.
4. Shafizadeh, F.: *Pyrolysis and combustion of cellulosic materials.* In: Advances in Carbohydrate Chemistry, ed. M.L. Wolfrom & R.S. Tipson 23 (1968): 419–465.
5. Shafizadeh, F. & A.G.W. Bradbury: *Thermal degradation of cellulose in air and nitrogen at low temperatures.* Journal of Applied Polymer Science 23 (1979): 1431–1442.
6. Shafizadeh, F.: *Thermal degradation of cellulose.* In: Cellulose Chemistry and its Applications, ed. T.P. Nevell & S.H. Zeronian 1985: 266–289.
7. Daniels, V.: *The Russell Effect.* Studies in Conservation. 29 (1984): 57–62.
8. Daniels, V.: *A photographic method for detecting the oxidation of materials.* ICOM 7th. Triennial Meeting, Copenhagen. Preprints 1 (1984): 51–53.
9. Daniels, V.: *Monitoring the auto-oxidation of paper using photographic materials.* In: Historic Textile and Paper Materials, ed. H.L. Needles & S.H. Zeronian. Advances in Chemistry Series 212. Washington: . American Chemical Society 1986: 317–327.
10. Daniels, V.: *The discolouration of paper on ageing.* The Institute of Paper Conservation Conference, Oxford 1986. Published 1988: 93–100.
11. Hon, D.N-S.: *Yellowing of modern papers.* In: Preservation of Paper and Textiles of Historic and Artistic Value I. Advances in Chemistry Series 193. Washington: American Chemical Society, 1981: 119–41.
12. Hon, D.N-S.: *Discoloration and deterioration of modern papers.* Source unknown. Ca. 1982: 89–92.

13. Lewin, M.: *The yellowing of cotton cellulose pt. II & III.* Textile Restoration Journal.1965: 935–942, 979–986.
14. Blackshaw, S.M. & V. Daniels: *The testing of materials for use in storage and display in museums.* The Conservator 3 (1979): 16–19.
15. Feller, R.L., S.B. Lee & J. Bogaard: *The kinetics of cellulose deterioration.* American Chemical Society 1986: 329–347.
16. Du Plooy, A.B.J.: *The influence of moisture content and temperature on the aging rate of paper.* Australian Pulp and Paper Industry Technical Association 34 (1981): 287–292.
17. Duswalt, A.A.: *Thermal analysis study of paper permanence.* In: Preservation of Paper and Textiles of Historic and Artistic Value, ed. J.C. Williams. American Chemical Society Advances in Chemistry Series 164, Washington, D.C., 1977: 352–61.
18. Feller, R.L.: *Accelerated aging: photochemical and thermal aspects.* Marina del Rey: Getty Conservation Institute 1994.
19. Vitale, T. & D. Erhardt: *Changes in paper color due to artificial aging, and the effects of washing on color removal.* Source unknown. Ca. 1995: 1–12.
20. Erhardt, D., D. von Endt & W. Hopwood: *The comparison of accelerated aging conditions through the analysis of extracts of artificially aged paper.* AIC Annual Meeting 1987. Preprints. Washington: American Institute for Conservation 1995: 43–55.
21. Zou, X., N. Gurnagul, T. Uesaka & J. Bouchard: *Accelerated aging of papers of pure cellulose: mechanism of cellulose degradation and paper embrittlement.* Polymer Degradation and Stability 43 (1994): 393–402.
22. Wilson, W.K., J.L. Harvey, J. Mandel. & T. Worksman: *Accelerated aging of record papers compared with normal aging.* Tappi J. 38, 9 (1955): 543–548.
23. Cuddihy, E.F.: *The aging correlation (RH + t): relative humidity (%) + temperature (°C).* Corrosion Science 27, 5 (1986): 463–474.
24. Lee, S.B., J. Bogaard, J. & R.L. Feller: *Accelerated thermal degradation of pulp sheets: Effect of beating and importance of humidity.* In: Cellulose and Wood-Chemistry and Technology. 10th Cellulose Conference, Proceedings ed. C. Schuerch. Syracuse, N.Y. 1988: 863–84.
25. Arney, J.S. & Jacobs, A.J.: *Accelerated aging of paper – the relative importance of atmospheric oxygen.* Tappi J. 62, 7 (1979): 89–91.
26. Arney, J.S. & Jacobs, A.J.: *Newsprint deterioration – the influence of temperature on the relative contribution of oxygen-independent and oxygen-dependent processes in the total rate.* Tappi J. 63, 1 (1980): 75–77.
27. Lee, S.B., J. Bogaard & R. Feller: *Damaging effects of visible and near- ultraviolet radiation on paper.* In: Historic Textile and Paper Materials II: Conservation and Characterisation, ed. S.H. Zeronian & H.L. Needles. 19th. Meeting of the American Chemical Society, L.A. September 1988. Published 1989: 54–62.
28. Whitmore, P.M. & J. Bogaard, J.: *Determination of the cellulose scission route in the hydrolytic and oxidative degradation of paper.* Restaurator 15 (1994): 26–45.
29. Segal, J., & D. Cooper: *The use of enzymes to release adhesives.* The Paper Conservator 2 (1977): 47–50.
30. ASTM Standard Test D1926-63: *Standard test methods for carboxyl content of cellulose.*
31. Eusman, E.: *Tideline formation in paper objects: cellulose degradation at the wet-dry boundary.* In: Conservation Research 1995. Studies in the History of Art 51., Washington: National Gallery of Art 1995: 11–27.
32. Davidson, G.F.: *The acidic properties of cotton cellulose and derived oxycelluloses. Part II The absorption of methylene blue.* Journal of the Textile Institute 39 T65 (1948): 65–86.

33. Lomax, S.Q.: *Analysis of peroxides. and analysis of tidelines.*, Washington: National Gallery of Art, Scientific Research Department 1993.
34. Hon, D.N-S.: *Fourier Transform IR spectroscopy and electron spectroscopy for chemical analysis.* American Chemical Society 1986: 349–361.
35. Cardamone, J.M.: *Application of nondestructive FTIR spectroscopy for identification of textile materials.* Glasgow: Scottish Society for Conservation and Restoration 1991: 49–58.
36. Grosso, V.: *Fourier Transform Infrared and Raman Spectroscopy of ancient paper*, Ottawa: Canadian Conservation Institute 1994: 245–250.
37. Langkilde, F.W. & A. Svantesson: *Identification of celluloses with Fourier-Transform (FT) mid-infrared, FT-Raman and near infrared spectrometry.* Journal of Pharmaceutical and Biomedical Analysis 13, 4/5 (1995): 409–414.
38. Pande, A. & M.M Singh: *Studies of molecular structure of cellulose and chemically modified cellulose by infra-red spectroscopy.* Laboratory Practice 15, 5 (1966): 544–550.
39. Berben, S.A., J.P. Rademacher, L.O. Sell & D.B. Easty: *Estimation of lignin in wood pulp by diffuse reflectance Fourier-transform infrared spectrometry.* Tappi J. 70 (1987): 129–133.
40. Conley, R.J.: *Infrared Spectroscopy.* Boston: Allyn & Bacon 1972.
41. Dyer, J.R.: *Applications of Absorption Spectroscopy of Organic Compounds.* Eaglewood Cliffs: Prentice-Hall Inc., 1965.
42. Gueskens, G., D. Baeyens-Volant, G. Delaunois, Q. LuVinh,, W. Piret & C. David: *Photo-oxidation of polymers II.* European Polymer Journal 14 (1987): 299–303.
43. Feller, R.L.: *Accelerated aging: photochemical and thermal aspects.* Marina del Rey: Getty Conservation Institute, 1994.
44. Ranby, B.G.: *"Weak links" in polysaccharide chains as related to modified groups.* Journal of Polymer Science 53 (1961): 131–40.
45. Whitmore, P.M. & J. Bogaard, J.: *The effect of oxidation on the subsequent oven aging of filter paper.* Restaurator 16 (1995): 10–30.

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The Effect of Ageing, on Paper Irradiated by Laser as a Conservation Technique

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Is Deacidification a Step to the Rescue of Historic Newspapers?

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INTRODUCTION

The safeguard of information printed on acid-sized groundwood paper is today a first-rate problem of archive and library management. The most endangered batch is the paper made from the last century, but also the very short live span of modern papers[1] makes the solving of this problem very urgent. In our libraries almost 75% of book items are of such type of paper[2].

Newsprints of low quality form a special group of groundwood papers. They have not been made for long-term storage in archives and libraries. Since their acidity is a main reason for their disintegration, deacidification[3] seems to be a crucial step to make them apt for long-term storage. Deacidification of large batches, however, is difficult to perform, and it may be doubted whether they really extend the lifetime of groundwood paper – not regarding the undesirable side-effects of the relevant processes. In accordance with results gained from the accelerated ageing of papers, even deacidified papers come, within a relatively short period of their natural ageing, to a significant breakage in their strength[4]. In the context of the practical situation in a library or an archive deacidification treatment of these papers may afford essential time for their reproduction, but their physical rescue without any further reinforcing probably will not be possible.

In our research we tried to find a reason for the intensely reduced strength of historic groundwood papers during accelerated ageing. Our means was to analyse the amount of damage caused by oxidation which occurs simultaneously together with the decisive degradation process, i.e., acid hydrolysis of cellulose.

EXPERIMENTS

Paper samples

As sample papers for observing the newsprint durability we used the following:

1: Modern newsprint 1996, manufacturer: Jihočeské papírny a.s., Větrní, Czech Republic
ca. 66% bleached groundwood approximately,
ca. 24% unbleached sulfite pulps
7–8% kaolin
no sizing
produced in acid medium
retention of aluminum sulfate and polyethylendiamine
grammage 48,8 g/m^2.

2: Modern newsprint 1996, manufacturer: Norske Skog Štetí, Czech Republic
ca. 50% classic groundwood bleached by hydrogen sulfide
ca. 15% half-bleached sulfate pulp
35% recycled material consisting of newspaper/magazine mixture (1:1)
all fillers supplied by the recycled material
no sizing
made in a slightly acid medium: pH ca. 6,8
retention of filler by NALCO 74508®, a product on polyacryl amide base
little amount of aluminum sulfate
grammage 48,8 g/m^2.

3: the *Hlas našej dediny* newspaper, 1956, Slovak Republic

4: the *Neue Ordnung* newspaper, 1942, Croatia

5: the *Pesti Hirlap* newspaper, 1881

The samples 6x1 cm were cut out of the modern newsprint in machine direction. Other samples were cut out of the rest of newspapers in machine direction from the outer margin (at least 1 cm from the page margin), always from the same issue or from consecutive issues. The papers were divided into 2 groups:

- Control papers (C). Soaked for 5 minutes in 50 ml pure methanol. Yellow degradation products of paper disintegration were passing into the methanol.

- Deacidified papers (D). Soaked for 5 minutes in 4% methanol solution of magnesium methyl carbonate (MMC: $(CH_3\text{-}O\text{-})_2\ MgCO_2$). As with the C-samples, coloured degradation products were passing into the methanol MMC solution. The alkaline reserve ($MgCO_3$) created from MMC after evaporation of methanol was determined as a difference of weight of C and D samples after 48 hours of sample conditioning.

Microscopic characteristics

Samples were soaked in deionized water for 24 hours and were non-destructively blended in a homogenizer for the period of 10 minutes at laboratory temperature and at 2450 rpm (revolutions per minaute). With the modern papers (sample 1 and 2) the homogenizing worked better than with the same samples after 12 days of accelerated ageing. With the historic papers samples the homogenizing worked better after deacidification. The course of homogenizing is given in Table 1.

Light microscopy of the samples was done with the magnification factors 63 and 100. (Fig. 1)

Light microscopy of the newsprint fibres points out a very complicated product after the homogenization in water. There is an obvious difference between modern and historic newsprints. Modern papers contain relatively more long intact cellulose fibres and less other accompanying products. Sample 5 contains the most of this "crushed material". In a microscopic picture there were no differences between C- and D-samples and no differences between the samples before and after accelerated ageing.

Means and methods

- Conditioning. Before setting the grammage and double folds, the samples were conditioned for 48 hours at RH 45% and temperature 21± 2°C.
- Accelerated ageing. Considering better separation of results caused by accelerated ageing we set the temperature at 103° C for 12 days. We assume that every 3 days exposure at this temperature corresponds to 25 years of natural ageing[5].
- Double folds. The samples after conditioning were tested for the number of double folds according to Schopper[6]. Induced tension was 10 N in the samples 1 and 2 and 2,5 N in the samples 3, 4 and 5. The brightness (reflectance) of samples was set, as determined in the preceding work, at 457 nm[7]. The reflec-

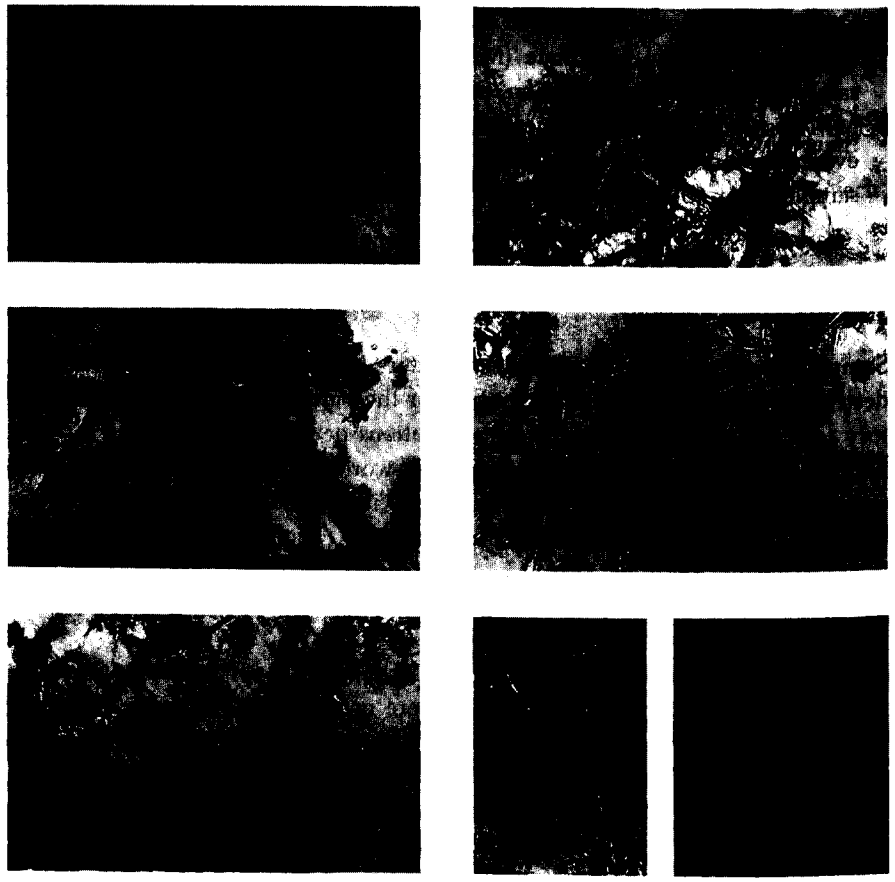

Fig. 1: Sample 1–5, disintegrated, under the microscope with magnification factor 63, and a specimen of groundwood in the samples 1 and 2 with the magnification factor 100.

Table 1: The behaviour of paper in the homogenizer, before (C0, D0) and after accelerated ageing (C12, D12). 1: beginning of disintegration ... ... 5: complete slush.

	5 minutes				10 minutes			
Sample	C_0	D_0	C_{12}	D_{12}	C_0	D_0	C_{12}	D_{12}
1	5	5	2	3	5	5	2	3
2	5	5	2	2	5	5	2	3
3	3	3	2,5	3	4	4,5	3,5	5
4	2	4,5	3	2,5	3	5	3	4
5	3,5	5	3,5	5	4,5	5	4,5	5

tance of samples before and after deacidification was measured in the visible spectrum area in the range of 375–700 nm (Fig. 2).

- Acidity. The samples 3x1 cm were extracted in 2 ml of deinozed water (pH 7) at 100°C for 1 hour. Acidity in the extract was determined using a pH-meter M-120 Mikrotechna (Czech Republic). The samples were dried and pressed before again determining the brightness as described above.
- Extractable agents. Light absorbance (optical density) of the extract before determining the pH was measured at 457 nm by the photocolorimeter Specol 11 (Carl Zeiss, Jena, Germany).
- Carbonyl content in individual samples was determined by the hydrazine photocolorimetric method according to Albertsson and Samuelson[8].
- Carboxyl content was determined by the photocolorimetric reaction with methylene blue (MB) according to the method T237 su-639 with modification for the low weight samples.
- Lignin content. So-called Klason's lignin in the samples of individual kinds of newsprint was determined by Koenig and Rump's method[10]. The amount has been determined as a weight percentage of lignin in dry sample of paper.

RESULTS AND DISCUSSION

Characteristics before deacidification

Basic characteristics of selected types of groundwood paper (C-samples) before accelerated ageing are given in Table 2.

- Grammage. The weight of modern newsprints is approximately the same as indicated by their manufacturers. The weight of historic papers is heavier, and groundwood papers from the last century are of the heaviest weight because of their greater amount of sizing and filler.
- Acidity of modern papers is not critical; in sample 2 the acidity is even considerably in the alkaline area. The most acid among historic papers was, as expected, sample 5.
- Double folds. Modern newsprint (sample 2) has twice the resistance than sample 1. Historic papers were being torn at four times lower tension, and they vary in degree of endurance. The higher endurance of sample 4 can partly be attributed to heavier grammage. Sample 5 is of very low folding endurance, which is a characteristic feature of low-pH-groundwood paper from the end of the last century.

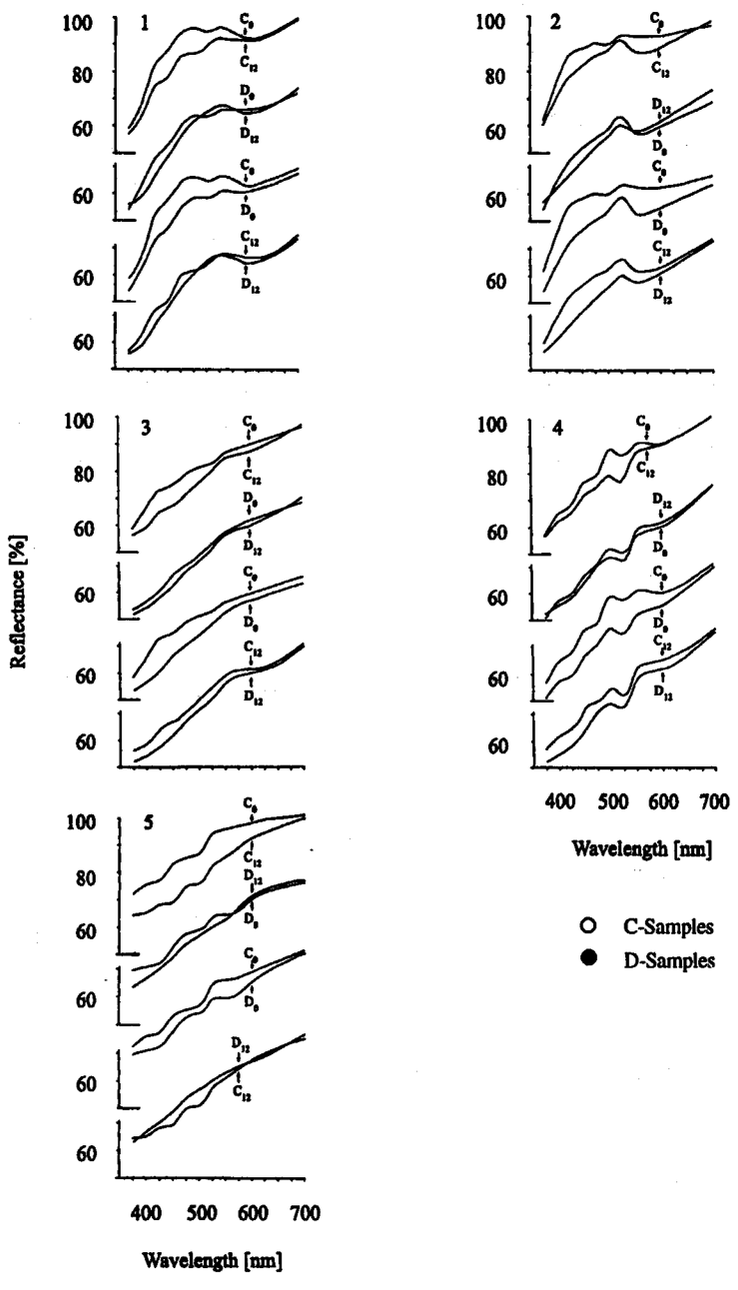

Fig. 2: Reflectance of samples in the visible spectrum area, C- and D-samples before (C_0, D_0) and after accelerated ageing (C_{12}, D_{12}).

- Brightness reflects the range of damage of historic paper only to some extent, as well as the amount of lignin present. The evidence of this is the brightness of sample 5: it is more than that of the samples 3 and 4, while the number of double folds of this paper is much lower and its grammage much higher. Extraction in methanol removes some of the yellow degradation products (exception: sample 5). This way the brightness rises about 0,7–1,1% in modern and about 1,8% in historic newsprint (sample 5: 2% decrease). This is not very much. The amount of agents extractable in methanol is 0,12–0,9% in modern and 0,5–1,35% in historic papers (Table 2: decrease of weight). After soaking in water the increase of brightness in historic papers is substantially more significant and higher. The optical density of the water extracts support this fact. Reflectance spectra of modern newsprints (Fig. 2) are very similar, and they are different from those of historic newsprints. It seems that historic newspapers absorb the light in visible area of radiance much more than modern pa-

Table 2: Basic characteristic of the tested papers (C-samples) after the extraction in methanol before accelerated ageing, average and standard deviation.

	Number of probes	Sample 1	2	3	4	5
Grammage (g/m²)	10	49,81 ±0,87	48,33 ±0,76	61,71 ±3,51	68,77 ±1,06	86,08 ±3,48
pH	10	6,89 ±0,14	7,8 ±0,24	6,21 ±0,31	5,58 ±0,11	5,47 ±0,32
Double folds (tension 10 N, * 2,5 N)	8	573 ±160	1226 ±207	*1136 ±327	*2682 ±369	*207 ±90
Brightess (%)	10	78,28 ±0,91	78,12 ±1,20	64 ±1,73	67,31 ±2,22	73,52 ±1,65
Brightness (%) after methanol extract	10	78,81 ±1,59	79,01 ±1,75	65,15 ±1,99	68,53 ±1,67	72,06 ±1,43
Brigtness (%) after aqueous extract	10	78,19 ±1,55	78,27 ±1,69	67,51 ±1,22	71,32 ±2,15	76,69 ±1,27
Optical density ($\cdot 10^{-2}$) of aqu. extr. at 457 nm	10	1,34 ±0,30	0,31 ±0,28	3,56 ±0,39	4,63 ±0,45	6,12 ±0,59
Carbonyls (mmol/100g)	5	3,24 ±0,37	3,69 ±0,12	5,14 ±0,17	6,61 ±0,48	7,33 ±0,14
Carboxyls (mmol/100g)	5	7,42 ±0,18	7,36 ±0,32	6,59 ±0,28	7,09 ±0,31	2,62 ±0,11
Carbonyls / Carboxyls	5	0,44	0,5	0,74	0,93	2,79
Lignin (g/100g)	3	18,5	17,5	17	21,3	15
Decrease of weight (%) after methanol extraction		-0,9	-0,12	-0,49	-1,24	-1,35

pers, which is indicated by the steepness of the curves. During accelerated ageing the spectra do not change significantly.

- Lignin. The amount of lignin indicates the content of groundwood in paper. The amount of ascertained lignin in modern papers is approximately the same as indicated by their manufacturers. As for historic papers, sample 4 contains more and the sample 5 less lignin in comparison with the samples 1 and 2.
- Carbonyl groups. The analysis of functional carbonyls shows the range of oxidation of all paper components, i.e. cellulose, lignin, sizing agents, etc. The historic papers analyzed for our research contained 1,4 to 2,0 times more carbonyls compared to modern papers; sample 5 had the highest carbonyl content.
- Carboxyl groups. The amount of carboxyls in papers represents paper oxidation, but the amount of ascertained function carboxyls can be influenced also by the presence of further various paper components such as cation active starch used in the production of modern newsprints. High values of carboxyls in the samples 1 and 2 probably do not pertain to actual oxidation. They may originate from the changes in paper during the production process. The carboxyls in the historic paper samples 3 and 4 are at the same value as in modern papers, but the carbonyls versus carboxyls ratio is nearly two times higher. Sample 5, a paper from the last century, has significantly low content of carboxyls, what is raising the ratio carbonyls versus carboxyls in a considerable amount. It is possible that this ratio is increased with the age of the paper.

After deacidification

Characteristics of paper after deacidification with MMC before ageing are given in Table 3.

- Grammage. The grammage increased after forming an alkaline reserve in papers in the amount of more than 5%, again with the exception of sample 5. After deacidification the alkalinity of samples considerably increased from slightly acidic to slightly alkaline (sample 5: pH 5,5 up to pH 8.2), from neutral to distinctly alkaline (sample 1: pH 7 up to pH 9.5). There is no direct relation between the amount of alkaline reserve and pH[4].
- Folding endurance. After deacidification, at the amount of alkaline reserve given in Table 3, the folding endurance is lower than before: the mineral added by the deacidification process is resulting in increased fragility. This phenomenon is less significant in strong modern papers, but it considerably high in historic ones.

- Brightness. It is known that after deacidification of paper in solutions containing Mg^{2+}, and particularly after deacidification with MMC, yellowing of paper takes place[7, 11]. In modern papers the decrease of brightness is about 13–15%, in historic papers 3–16%. The brightness of the historic C-samples after the extraction in water is significantly increased, as well as that of all D-samples. Differences between C-samples and D-samples are considerably reduced making an aqueous extract. Again the optical density of extracts confirms the fact that decrease of paper brightness was caused by the water soluble degradation products of low molecular weight. The lines in Fig. 2 representing deacidification (D_0 and D_{12}) are considerably lower than the those representing the samples before treatment (C_0 and C_{12}). The reason for this is the presence of Mg in paper and its bond to lignin. The same fact is also the rea son for the yellowing observed not only in modern, but also in some historic papers. The difference is lessened increasing the wavelength.
- Carbonyl and carboxyl groups. Deacidification of newsprints with MMC has no direct impact on the amount of carbonyls and carboxyls in paper: Those of C- and D-samples are approximately at the same level. The only exception is sample 5, where we found a bigger amount of carboxyls after deacidification. This is displayed by the decrease of carbonyls/carboxyls ratio.

Table 3: Basic characteristics of the tested papers after deacidification in MMC (D-samples) before accelerated ageing.

	Number of probes	Sample 1	2	3	4	5
Grammage (g/m2)	10	52,71 ±1,38	51,13 ±1,17	64,94 ±1,25	72,45 ±1,72	87,70 ±4,03
Alkaline reserve (%)	10	5,82	5,79	5,23	5,35	1,88
pH	10	9,54 ±0,18	9,26 ±0,23	9,01 ±0,29	8,67 ±0,17	8,23 ±0,22
Double folds (tension 10 N, * 2,5 N)	8	358 ±61	1171 ±214	*640 ±212	*1201 ±340	*122 ±31
Brightness (%)	10	66,68 ±1,61	69,05 ±1,63	59,28 ±1,43	57,27 ±1,72	70,05 ±1,70
Brigtness (%) after aqueous extract	10	71,99 ±0,81	74,51 ±1,81	66,7 ±1,11	63,68 ±1,21	73,65 ±1,79
Optical density ($\cdot 10^2$) at 457 nm (aqu. extr.)	10	3,93 ±1,01	0,98 ±0,23	8,73 ±1,13	11,87 ±1,04	9,43 ±1,41
Carbonyls (mmol/100g)	5	2,92 ±0,41	3,12 ±0,19	5,02 ±0,19	5,97 ±0,17	7,31 ±0,12
Carboxyls (mmol/100g)	5	7,8 ±0,35	7,41 ±0,26	6,88 ±0,22	6,87 ±0,29	3,98 ±0,23
Carbonyls / Carboxyls	5	0,37	0,42	0,73	0,87	1,84

Table 4: Basic characteristics of the tested papers (C-samples) after 12 days of accelerated ageing.

	Number of probes	Sample 1	2	3	4	5
Grammage (g/m2)	10	49,24 ±1,12	47,71 ±1,94	60,19 ±3,09	70,72 ±1,41	81,82 ±1,78
pH	10	6,52 ±0,14	7,65 ±0,34	5,12 ±0,19	5,41 ±0,25	5,06 ±0,16
Double folds (tension 10 N, * 2,5 N)	8	466 ±139	993 ±228	*9 ±4	*107 ±46	*2,5 ±0,9
Brightness (%)	10	69,60 ±1,13	72,96 ±1,56	58,74 ±1,59	64,49 ±2,16	68,96 ±1,86
Brigtness (%) after aqueous extract	10	72,78 ±2,12	73,81 ±1,02	63,84 ±2,21	65,98 ±1,45	73,59 ±1,08
Optical density ($\cdot 10^{-2}$) at 457 nm (aqu. extr.)	10	4,59 ±0,53	3,54 ±0,30	8,25 ±1,21	7,81 ±0,74	8,93 ±0,47
Carbonyls (mmol/100g)	5	6,59 ±0,42	3,89 ±0,25	8,91 ±0,39	7,82 ±0,46	6,98 ±0,22
Carboxyls (mmol/100g)	5	7,51 ±0,29	7,82 ±0,14	7,11 ±0,15	6,23 ±0,24	2,95 ±0,17
Carbonyls / Carboxyls	5	0,92	0,50	1,25	1,26	2,13

Table 5: Basic characteristics of the tested papers after deacidification in MMC (D-samples) after 12 days of accelerated ageing.

	Number of probes	Sample 1	2	3	4	5
Grammage (g/m2)	10	54,24 ±1,06	51,99 ±1,00	63,11 ±3,98	73,57 ±1,86	85,45 ±3,25
pH	10	9,76 ±0,20	8,85 ±0,24	8,15 ±0,19	8,65 ±0,21	7,85 ±0,15
Double folds (tension 10 N, * 2,5 N)	8	316 ±148	827 ±225	*195 ±58	*281 ±129	*5,5 ±2,2
Brightness (%)	10	59,44 ±2,09	64,08 ±1,72	54,67 ±1,66	56,66 ±1,60	65,98 ±1,76
Brigtness (%) after aqueous extract	10	68,05 ±1,17	70,44 ±2,15	62,13 ±1,16	62,79 ±0,87	70,60 ±1,73
Optical density ($\cdot 10^{-2}$) at 457 nm (aqu. extr.)	10	12,51 ±0,38	5,11 ±0,44	14,63 ±2,12	19,93 ±1,23	12,44 ±0,62
Carbonyls (mmol/100g)	5	4,75 ±0,32	3,47 ±0,21	6,46 ±0,22	6,27 ±0,32	5,89 ±0,54
Carboxyls (mmol/100g)	5	7,84 ±0,26	8,04 ±0,20	7,45 ±0,19	6,54 ±0,30	4,29 ±0,19
Carbonyls/ Carboxyls	5	0,61	0,43	0,87	0,96	1,20

After accelerated ageing

Accelerated ageing of samples before and after deacidification (Table 4 and 5) was not significantly reflected by a change in their acidity during the all the 12 days of accelerated ageing (Fig. 3).

We presume that during dry accelerated ageing of slightly acid or neutral modern newsprints hydrolysis forming sulfuric acid out of alum does not take place. Only organic acids, characterized by carboxyl groups, are formed, and this is true even for historic papers. The acidity of paper is only slightly increased in the course of accelerated ageing (Table 2+4, Fig. 3: decrease of pH).

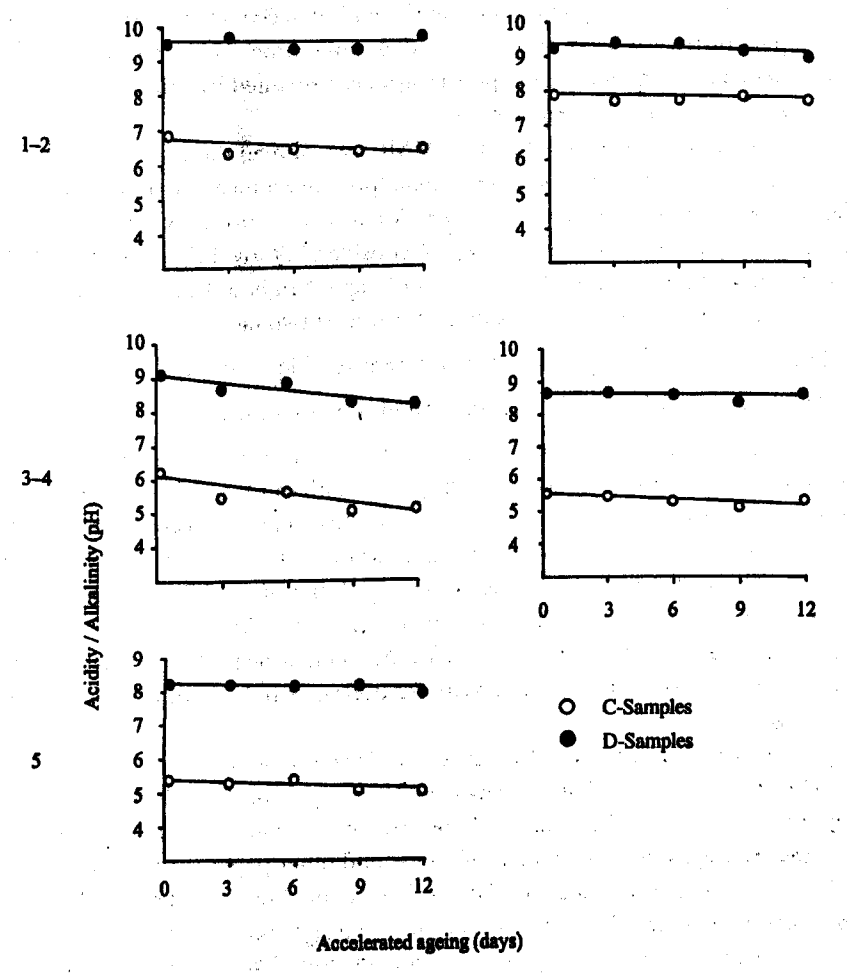

Fig. 3: Acidity of papers during accelerated ageing.

The most considerable decrease takes place with folding endurance of C-samples in the first three days of ageing (Fig. 4). D-samples are of similar course. The decrease in folding endurance in C-samples of historic newspapers is very precipitous right from the beginning. Significant deterioration of mechanical qualities (breakage) takes place in samples 3 and 4 on the ninth day of ageing, and in sample 5 as early as on the third day. Compared to C-samples the loss of strength of D-samples is considerably slower, but the course of ageing is similar. After a period of slow decrease the strength of D-samples deteriorates very quickly. The strength of sample 3 deteriorates on the eighth/ninth day, of sample 4 on the third, 5 on the sixth/seventh day. The result is that deacidified historic papers have better ageing endurance at the end of accelerated ageing, but finally the papers turn very weak and fragile; after some time they are of no use. The loss of mechanical qualities of papers is also accompanied by other changes. One of them is yellowing of paper (Fig. 5).

Besides the yellowing provoked by MMC[7] (cf. above) the extent of yellowing of paper in the course of accelerated ageing provides a measure of the amount of degradation products formed in paper. Modern newsprints (C and D) yellow more quickly than historic ones being of considerably low brightness already before the test. As showed by the measures of paper brightness before and after the extraction in water, yellowing is caused by at least two factors:

- Substances bound to paper and therefore insoluble in water,
- The low molecular weight degradation products extractable in water[11, 12].

Considerable increase of these substances was observed in the water extracts already at the third day of accelerated ageing, both in C- and D-samples. This increase was somewhat slower in a later period. The values of brightness in C- and D-samples approached each other significantly after washing out these substances. This refers to the fact that yellowing during deacidification is to a considerable extent caused by the reaction of lignin with MMC. The alkaline medium facilitates the creation of low-molecular weight degradation products. The most of these degradation products are formed in sample 4 with the highest lignin content.

We cannot eliminate even the oxidative degradation influence of oxygen on cellulose in alkaline medium[13]. Only detailed analysis of these degradation products could determine the share and mechanism of oxidation and hydrolyzation reactions in degradation of lignin, cellulose, and other paper components[12, 14, 15].

In order to explain changes in the mechanical qualities of papers we have also analyzed the amount of carbonyls and carboxyls (Fig. 6).

We realize that the crucial process of degradation of acid papers is the acid hydrolysis. The share of oxidation reactions in paper degradation primarily de-

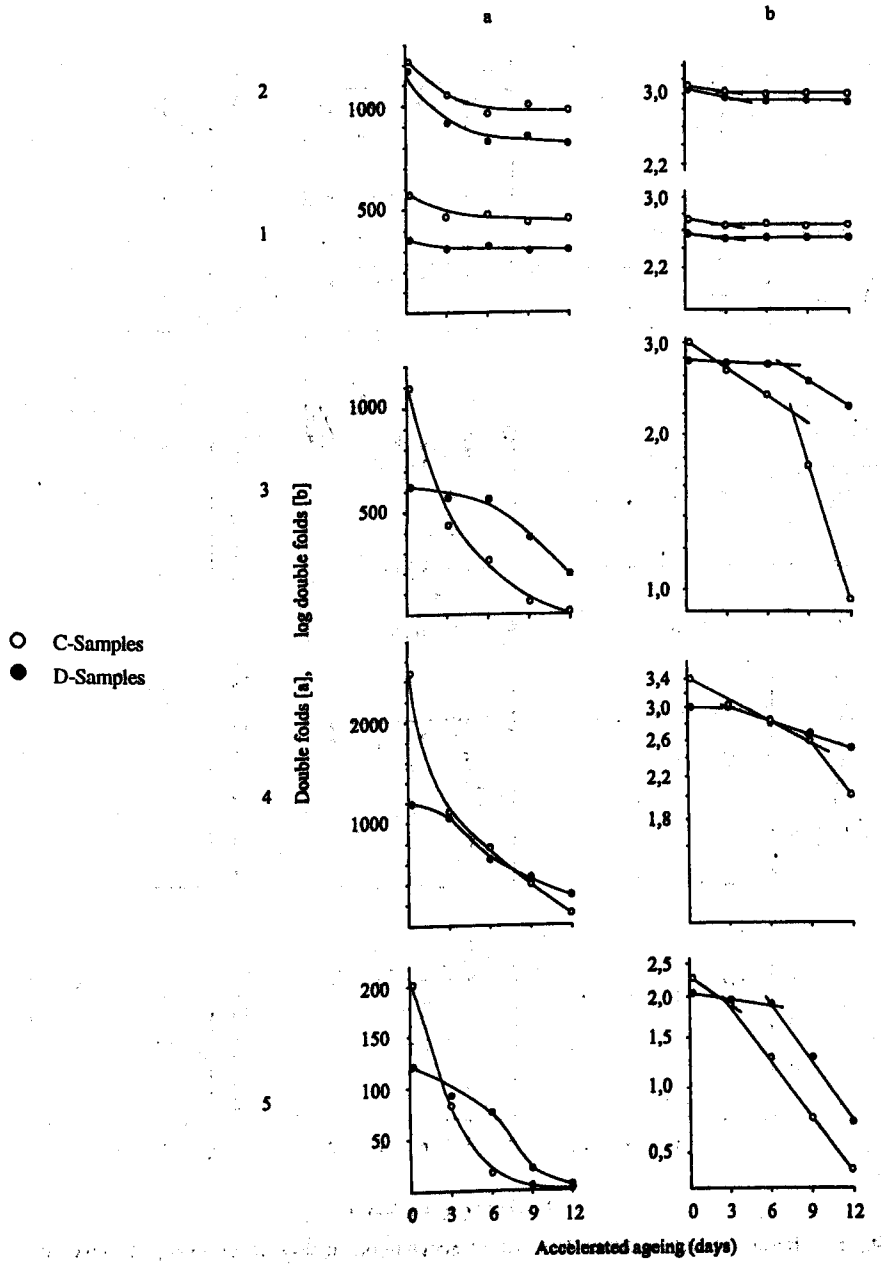

Fig. 4: Folding endurance during accelerated ageing.

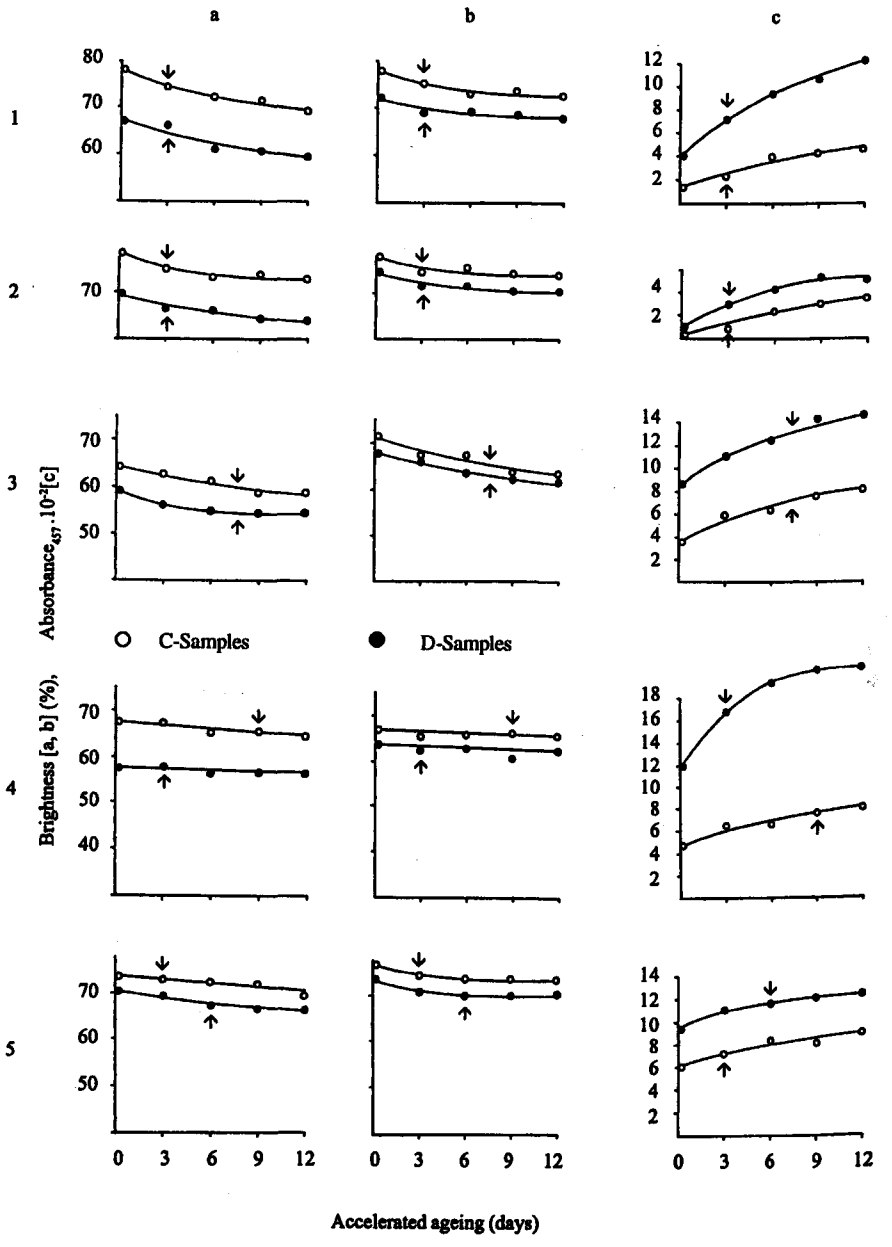

Fig. 5: Change of optical properties during accelerated ageing; a: yellowing; b: change of brightness after the extraction in water; c: optical density of degradation products in the aqueous extracts. Arrows indicate where damage of mechanical strength occurs.

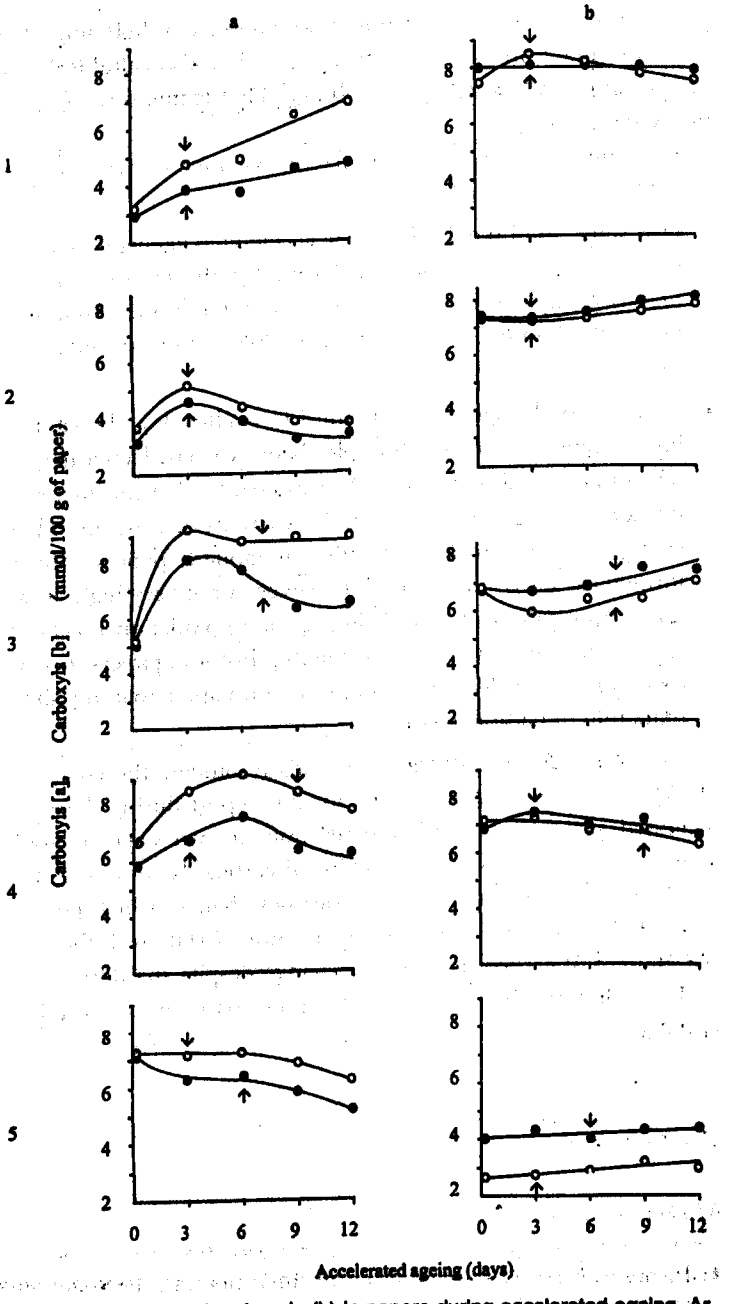

Fig. 6: The amount of carbonyls (a) and carboxyls (b) in papers during accelerated ageing. Arrows indicate the places of sharp damages in the mechanical strength of paper.

pends on the content of lignin and the intensity of lightning of paper. This kind of environment primarily degrades lignin, but also cellulose[13]. The final product of hydrolysis and oxidation was observed in the intensity of coloration of the water extracts.

For sample 2, 3 and 4 the course of oxidative changes can be seen as having two stages.

- First stage: until the third day the accelerated ageing goes on similarly in these three samples; its characteristic feature is the increase of the amount of carbonyls. Sample 1, however, shows a constantly increasing amount of carbonyls, while sample 5 seem to have the maximum carbonyl content already before accelerated ageing.
- In the second stage, from the third to twelfth day, the gained amount of carbonyls does not change (sample 3) or is even decreasing, except sample 1, wherein it unceasingly rises. We can assume that this increase indicates a significant boost of thermo-oxidation reactions that has an influence even on the changes in the physical qualities of modern papers. The total amount of formed carbonyls in sample 1, however, is not very high; it does not reach the maximum values observed during photo-oxidation reactions[7]. This correlation is not strictly clear-cut among historic papers because the thermo-oxidation of accelerated ageing starts on papers that are already damaged by oxidation of natural ageing.

The deacidification of the paper clearly hinders the creation of carbonyls in all types of paper under research for this report during the whole course of accelerated ageing. The oxidation reactions in two stages is also true for the D-samples. Observation of the content of carboxyls showed that even in the first stage of oxidation their amount does not change, which points out slow transformation of carbonyls into carboxyls. Similar state is in the second stage where the content of carboxyls does not change despite the decrease of carbonyl content. The intense changes in the strength of paper were not reflected at all in the content of carboxyls.

Conclusion

Modern newsprint

- In both observed papers – one of them neutral, the other slightly alkaline – the share of hydrolysis reactions in the degradation process was considerably lowered by the deacidification treatment.

- Both papers have high carboxyl content which is nearly not changed in the course of accelerated ageing.
- Certain deterioration of the mechanical qualities of paper in the first stage of accelerated ageing seems to be the result of oxidative degradation.
- Deacidification with MMC results not only in a significant shift to the alkaline area, but also in significant yellowing.
- Substantial parts of this yellowing are extractable; they include even non-oxidative degradation products of lignin.
- Deacidification inhibits oxidation reactions.

Historic newsprint

- The mechanical strength of the three papers under research was considerably low, what points to substantial degradation.
- Considering the presence of sulfuric acid in the paper during accelerated ageing, hydrolysis and oxidation go on simultaneously, with hydrolysis reactions to a greater extent.
- During accelerated ageing, under the influence of acid hydrolysis, the papers lose their mechanical strength very quickly.
- The papers have high content of carbonyls and relatively less carboxyls. Carbonyl content is not increased in the second stage of accelerated ageing.
- Intense deterioration of the mechanical qualities takes place at the beginning of the second stage of accelerated ageing. This process is connected to maximum content of carbonyls. The share of oxidation reactions in it is not unambiguously clear.
- Deacidification of paper hinders the acid hydrolysis of cellulose, but it facilitates lignin degradation.
- MMC used as deacidification agent binds to lignin and causes increased yellowing.
- Deacidification considerably slows down thermo-oxidation reactions.

Altogether, we can assume that deacidification of historic groundwood papers slows down their destruction for a certain period (possibly 30 years), but, despite the created alkaline reserve and the inhibition of oxidation, deacidification does not hinder their further destruction. Therefore, if those papers are to be pre-

served for longer or even indefinite time, it is necessary to reinforce them simultaneously with deacidification. It seems to be more advantageous to transmit information from them to other carriers. On the other hand, it is necessary to note that deacidification of modern newsprints, or their production in neutral or alkaline medium respectively, has considerably positive influence on their lifetime in a process of long-term storage, despite the presence of lignin[16, 17].

SUMMARIES

Is deacidification a step to the rescue of historic newspapers?

Acidity of groundwood paper has a decisive influence on its lifetime. Slightly acid or neutral modern newsprints loose their strength during accelerated ageing very slowly; very acid historic newsprints, however, are already in a higher stage of degradation and still lose further their strength: after a certain time of accelerated ageing even very intensively. Deacidification treatment considerably slows down the loss of strength in these papers; unfortunately, despite the elimination of acidity, intensive deterioration of the paper affecting its mechanical properties takes place after some time. In this research we tried to find a reason of this phenomenon. We presume that, besides acid hydrolysis, thermo-oxidation reactions on cellulose and lignin as well as decomposition reactions of lignin in the newly created alkaline medium cause the intense deterioration of the paper strength during accelerated ageing.

La désacidification est-elle un moyen approprié pour sauver les gazettes historiques ?

L'acidité du papier fait à base de pâte mécanique a une influence décisive sur sa longévité. Le papier journal moderne légèrement acide ou neutre ne perd sa solidité que très lentement lors de la procédure du vieillissement accéléré; par contre le papier journal historique, très acide, ayant déjà atteint un fort degré de dégradation, continue de perdre sa solidité et, après un certain temps de vieillissement accéléré, de façon même très accentuée. Le traitement de désacidification du papier ralentit considérablement sa perte de solidité; ce processus de détérioration des propriétés mécaniques du papier reprend cependant quelque temps plus tard malgré le traitement de désacidification. On a cherché dans cette étude à trouver une explication à ce phénomène. On présume que, à côté de l'hydrolyse induite par l'acide, des réactions de thermo-oxydation sur la cellulose et la lignine ainsi que des réactions de décomposition de la lignine dans le milieu alcalin nouvellement créé, provoquent une détérioration intense de la solidité du papier au cours du vieillissement accéléré.

Ist Neutralisieren ein geeignetes Mittel zur Rettung historischer Zeitschriften?

Säure hat den entscheidenden Einfluß auf den Zeitraum in dem Holzschliffpapier benutzbar bleibt. Leicht saures oder neutrales modernes Zeitungspapier verliert beim beschleunigten Altern

seine Festigkeit nur langsam, stark saures historisches hingegen ist bereits in einem fortgeschrittenen Stadium des Abbaus und verliert noch weiter an Festigkeit, nach einer gewissen Zeit beschleunigter Alterung sehr intensiv. Entsäuerung verlangsamt den Festigkeitsverlust dieses Papiers beträchtlich; nach einiger Zeit setzt dieser jedoch trotz des Entfernens der Säure wieder ein. In dieser Studie wird versucht, für dieses Phänomen eine Erklärung zu finden. Es wird vermutet, daß neben der säurekatalysierten Hydrolyse auch Reaktionen einer wärmeinduzierten Oxidation an Cellulose und Zersetzungsreaktionen am Lignin in dem durch die Neutralisierungsmaßnahme geschaffenen alkalischen Medium eine deutlichen Rückgang der Papierfestigkeit während einer beschleunigten Alterung bewirken.

REFERENCES

1. Smith, R. D.: *A comparison of paper in identical copies of books from Laurence University, the Newberry, and the New York Public Libraries.* Restaurator suppl. 2 (1972).
2. Bukovský, V., & I. Kuka.: *Ochrana historických knižných fondov pred kyslou deštrukciou (Preservation of historic books before acid destruction).* Knižnice a informácie 29 (1997): 256–260
3. Porck, H. J.: *Mass deacidification. An update of possibilities and limitations.* Amsterdam: European Commission on Preservation and Access 1996: 54.
4. Bukovský, V.: *Poznatky z neutralizácie papiera s karboxymetanolátom horečnatým (Knowledge from deacidification of paper with methoximagnesium carbonate).* Proceedings from 8th Workshop of Restorers and Historians. SÚA Praha, Železná Ruda 1991: 173–188.
5. Moravová, J., M. Libnarová & B. Loffajová: *K technologickým aspektum stárnutí papíru. (To technological aspects of paper ageing).* Papír a Celulóza 45 (1990): 97–100.
6. Souček, M.: *Zkoušení papíru (Testing of paper).* Praha: STNL 1977: 66.
7. Bukovský, V.: *Yellowing of newspaper after deacidification with methyl magnesium carbonate.* Restaurator 18 (1997): 25–38.
8. Albertsson, U., & O. Samuelson: *A colorimetric method for the determination of carbonyl groups in cellulose.* Chim. Acta 12 (1962): 434–440.
9. *Carboxyl content of cellulose.* T237 su–63 (1963).
10. Nikitin, V. M.: *Chémia dreva a celulózy (Chemistry of wood and cellulose).* Bratislava: SVTL 1956: 78.
11. Bukovský, V.: *Záchrana historických novín (Rescue of historic newspapers).* Proceedings of conference: Chemical Technology of Wood, Pulp and Paper. Bratislava: CHTF-STU 1998: 222–225.
12. Krkoška, P.: *Zafarbenie papiera pri dlhodobom používaní a uchovávaní (Coloration of paper during long-term use and stocking).* Proceedings of conference: Chemical Technology of Wood, Pulp and Paper. Bratislava: CHTF-STU 1998: 228–232.
13. Kolar, J., M. Strlič, G. Novák & B. Pihlar: *Aging and stabilization of alkaline paper.* J. Pulp Paper Sci. 24 (1998): 89–94.
14. Reinprecht, L.: *Procesy degradácie dreva (Processes of wood degradation).* Zvolen Technical University 1997:103.
15. Dupont, A.L.:*Degradation of cellulose at the wet/dry interface. II. An approach to the identification of the oxidation compounds.* Restaurator 17 (1996): 145–164.
16. Grattan, D., & N.Gurnagul: *Government and industry join forces in research project to understand effect lignin has on paper permanence.* Ottawa 1996: 1–7.

17. Bégin, P, S. Deschâtelets,, D. Grattan, N. Gurnagul, J. Iraci, E. Kaminska, D. Woods & X. Zou: *The impact of lignin on paper permanence. A comprehensive study of the ageing behaviour of handsheets and commercial paper samples.* Restaurator 19 (1998): 135–154.

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Fungal Growth on Samples of Paper: Inhibition by New Antifungals

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INTRODUCTION

Biotic factors, such as fungi and other micro-organisms, can play an important role in paper deterioration[1] and paper ageing phenomena[2], but they are usually underestimated in comparison with abiotic factors, both environmental (light, temperature, oxygen, humidity changes, air pollutants)[3] and related to manufacturing processes, such as the use of modern high yield chemi-thermomechanical pulp[4]. Since paper of high resistance is generally characterized by minimal alteration of its chemical components with time, most paper-making processes are commonly focused on improving the resistance of paper to abiotic factors[5].

On the contrary, fungi are well-known dangerous agents responsible for paper biodeterioration, because of their hydrolytic enzymatic activities[6–9]. In particular, cellulase activities cause the most severe damages on paper and recently it has been reported that the amorphous fraction of cellulose (the main component of paper) is the most affected by the endoglucanase enzymatic attack of fungi[10]. However, different kinds of paper are characterized by quali-/quantitative differences that can affect the biotic and abiotic paper deterioration processes. In a previous work we have shown that the mechanism of paper deterioration due to micro fungi can change according to the characteristics of the paper[11].

In the present work we show that even high quality and low chemical deterioration samples of paper can be badly affected by fungal attack and we describe the inhibition effect of some new synthesized compounds, which were already shown to inhibit some plant pathogenic fungi[12].

EXPERIMENTAL PART

Fungi Tested

The fungi tested were: ***Penicillium chrysogenum Thom, Aspergillus terreus Thom, Stachybotrys atra Corda and Chaetomium elatum Kunze.*** All these strains were isolated from different samples of biodeteriorated paper incubated in mycological agar medium (Difco) at 25°C for 7 days as previously described[8].

The isolated strains were maintained on PDA (Potato Dextrose Agar) at 25°C for 15 days.

Fungal Inoculum of Different Kinds of Paper

The fungal inoculum was carried out on three samples of paper (kindly supplied by Istituto Poligrafico e Zecca dello Stato, Rome, Italy) of different composition and different resistance in time. The characteristics of the three kinds of paper are shown in Table 1.

Table 1: The samples

Sample	Pulp Composition	Additives
A:	bleached hardwood cellulose bisulfite 5%)	kaolin (14%)
sizing with rosin	bleached hardwood cellulose sodium	starch (4%)
and $Al_2(SO_4)_3$ sulfite	(25%)bleached softwood cellulose sodium	rosin (0.5%)
pH 5.5	(55%)	aluminum sulfate (0.8%)
	bleached softwood cellulose bisulfite (8%)	optical bleach liquor (0.3%)
	bleached semichemical cellulose (7%)	sodium chloride (0.4%)
B:	bleached hardwood cellulose bisulfite (8%)	calcium carbonate (18%)
sizing with AKD	bleached hardwood cellulose sodium (37%)	starch (4%)
without Al2(SO4)3	bleached softwood cellulose sodium (55%)	AKD (0.5%)
pH 8–8.5;		optical bleach liquor (0.8%)
permanent durable		sodium chloride (0.3%)
paper		
C:	cotton bleached cellulose, linters (100%)	calcium carbonate (4%)
sizing with AKD		starch (3%)
without Al2(SO4)3		AKD (0.3%)
pH 8–8.5;		gelatin (2%)
permanent durable		acrylic copolymer (0.1%)
paper of highest		
quality		

Paper stripes (100mg) were inoculated with $5x10^5$ conidia or spores suspended in synthetic culture medium, Czapek Dox Broth (CDB) with carboxy methyl cellulose (CMC) (0.2% w/v) as carbon source, without sucrose and incubated in Petri dishes at relative humidity (RH) of 95% at 27°C up to 30 and 60 days.

Fungicides

The new chemicals assayed (cf. Fig. 1) were: some 2,4,6-trisubstituted 1,3,5-triazines (1–3)[13], two macrocyclic structures containing two 1,3,5-triazine units (4, 5)[13] and two modified dihydro-isocoumarines (6, 7)[14]. In detail their chemical names are:

(1) (R)-2,4,6-tri[3'-N'(1"-α-naphtylethyl)aminopropyl]amino-1,3,5-triazine;

(2) (S)-2,4,6-tri[3'-N(1"-phenylethyl)aminopropyl]amino-1,3,5-triazine (2)[15];

(3) 2,4-di[3'-N'[(1"R)-1"α-napthylethyl]aminopropyl]amino-6-n.hexylamino-1,3,5-triazine;

(4) (S)-4,29-di(1'-c.hexylethyl)amino-5,8,20,23-tetraoxa-2,11,13,15,17,26,28,30,31,32- deca-azatricyclo[25.3.1.1] dotriaconta-1(31),12,14,16(32),27,29-hexane;

(5) (S)-14,29(1'-phenylethyl)amino-5,8,20,23-tetraoxa-2,11,13,15,17,26,28,30,31, 32-deca-azatricyclo[25.3.1.1]dotriaconta-1(31),12,14,16(32),27,29-hexane;

(6) 3(R,S)-6,8-dihydroxy-3-hydroxymethyl-3-4-dihydroisocoumarine;

(7) 3(R,S)-8-hydroxy-3-hydroxymethyl-6-methoxy-3,4-dihydroisocoumarine.

Tests of Antifungal Activity

Tests *in vitro*

Conidia or spores (5×10^5) were placed in test tubes containing CDB and each antifungal compound at the concentration of 5×10^{-4} M and 5×10^{-5} M for 12 ,24 and 72 h at 25°C. The efficacy of the new tested compounds was evaluated by counting the number of germinated spores or conidia and the percentage of their inhibition with time.

Tests *in vivo*

The paper stripes were inoculated with the antifungal compounds (at the same concentration used in the test *in vitro*) together with the conidia/spores of tested fungi (5×10^5) to verify their action on fungal growth.

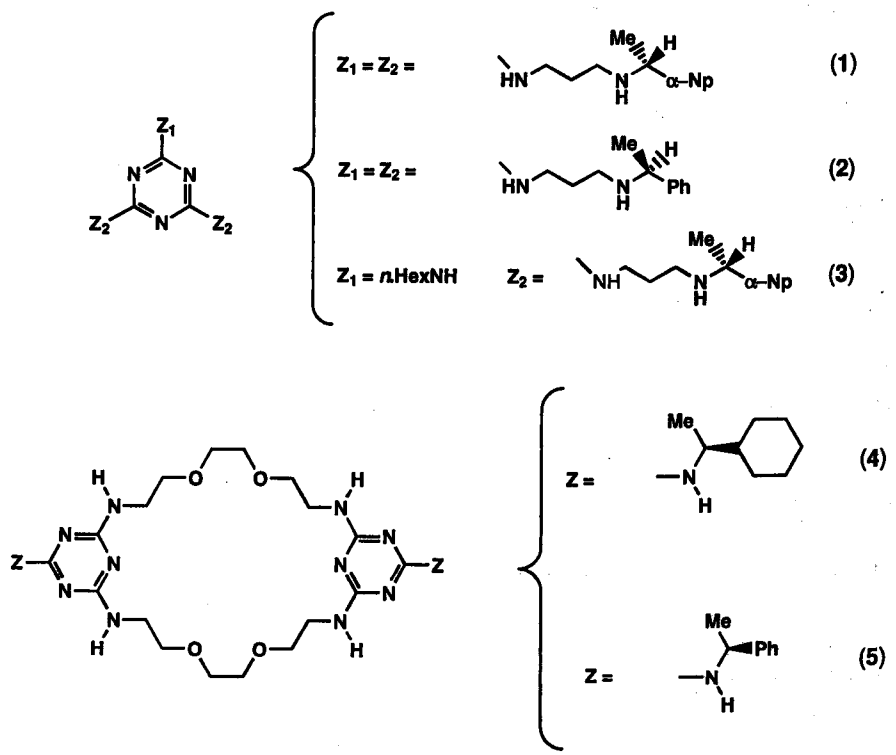

Fig. 1: Chemical constitution of the antifungal compounds

Tests on the effect of AKD

The effect of the sizing agent AKD (alkyl ketene dimer, kindly supplied by AKZO, Chem.Div.) on the fungal growth was tested by adding the sizing agent (5% w/w in CZB without sucrose) to the fungi. All the tested fungi were incubated for 4, 7 and 10 days at 25°C and the fungal growth was evaluated as ergosterol content as described in the following section.

Fungal Growth Determination

Fungal growth was evaluated as ergosterol content modifying a previously reported procedure[16]. The paper stripes were washed with 20 ml of $CHCl_3$/CH_3OH (2/1 v/v) containing 2,6-di t.butyl-4-methylphenol (BHT), the solution was filtered on Na_2SO_4 and concentrated with a stream of N_2. The recovered samples were treated with 5 ml of KOH 2M in methanol at 70°C for 20 minutes and finally extracted with pentane (3 x 5 ml).

The solvent was removed under a stream of N_2 and the crude product was dissolved in methanol and analyzed by HPLC using a Perkin-Elmer Series 3 equipped with a Perkin-Elmer LC75 UV detector [analysis conditions: reverse phase LC-18-DB (25cm x 5µm, Supelco), 30°C, CH_3OH/H_2O(95/5 v/v) 1.5ml/min., 282 nm].

RESULTS

Fungal growth (estimated as ergosterol content) of all tested fungi on samples of paper of different chemical resistance (A , B and C) is reported in Table 2. Collected data pointed out that all the tested kinds of paper allow fungal growth, though in different extent: in general *S.atra* shows the highest fungal growth and the *C. elatum* the lowest one.

It is noteworthy that sample C is the best substrate for the growth of all the tested fungi.

Table 2: Fungal growth (as ergosterol content) of different fungi on paper samples A, B and C after 30 and 60 days of incubation at 25°C and at 95% relative humidity.

	ERGOSTEROL: µg/100 mg of paper	
	30 days	60 days
Sample A *A. terreus*	6.03±0.41	7.22 ± 0.53
P. chrysogenum	6.6 ± 0.4	8.07 ± 0.71
S. atra	9.12 ± 0.78	11.21 ± 0.88
C. elatum	4.33 ± 0.32	5.22 ± 0.41
Sample B *A. terreus*	6.55 ± 0.52	7.44 ± 0.63
P. chrysogenum	7.04 ± 0.61	8.21 ± 0.65
S. atra	10.40 ± 0.79	11.7 ± 0.8
C. elatum	5.30 ± 0.46	6.7 ± 0.5
Sample C *A. terreus*	8.98 ± 0.70	10.8 ± 0.8
P. chrysogenum	9.94 ± 0.80	11.5 ± 0.9
S. atra	12.6 ± 1.3	14.2 ± 1.3
C. elatum	6.8 ± 0.5	8.7 ± 0.7

A
VI: 88/m, N79
N99, 20-2

The inhibiting effect of some antifungals on conidia or spore germination inoculated on synthetic medium CDB is shown in Table 3.

Among the tested compounds, (3) and (4) show a strong inhibiting effect on all the assayed fungi (the fungal growth was not detected or detected only in traces). The other chemicals, i.e. (1), (2), (5), (6) and (7), are less efficient, (1) and (7) higher than (2), (5) and (6). However, the behaviour of all the tested antifungals is alike.

The same compounds were also tested on different samples of paper A, B, C previously inoculated with conidia or spores of *P.chrysogenum, S.atra, A.terreus* and *C.elatum*. The obtained results (Table 4) show that the fungal growth of all fungi in these conditions is similar to that reported in Table 2 and the inhibiting effect of antifungals is similar to that reported in Table 3. As a matter of fact the compounds (3) and (4) show a strong inhibiting effect and the others a lower efficacy.

Among the sizing agents commonly used in paper-making processes we have tested the effect of AKD on fungi inoculated on synthetic medium, since AKD is known to afford paper higher chemical resistance.

Table 3: Effect of some antifungals on conidia or spores germination (%) inoculated on CDB after 12, 24 and 72 hours at 25°C.

	A. terreus			*P. chrysogenum*		
	12h	24h	72h	12h	24h	72h
Control	78	93	96	76	87	93
1	12	22	28	11	20	25
2	55	67	81	49	65	49
3	0	2	3	1	2	3
4	0	1	2	0	2	3
5	34	48	68	27	45	65
6	36	55	69	28	51	65
7	14	19	25	11	20	22
	S. atra			*C. elatum*		
	12h	24h	72h	12h	24h	72h
Control	81	90	95	90	93	96
1	21	23	29	22	24	31
2	66	69	75	62	72	79
3	0	2	3	0	1	2
4	0	1	2	0	1	2
5	41	43	57	32	36	41
6	34	37	41	30	35	41
7	11	14	19	10	16	19

The overall results (Table 5) show that AKD supports fungal growth without inhibition effects and in some cases (*P.chrysogenum* and *C.elatum*) it can even enhance fungal development.

CONCLUSIONS

The laws concerning common paper-making processes tend to underestimate the role of fungi and other micro-organisms in paper deterioration. As a matter of fact, high resistance to abiotic deteriorative agents is usually considered the most important feature of paper. Thus, biocides are commonly used as "control additives" during the manufacturing processes, but they are hardly retained on the final product[17]. On the contrary, not only are fungi dangerous deteriorative agents during the paper-making process, but also during the storage of paper material in libraries and bookcases.

Table 4: Fungal growth (as ergosterol content) of paper deteriorative fungi grown on paper stripes (samples A, B and C) after 30 days incubation at 25°C and 95% relative humidity in the presence of antifungals 1–7.

	Ergosterol content (mg/100 mg paper stripes)					
	A. terreus			*P. chrysogenum*		
	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
Control	6.08±0.41	6.55±0.52	8.98±0.7	6.6±0.45	7.04±0.61	9.94±0.8
1	1.03±0.11	1.23±0.12	2.34±0.15	1.22±0.11	2.34±0.2	3.44±0.23
2	5.5±0.41	5.89±0.47	7.12±0.67	4.88±0.39	1.44±0.12	6.88±0.55
3	nd[a]	nd[a]	tr[b]	nd[a]	nd[a]	tr[b]
4	nd[a]	nd[a]	tr[b]	nd[a]	nd[a]	tr[b]
5	4.32±0.32	4.59±0.33	6.88±0.55	5.23±0.44	6.44±0.56	7.55±0.56
6	3.47±0.22	4.05±0.34	6.47±0.34	4.44±0.38	5.49±0.47	7.32±0.61
7	1.33±0.11	1.53±0.11	2.03±0.15	1.44±0.17	1.67±0.12	1.37±0.12
	S. atra			*C. elatum*		
Control	9.16±0.78	10.4±0.79	12.6±1.3	4.33±0.32	5.3±0.46	6.8±0.5
1	1.8±0.11	2.1±0.18	2.6±0.23	0.55±0.04	1.22±0.13	2.1±0.14
2	7.2±0.61	6.8± 055	9.0±0.87	3.7±0.25	4.3±0.34	5.1±0.38
3	tr[b]	tr[b]	tr[b]	nd[a]	nd[a]	tr[b]
4	nd[a]	nd[a]	tr[b]	nd[a]	nd[a]	tr[b]
5	4.4±0.33	5.9±0.48	6.7±0.60	4.1±0.34	3.5±0.44	4.7±0.58
6	2.9±0.22	4.8±0.44	6.8±0.59	3.4±0.29	3.5±0.24	4.1±0.34
7	1.88±0.12	2.04±0.18	2.22±0.19	1.25±0.11	1.66±0.15	2.22±0.19

[a] Not detected [b] Detected in traces (<0.1 µg/100 mg paper stripes)

It is reasonable to suppose that in sample C a higher concentration of gelatin is responsible for the higher fungal growth observed.

Among *P.chrysogenum*, *C.elatum*, *A.terreus* and *S.atra*, *S.atra* is the most efficient in colonizing paper substrates, probably due to its higher hydrolytic enzymatic activity.

The alkaline treatment with internal sizing agent AKD, used in manufacture of samples B and C is usually preferred to rosin sizing process that is carried out at pH 4–6. As a matter of fact the alkaline paper-making procedure allows to minimize the hydrolytic degradation of carbohydrate moieties, usually due to traces of acidic impurities[17].

According to previously reported data[18], it was found (Table 5) that AKD supports fungal growth and in some cases can even enhance it. It was also shown (Table 2) that differences in pH values of the rosin and alkaline sizing procedures (pH=4–6 and pH 8 respectively) do not affect the fungal growth significantly.

All the new antifungals tested (some 2,4,6-trisubstituted 1,3,5-triazines, macrocyclic structures containing 1,3,5-triazine units and modified dihydro-isocoumarines) showed inhibition effects on the growth of the tested fungi, but only the triazinic derivatives (3) and (4) completely stopped the fungal growth.

Although nothing is known about the mechanism of action of (3) and (4), collected data seem to suggest that the inhibition mechanism involves a metabolic target common to all the tested fungi .

The hereby reported results point out the importance of biotic factors in paper deterioration and suggest the necessity of introducing antifungals in paper

Table 5: Effect of AKD on fungal growth (as ergosterol content) of *A. terreus*, *P. chrysogenum*, *S. atra* and *C. elatum* inoculated on CDB for 4, 7 and 10 days at 25°C.

	Ergosterol content[a] (μg/10 mg CDB)					
	A. terreus			*P. chrysogenum*		
	4 days	7 days	10 days	4 days	7 days	10 days
Control	tr[b]	2.52±0.22	3.55±0.33	tr[b]	1.28±0.10	2.58±0.16
AKD	tr[b]	2.08±0.19	2.97±0.44	0.57±0.30	1.51±0.19	3.22±0.28
	S. atra			*C. elatum*		
	4 days	7 days	10 days	4 days	7 days	10 days
Control	2.88±0.7	2.20±0.29	2.22±0.31	tr[b]	tr[b]	0.56±0.05
AKD	tr[b]	tr[b]	2.07±0.18	0	tr[b]	1.44±0.12

[a] Each value represents the mean ± S.E.M. of three determinations.
[b] Detected in traces (<0.1 μg/10 mg CDB).

manufacturing processes as "functional additives"[17], which can be retained in the final product.

We feel that the use of *ad hoc* planned preventive chemicals as antifungals could provide an important aid in preserving the cultural heritage contained in books.

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SUMMARIES

Fungal growth on paper of different composition: inhibition by new antifungals

The fungal growth on paper samples of different chemical composition due to some paper deteriorative fungi *(Aspergillus terreus, Chaetomium elatum, Stachybotrys atra and Penicillium chrysogenum)* is reported. All the tested samples, stored at high relative humidity, show low resistance to fungal attack and allow the fungal growth. The addition of some new synthesized compounds to the different samples of paper inhibits the fungal growth of all the paper deteriorative fungi tested.

Développement de champignons sur des papiers de différentes compositions: lutte au moyen de nouveaux fongicides

Sur des échantillons de papier de différentes compositions chimiques on a observé le développement de certains champignons *(Aspergillus terreus, Chaetomium elatum, Stachybotrys artra et Penicillium chrysogenum)* qui détérioraient le papier. Tous les échantillons étudiés, conservés dans un environnement d'un degré d'humidité relativement haut, n'opposaient que très peu de résistance à l'attaque des champignons et leur permettaient de proliférer. L'addition de certaines nouvelles substances fongicides synthétiques a permis d'enrayer complètement le développement de ces champignons destructeurs de papier.

Schimmelwachstum auf Papierproben: Bekämpfung durch neue Fungizide

Es wird das Wachstum von Schimmelpilzen *(Aspergillus terreus, Chaetomium elatum, Stachybotrys atra und Penicillium chrysogenum)* auf Papierproben verschiedener Zusammensetzung beschrieben.

Alle Proben zeigten bei hoher Luftfeuchtigkeit nur geringen Widerstand gegen Schimmelwachstum. Der Zusatz von einiger neuen synthetischen Fungiziden verhinderte das Wachstum vollständig.

References

1. Dhawan, S., & O.P. Agrawal: *Fungal flora of miniature paper paintings and lithographs.* International Biodeterioration 22, 2 (1986): 95–99.
2. Havermans, J.B.: *The effect of air pollutants on accelerated ageing of cellulose containing materials: preliminary results of the project STEP (CT 90-0100).* Environment et Conservation de l'Écrit, de l'Image et du Son. Actes des Douxiemes Journées Internationales d'Études de l'ARSAG. Paris 16/20-5-94 (1994): 39–47.
3. Lanting, R.W.: *Air pollution in archives and museums: Its pathways and control.* Indoor Air '90. Toronto 1990.
4. Priest, D.J., & J. Stanley: *The ageing of paper containing chemithermomechanical pulp.* Environment et Conservation de l'Écrit, de l'Image et du Son. Actes des Douxiemes Journées Internationales d'Études de l'ARSAG. Paris 16/20-5-94 (1994).:154–160.
5. ISO 9706. *Information and documentation – Paper for document – Requirements for permanence.* 1994.
6. Coughlan, M. P., M.G. Touhy, X.F. Filho, J. Puls, M. Claeyssens, M. Vrsanska. & M.M. Hughes: *Enzymological aspects of microbial emphasis on fungal system.* Hemicellulose and Hemicellulase ed. M.P. Coughlan & G.P.Hazlewood. London: Portland Press 1993: 53–85.
7. Zabel R. A., & J.J. Morrell: *Wood microbiology decay and its prevention.* New York: Academic Press Inc. 1992: 476.
8. Wood, T. M., & V. Garcia-Campayo: *Enzymes and mechanisms involved in microbial cellulolysis.* Biochemistry of Microbial Degradation, ed. C. Ratledge. Dordrecht: Kluver 1994: 197–231.
9. Teeri, T. T., & A. Koivula: *Cellulose degradation by native and engineered fungal cellulase.* Carbohydrates in Europe. May 1995: 28–33.
10. Capitani, D., M.C. Emanuele., A. L. Segre, C. Fanelli, A.A. Fabbri, D. Attanasio, B. Focher & G. Capretti: *Early detection of enzymatic attack on paper by NMR relaxometry, EPR spectroscopy and X-ray power spectra.* Nordic Pulp and Paper Res. J. 13,2 (1998): 95–100.
11. Fabbri, A. A., A. Ricelli, S. Brasini & C. Fanelli: *Effect of different antifungals on the control of paper deterioration caused by fungi.* International Biodeterioration and Biodegradation 39,1 (1997): 61–65.
12. Fanelli ,C., A.A. Fabbri, S. Monti, R. Menicagli, D. Pini, S,M. Rapaccini, S. Samaritani & P. Salvadori: *Effect of some novel antifungals on different pathogenic fungi.* 7th International Congress of Plant Pathology 3 (1998): 5.6.8..
13. Work in preparation.
14. Superchi, S.:. *Reazioni di metallazione e di cross-coupling per l'alchilazione di substrati aromatici: sviluppi sintetici ed applicazione alla sintesi di diidroisocumarine..* Tesi di Dottorato in Scienze Chimiche. Pisa 1994.
15. Peluso, P., *Approccio alla sintesi di fasi stazionarie chirali contenenti derivati otticamente attivi della 1,3,5-triazina.* Tesi di Laurea in Chimica. Pisa 1993.
16. Padgett, D. E., & M.H. Posey: *An evaluation of the efficiencies of several ergosterol extraction techniques.* Mycological Research 97, 12 (1994): 1476–1480.

17. Biermann, C. J.: *Essential of pulping and papermaking.* San Diego: Academic Press 1993: 194–199.
18. Gallo, F., G. Pasquariello & F. Rocchetti F.: *Biological investigation on sizing for permanent paper.* Restaurator 19 (1998): 61–84.

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Ageing Behaviour of Encapsulated Paper

by JOHN B. G. A. HAVERMANS

INTRODUCTION

One of the preventive conservation measures to be undertaken is to avoid contact of the paper, stored, e.g., in an archive, with the polluted air. This can be done by applying an air purification system or by storing paper in a closed environment. However, wrapping of paper with a synthetic polymer (encapsulation) is under discussion since many years[1]. Depending on the material used for wrapping, papers ageing due to acid contaminants will be reduced as the polymer will act as a barrier against the surrounding air. Besides protecting paper against its deteriorative environment, the microclimate in the bundle of paper will have its own behaviour and may contribute to the ageing of the wrapped or boxed object[2]. In 1980 the Library of Congress reported that PE encapsulation of paper would not enhance the ageing, especially if alkaline (deacidified) paper is applied[3]. This conclusion was contradicted by other researchers. Passaglia (1987) concluded that the microclimate inside the encapsulation could be a danger for the encapsulated paper as degradation products coming from the paper remain in the closed environment and therefore could affect the stored paper[4]. Pauk and Pork showed by their research, that after subjecting sealed paper to accelerated ageing (alternating climate) and at using different polymer films, the deterioration was enhanced[5].

Once the paper is encapsulated, also no oxygen will enter the paper. As shown by several researchers, a reduced oxygen environment will reduce the deterioration of paper however for acid paper the deterioration by acid catalysed hydrolyses may continue[6–8].

Looking at research undertaken with encapsulated paper, one critical point has to be considered: The way of ageing applied. During ageing the climate in the polymer bag or pouch has to be considered and none of the researchers who investigated paper encapsulation have taken this phenomena into account. Sealed or encapsulated paper will create its own environment as there always is an equilibrium of the water in the (micro)environment and the paper. The water activity in the pouch is therefore seldom comparable to the water activity of the ageing environment, and more importantly, results therefore obtained of paper

artificial aged in a pouch and in a climate oven are not comparable. The aim of our work is to understand the way of ageing of paper wrapped and unwrapped by investigating the most comparable ageing conditions of wrapped (inpouch climate) and unwrapped (outpouch climate) paper.

MATERIALS

Two different papers were used. These papers were the same as used during previous paper ageing studies[6]: a bleached softwood cellulose paper and an acid mechanical pulp paper. The pouches applied came from Archipress and are based on laminated uncoated polyester. Bundles of 50 sheets were encapsulated according to the Archipress specifications[9] using the Archipress H 1000 machine (vacuum 2–3 mbar, reached within 25 seconds).

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

EXPERIMENTAL

Usually the ageing conditions are given in international standards, e.g., 90°C and 50% relative humidity. However it is obviously clear, that due to the paper content and the way of sealing the inpouch climate differs from the outpouch climate. Therefore water sorption and desorption behaviour of the papers used and the inpouch and outpouch water activity were measured in a climate chamber for in which firstly the climate varied from 20 to 90°C at a constant relative humidity of 50%. Subsequently the relative humidity was changed from 50% to 80% and back to 50% using an interval of 5% at constant equilibrium temperature. Based on the experimental values, we found an equilibrium environment at 70°C and 55–57% RH. Therefore we decided to apply an ageing climate of (70.0 ±0.5)°C and (55±2)% RH.

Chemical deterioration is dependent on the temperature applied as can be shown using the Arrhenius equation[10]. Therefore we decided to apply an ageing time of 24 days at the conditions as were established above.

After the ageing period, chemical, physical and mechanical paper properties were evaluated, *i.e.*, pH of the cold waters extract of the paper, total organic water soluble fraction, copper number, whiteness, folding number and tear strength[11–17].

RESULTS AND DISCUSSION

Looking at the acidity of the papers used, it was found that for both used papers the pH decreases after ageing (see Fig. 1), especially for the encapsulated acid mechanical paper.

The acidity of the unwrapped acid mechanical paper (outpouch), however, was not significantly affected. Therefore it is suggested, that the acidification will continue more extensively for the wrapped papers. This effect can be due to the microclimate created. Comparable results on acidification were found in a previous research where the effects of an inert gas on the ageing of paper were examined[18].

The copper numbers of the papers as shown in Fig. 2 represents the reducing aldehydes and reactive keto groups and therefore it indicates the amount of degradation. For the softwood cellulose paper the copper number was increased

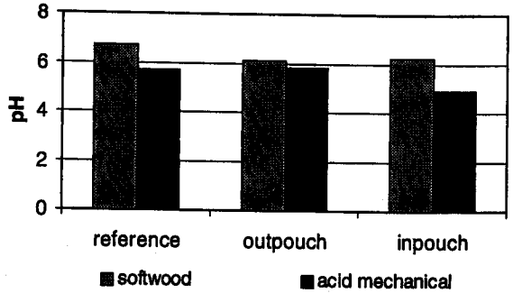

Fig. 1: The pH of the cold water extract of the softwood cellulose and the acid mechanical paper before ageing (reference), after ageing in a stock directly in the climate chamber (outpouch) and after ageing of the encapsulated paper (inpouch).

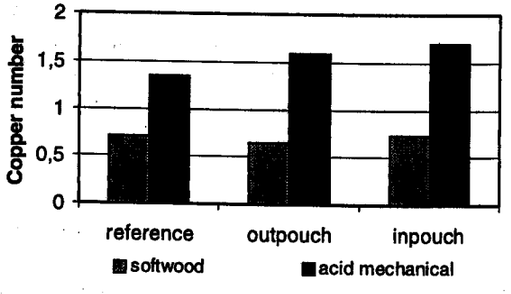

Fig. 2: The total amount of aldehyde and reactive keto groups, represented by the copper number of the softwood cellulose and the acid mechanical paper before ageing (reference), after ageing in a stock directly in the climate chamber (outpouch) and after ageing of the encapsulated paper (inpouch).

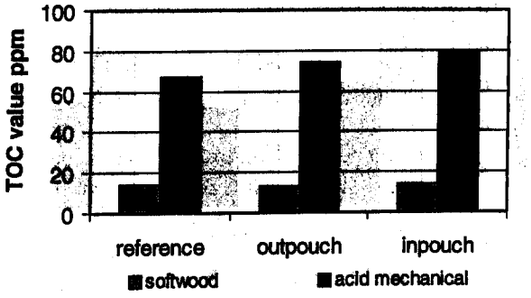

Fig. 3. The total organic soluble compounds represented by the TOC value in ppm of the cold water extract of the softwood cellulose and the acid mechanical paper before ageing (reference), after ageing in a stock directly in the climate chamber (outpouch) and after ageing of the encapsulated paper (inpouch).

only for the encapsulated paper, while for the acid mechanical paper the copper number increased for both the wrapped and unwrapped paper. From this point we suggest that although no oxygen could enter the inpouch climate, the microenvironment contains enough oxygen to continue the (thermal)oxidation more extensively for the wrapped acid mechanical pulp paper.

The water soluble degradation products formed during ageing can be presented by the TOC number. Here it was found that the acid mechanical paper deteriorates more extensively than the softwood cellulose paper. However, the degradation was somewhat reduced due to the used encapsulation (see Fig 3). From these results it is suggested that encapsulated paper degradates in such a case, that no small deterioration compounds are formed, thus no kind of peeling degradation reaction occurs. This as a base, combined with the increased copper number, we suggest that the paper polymers (the polysaccharides and lignin) will be depolymerized into larger pieces. And that the responsible mechanism can be attributed to the acid catalysed hydrolyses.

The whiteness of the papers used was decreased after ageing (see Fig. 4), however no significant differences were found due to the way of ageing, i.e., wrapped or unwrapped as presented as the inpouch and outpouch values. This is in accordance with the TOC number, as no enhancement of water soluble particles were found like acetic acid and 2-furaldehyde.

Looking finally at the mechanical properties of the paper we found that there were no significant differences for both papers related to the wrapping as presented by the inpouch and outpouch values (see Figs 5 and 6). Here in both figures the cheometrical mean (sqrt(MD*CD)) is presented.

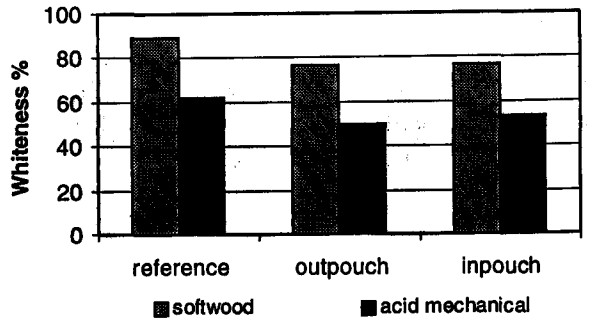

Fig. 4: The whiteness of the softwood cellulose and the acid mechanical paper before ageing (reference), after ageing in a stock directly in the climate chamber (outpouch) and after ageing of the encapsulated paper (inpouch).

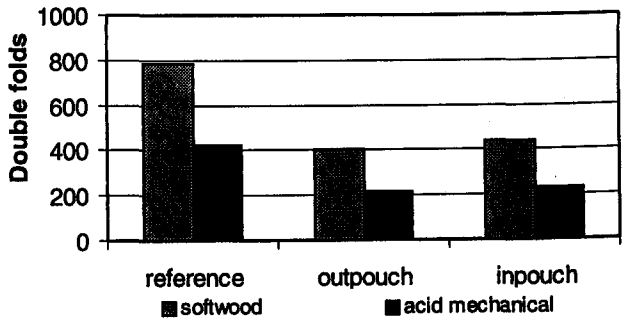

Fig. 5: The cheometrical mean number of double folds of the softwood cellulose and the acid mechanical paper before ageing (reference), after ageing in a stock directly in the climate chamber (outpouch) and after ageing of the encapsulated paper (inpouch).

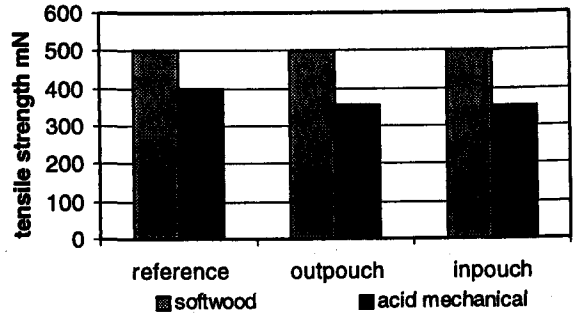

Fig. 6: The calculated cheometrical mean number of tensile break in mN of the softwood cellulose and the acid mechanical paper before ageing (reference), after ageing in a stock directly in the climate chamber (outpouch) and after ageing of the encapsulated paper (inpouch).

For both papers the mechanical properties, represented by the number of double folds and tear strengths (mN), dropped after the accelerated ageing seriously. Therefore we suggest that the way of wrapping used has not an effect on the mechanical strength properties during the applied artificial ageing, i.e., exposing the papers for 24 days at 70° and 55% RH.

CONCLUSIONS

Based on the approach, that the inpouch environment has to be equal to the outdoor environment during ageing studies, in our case 24 days at 70°C and 55% RH, the conclusion can be drawn that encapsulation of paper using a laminated uncoated polyester pouch and a slight vacuum, will neither influence the mechanical paper properties in a positive or negative way in time.

However, paper deterioration will continue and paper acidification will even be enhanced by the paper encapsulation. It is suggested therefore that only for deacidified papers this accelerated acidification will not occur. Based on the artificial ageing experiments, care has to be taken for storing acid papers encapsulated.

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The results represented in this paper were obtained during our research programme on the development of the Armacon-P method. The contribution of our co-funders, especially Mr. Kissing, therefore was highly acknowledged. Mr. Ronald van Deventer is also highly acknowledged for his effort.

SUMMARIES

Ageing Behaviour of Encapsulated Paper

This paper presents a study on the effects of paper encapsulation using a laminated uncoated polyester pouch and a slight vacuum. Because due to wrapping the environment inside of the pouch differs to the environment outside, the so-called inpouch and outpouch environment was investigated firstly. After adjusting the climate conditions two papers, wrapped and unwrapped, were subjected to an artificial ageing. The chemical, mechanical and physical changes of the papers were evaluated. It was concluded that paper encapsulation has no direct effect on the exchange of mechanical properties during artificial ageing. However, paper acidification, for example, was more extensively during artificial ageing for the papers stored in the pouches and thus care has to be taken for storing acid papers encapsulated.

Réaction du papier au vieillissement à l'intérieur d'une enveloppe de matière plastique

On présente une étude sur les effets causés sur le papier par une enveloppe ou un sac en polyester non enduit, fermé hermétiquement de tous les côtés et étanche à l'air. Etant donné qu'en raison de la fermeture hermétique l'air contenu à l'intérieur de l'enveloppe (ou du sac) réagira différemment aux fluctuations climatiques que l'air se trouvant à l'extérieur, on a d'abord analysé le climat interne et externe. Après avoir adapté les conditions climatiques on a soumis deux échantillons de papier, l'un enveloppé, l'autre sans enveloppe au vieillissement artificiel. Puis on a évalué les modifications des propriétés chimiques, mécaniques et physiques de ces échantillons. Les résultats obtenus indiquent que l'enveloppe étanche à l'air n'avait pas d'influence directe sur les propriétés mécaniques. On a constaté cependant que le taux d'acidité du papier, au cours du vieillissement artificiel, augmentait davantage à l'intérieur de l'enveloppe qu'à l'extérieur, ce dont il faudra tenir compte pour la conservation de papiers acides par la méthode de l'enveloppe.

Das Alterungsverhalten von Papier in Kunststoffhülle

Es wird eine Studie vorgelegt über die Wirkung einer allseitig fest und durch Schweißnähte luftdicht luftdicht geschlossenen Hülle oder Tasche aus unbeschichtetem Polyester. Da wegen des festen Abschlusses die Luft innerhalb der Tasche anders auf Klimaschwankungen reagiert als außerhalb, wurde das sog. Innen- und das Außenklima zuerst untersucht. Nach Festlegung der Klimabedingungen wurden das gleiche Papier, teils in in einer Hülle, teils frei, einer beschleunigten Alterung unterworfen und dann in seinen chemischen, mechanischen und physikalischen Eigenschaften untersucht. Es ergab sich, daß die luftabgeschlossene Hülle keinen direkten Einfluß auf die mechanischen Eigenschaften hat. Es zeigte sich jedoch, daß der Säuregehalt im Papier in der Hülle stärker zunahm als außerhalb, was als Warnung vor der Konservierung von säurehaltigem Papier durch die Methode der Umhüllung zu verstehen ist.

REFERENCES

1. Kissing, P.P.: *De Armacon methoden in historisch perspectief.* Written Communivation. 1993.
2. Hanus, J., M. Komorníková & J. Mináriková: *Influence of boxing materials on the properties of different paper items stored inside.* Restaurator 16 (1995): 194–208.
3. Brown, M.R.: *Polyester film encapsulation.* LC Publications on Conservation of Library materials. Preservation Office Research Services, Library of Congress: Washington D.C., 1980.
4. Passaglia, E.: *The characterization of microenvironments and the degradation of archival records: a research program.* Gaithersburg: U.S. Department of Commerce, National Bureau of Standards, Institute for Materials Science and Engineering 1987.
5. Pauk, S. and H. Porck, *De invloed van verschillende folies en verschillende manieren van insealen op papier bij kunstmatige veroudering.* Restaurator 23 (1993): 56–57.
6. Havermans, J.B.G.A., et al.: *The effects of air pollutants on the accelerated ageing of cellulose containing materials – Paper.* EC/DGXII/STEP Project CT 90-0100. Delft: TNO 1994.
7. Arney, J.S. and A.J. Jacobs, *Newsprint deterioration. The influence of temperature on the relative contribution of oxygen-independent and oxygen-dependent processes in the total rate.* Tappi Journal, 63,1 (1980): 75–77.
8. Anonymous: *Preservation of the Declaration of Independence and the Constitution of the United States.* Washington: United States Department of Commerce, National Bureau of Standards 1951.
9. Deventer, J. P. & J. B. G. A. Havermans: *Ontwikkeling van de Armacon-P methode.* Delft: TNO Paper and Board: 1994.
10. Priest, D. J.: *Artificial ageing of paper: Correlation with natural ageing,* Workshop on the effects of aging on printing and writing papers. Philadelphia PA: ASTM Headquarters 1994: 59–71.
11. *Bepaling van de pH van een waterige suspensie.* NEN 2151 (1981).
12. *Paper – Determination of tearing resistance.* ISO 1974 (1985).
13. *Paper – Determination of folding endurance.* ISO 5626 (1978).
14. *Paper and board – Measurement of diffuse blue reflectance factor (ISO brightness).* ISO 2470 (1977).
15. Sprokkelt, R.P.A.: *Het meten van de totale hoeveelheid opgelost en colloidaal organisch en anorganisch koolstof in de waterfase met behulp van de TOC-analyzer.* Report No. PK 92.9002, , Delft: Centrum TNO Papier en Karton 1992.
16. *Copper number of pulp, paper, and paperboard.* TAPPI T 430 (1988).
17. *pH and electral conductivity of hot water extracts of pulp, paper, and paperboard.* TAPPI T 252 (1990).
18. Havermans, J. B. G. A.: *Vergelijkend onderzoek naar de houdbaarheid van papier onder gangbare klimatologische omstandigheden en papier bewaard in een intert gas.* Delft: TNO Centrum voor Papier en Karton 1992.

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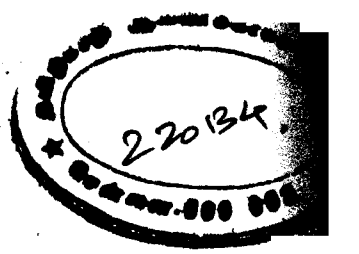

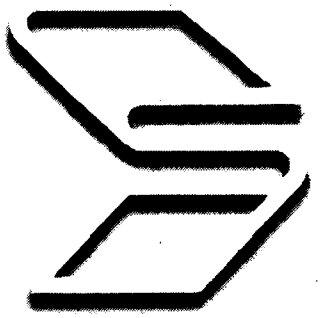

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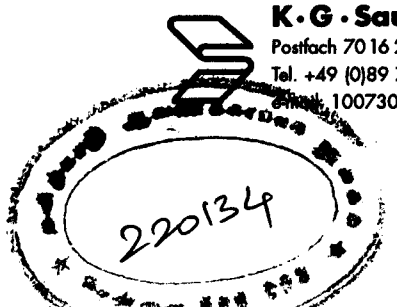

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