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Degradation of Cellulose at the Wet/Dry Interface

I. The Effect of Some Conservation Treatments on Brown Lines

by A.-L. DUPONT

INTRODUCTION

In 1934, Bone noted that when a strip of pure bleached cotton was dipped with one end into pure water, a brown line developed at the edge separating wet and dry material.[1] This problem was studied in the dye and textile industry and overcome by the development of better drying techniques in the mid-1960's. More recently, the problem of water-stained cellulosic material has been encountered by paper and textile conservators.

The browning is produced by the formation of unsaturated compounds with the presence of conjugated double bonds. Most chemical systems in which browning occurs contain carbonyl or potential carbonyl groups as the reducing sugars which are further transformed into unsaturated colored compounds. Polyhydroxy compounds in which the carbonyl group is blocked, such as sugars in their cyclic form, do not directly give rise to browning.[2] At first, they should undergo oxidation. In the macromolecule of cellulose, glucose residues are in their cyclic form (Fig.1). Oxidation reactions which involve the presence of oxygen are a common cause of browning. The very particular micro environment of the cellulose at the wet/dry interface might be necessary for oxidation to occur at this location. This article contains results of an investigation of the effect of washing and bleaching with the reducing agent sodium borohydride on artificially aged brown lines and brown lines freshly formed at wet/dry interfaces on Whatman filter paper no. 5. Other current paper conservation treatments involving local or global wetting are also studied in this paper for their degrading action on the cellulose if the conditions for the formation of brown lines are fulfilled. The degradation was evaluated qualitatively by observation under natural light, ultraviolet (UV) light at 366 nm and by methylene blue absorption.

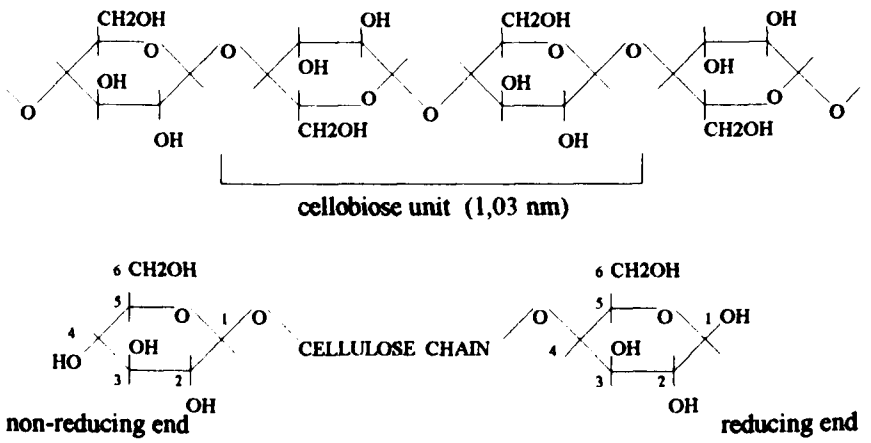

Fig. 1. Formula of cellulose.

MATERIALS AND METHODS

Test samples

Test samples were prepared using Whatman filter paper no. 5. Brown lines at the wet/dry interface were obtained by dipping few centimeters of one end of the test samples (8×28.5 cm) in distilled water, in ethanol or in acetone for approximately 18 hours.

Rings of brown degradation products in the experiment of consecutive drops were obtained by pouring drops of water on test samples (4×28 cm).

Methods of detection

Three visual, qualitative methods were used for the detection of the degradation at the wet/dry interface. These included a visual inspection under natural light (1), under ultraviolet light (2), and after staining with methylene blue dye (3). The natural light was daylight from the window. Ultraviolet light at 366 nm was produced by a Fluotest lamp (Original) and the observation of the samples was done in a dark room. A 2 mM solution of methylene blue was prepared in distilled water. The samples were immersed in the solution for 10 to 15 minutes and thoroughly rinsed in several baths of warm water.

Artificial ageing conditions

Artificial ageing conditions were 80°C, 65% RH for 24 days (ISO 5630/3-1986). A Heraeus VTRK 150 ageing chamber was used. Each set of experiments reported below comprised besides unaged samples, a number of samples aged, to evaluate the long-term behavior of the brown lines after the treatments carried out.

Experiment of consecutive drops

1, 2, 4, 8, 12, 16 and 20 drops (30 µl) of distilled water were poured on 4 samples divided in 7 parts (4×4 cm each part). Samples were allowed to dry between each drop. Two of the four samples were artificially aged. One aged sample and one unaged sample were used for observation in daylight and under UV. The second aged sample and the second unaged sample were used for methylene blue absorption.

Solubility of the degradation products

The solubility of the degradation products was evaluated by the observation of the decrease in the coloration after washing the samples, using the three methods of detection described. Table 1 summarizes the reference samples used to compare each test sample within this experiment.

– *Solubility of fresh degradation products*

Solubility of the degradation products generated in water: the washing was carried out by immersing paper samples with fresh brown lines during 20 minutes in:

- a large range of solvents at room temperature, or
- distilled water at 50-60°C or at room temperature.

Table 1. Samples used as references to evaluate test samples on the basis of the three evaluation methods in testing the solubility of the brown lines

	Solubility of fresh brown lines		Solubility of aged brown lines	
	Originated in water	Originated in ethanol or acetone	Originated in water	Originated in ethanol or acetone
Reference samples	fresh brown lines not washed	fresh brown lines not washed	aged brown lines not washed	aged brown lines not washed
Test samples	brown lines washed in water or in a wide range of solvents	brown lines washed in water, in ethanol or in acetone	aged brown lines washed in water	aged brown lines washed in their originating solvent

Solubility of the degradation products generated in organic solvents: brown lines obtained with ethanol and with acetone were washed respectively in:

- ethanol or acetone for 20 minutes at room temperature, or
- distilled water at 50-60°C.

Three samples of brown lines were formed in each generating liquid: one was the unwashed reference and two others were washed. One of the two washed samples was used for daylight and UV observation and the other for methylene blue absorption.

– Solubility of aged degradation products

Samples of brown lines obtained with water, ethanol or acetone were artificially aged. The experiment comprised 6 samples of brown lines per each generating liquid.

Two samples of fresh brown lines were compared with the reference aged brown lines in order to evaluate the damage produced during the ageing:

- 1 for observation in daylight and under UV; and
- 1 for methylene blue absorption.

Four aged samples:

- 2 reference samples not washed: 1 for observation in daylight and under UV and 1 for methylene blue absorption; and
- 2 samples washed in their originating liquid: 1 for observation in daylight and under UV and 1 for methylene blue absorption.

Influence of the chemical condition of the cellulose on the formation of brown lines

– Effect of washing and reduction on unaged paper

Brown lines formed on paper not washed (1), paper washed (2) and paper washed and reduced with sodium borohydride ($NaBH_4$) (3) were compared.

Solutions of $NaBH_4$ 5 g/l in ethanol (96%) were prepared. Samples were immersed in the reduction bath for 20 minutes. After reduction, samples were first washed in a bath of ethanol, and consecutively thoroughly rinsed in water (method described by Burgess[3]). Samples were allowed to dry before the use for brown line formation.

– Effect of washing and reduction on artificially aged paper

Brown lines were obtained on:

- (1) paper not aged, not washed, not reduced (reference samples),
- (2) paper aged,
- (3) paper aged, then washed in water,
- (4) paper aged, then washed and reduced in $NaBH_4$.

Table 2. References used for each test sample on the basis of the three evaluation methods in the experiment of reduction with sodium borohydride

	Brown lines not aged	Brown lines aged
Reference samples	brown lines not reduced	brown lines not reduced
Test samples	brown lines reduced	brown lines reduced

Reduction with sodium borohydride of unaged or aged brown lines formed in water or in solvents

This experiment was carried out on fresh brown lines and on artificially aged brown lines obtained with water, ethanol or acetone. In order to avoid any washing effect of the $NaBH_4$ solutions and to evaluate only the effect of reduction on the brown lines, we used the following procedure:

reduction of samples of brown lines obtained with water was carried out in a solution of $NaBH_4$ in ethanol, further rinses also in ethanol; and

- reduction of samples of brown degradation products obtained with ethanol or acetone were carried out in aqueous solution of $NaBH_4$, further rinses also in water.

The experiment comprised 4 samples of brown lines per generating liquid:

- 2 reference samples not reduced (1 reference not aged and 1 reference aged),
- 2 test samples reduced (1 not aged and 1 aged).

Detection was done in daylight and under UV.

Table 2 summarizes the reference samples used for each test sample.

Formation of oxidized cellulose on the suction table

A test was carried out on the suction table with water, ethanol and acetone as liquids that might generate oxidation. Samples were divided in 3 parts in order to pour 200 µl, 1 ml and 5 ml of water, ethanol or acetone dropped on a surface as restricted as possible.

The experiment comprised 6 samples:

- 2 samples of paper not aged and not washed,
- 2 samples of paper not aged and washed,
- 2 samples of paper aged and not washed.

In each series, 1 sample out of the 2 was additionally aged.

Samples on which ethanol and acetone were poured were sprayed with water after the use on the suction table. At the end of the experiment, samples were allowed to dry slowly between two blotter papers.

Fig. 2. Brown line originated in water.

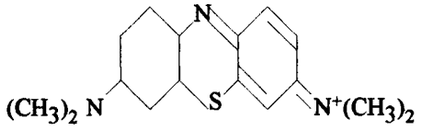

Fig. 3. Methylene blue molecule.

Results and Discussion

Methods of detection

In daylight, the visual aspect of brown lines originated in water is a thin line (0.1 to 1 mm thin). The color ranges from ocher to dark brown. They can form very fast (as fast as 15 minutes, but reach their maximal intensity around 5 to 10 hours), moving upwards and intensifying brown color at the wet/dry interface as water rises in the paper by capillarity (Fig. 2). The degradation products show a bright bluish fluorescence when exposed to the UV source. According to Hodge[2], fluorogens are thought to be precursors of browning. We know that numerous organic molecules as those containing benzenic or non-benzenic rings and molecules containing carbonyl groups (aldehydes and ketons) have a UV fluorescence.[4]

Methylene blue is a basic dye (Fig. 3) and reacts with acidic groups present on the oxidized cellulose by a typical cation exchange process.[5,6] The reaction for methylene blue absorption is the following:

$$R\text{-}COOH + Mb^+ \Leftrightarrow R\text{-}COOMb + H^+$$

Table 3. Effect of water drop test

Visual observation	Before ageing	After ageing
In daylight	–: no brown rings independently of the number of drops	+: brown rings independently of the number of drops
UV fluorescence	slight fluorescent ring after 1 drop, increasing with number of drops	+: bright fluorescent rings independently of the number of drops
Methylene blue absorption	slight blue ring from 4 drops, mildly intense after 8 drops and increasing	+: strong absorption independently of the number of drops

The brown line is stained dark blue and the paper light blue after the dyeing since methylene blue also can be absorbed as a direct dye on the -OH groups of the cellulose.

Experiment with consecutive drops

This experiment was carried out in order to investigate the lower limit (time, volume of water poured) of the presence of a wet/dry interface that creates a brown ring. The results are reported in Table 3. The results showed how water-rings that are invisible by the naked eye have a bright UV fluorescence and absorb methylene blue. Upon ageing, those fluorescent rings develop browning. Results showed that any wet/dry interface on the cellulose, even in a brief exposure (the time for one drop to dry out), may be a potential cause of degradation and may result in the development of brown coloration on ageing. UV fluorescence and methylene blue absorption are found to be very sensitive methods for the detection of degradation, which can develop brown marks on ageing. However, we observed that UV fluorescence was the more sensitive: four drops of water were necessary to observe a slight methylene blue absorption while only one drop was required to observe a fluorescent ring. For practical conservation work, methylene blue dyeing is not suitable to detect damaged areas, but UV fluorescence is found useful to detect those areas of the cellulose where browning could further develop.

Solubility of the degradation products

– Solubility of fresh degradation products

The results in Table 4 are based on the observation of the brown line area of the samples after washing. Observation in daylight showed clearly that the degradation products formed by water at the wet/dry interface were soluble in water exclusively. However, methylene blue absorption and UV fluorescence showed that there still were acidic groups and fluorescent compounds

Table 4. Solubility of the fresh degradation products. Observation of the brown line area on the samples (Table 1 gives the references used with each test sample)

	Solubility of brown lines orginated in water		Solubility of brown lines originated in ethanol or acetone	
Visual observation	Solubility in water	Solubility in organic solvents*	Solubility in water at 50–60°C	Solubility in respective originating solvent
In daylight	+: partly washed at room T° and totally between 40–60°C	totally insoluble, same as reference	totally insoluble, same as reference	totally soluble
UV fluorescence	slight	bright, same as reference	bright, same as reference	slight
Methylene blue absorption	slight	strong, same as reference	strong, same as reference	very slight

*Pure solvents used for testing the solubility in solvents of brown lines originated in water are (dipolar moment in Debye is indicated): acetonitrile (3.5), acetone (2.7), ethylmethylketon (2.7), ethanol (1.7) (warm and at room T°), methanol (1.65), chloroform (1.1), toluene (0.4), trichlorethylene (0), cyclohexane (0), carbon tetrachloride (0).

in the paper at the location of the brown line after the washing. These compounds not soluble in water are covalently bound to the cellulose. Degradation did not lead only to distinct compounds cleaved from the cellulose chain, but also to new oxidized groups on the cellulose chain. This result is consistent with that of Bone & Turner.[7] None of the pure organic solvents used did solubilize the brown degradation products originated in water. Ethanol, methanol, ethylmethylketon and acetone partly mixed with water were tested. Solubilization was found to be proportional to the part of water. However, the non-solubility in organic solvents needs to be qualified by the fact that the degradation of the cellulose at the location of the brown line could lead also, besides to the brown compounds, to uncolored and less polar compounds. Those compounds could possibly be extracted with some of the solvents tested. But the qualitative visual evaluation was not suitable to detect them. Infrared spectra of the residue obtained after evaporation of the organic phase of a partition ethyl acetate against an aqueous extract of the brown line compounds showed the presence of uncolored compounds of weak and mild polarity.[8]

The results showed that ethanol and acetone did produce degradation. Brown lines obtained with ethanol and acetone were less sharp, less colored (yellowish), more blurred and had a very strong methylene blue absorption as compared with brown lines formed with water. They seem to

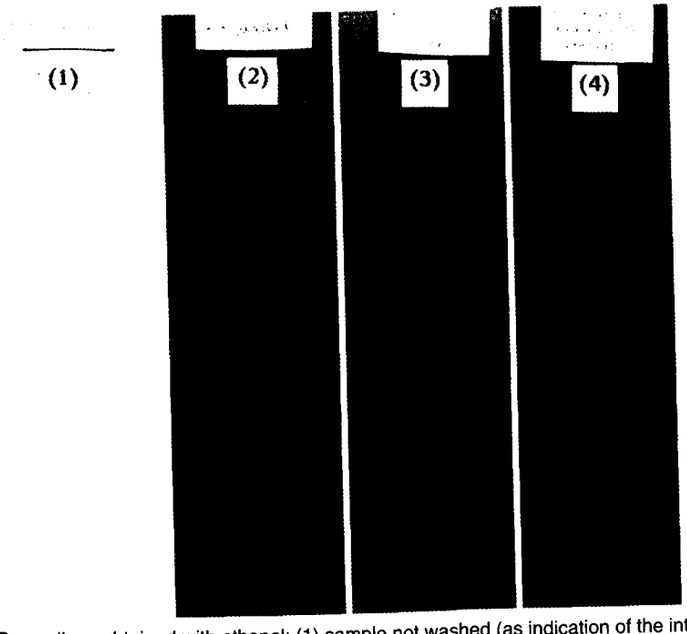

Fig. 4. Brown lines obtained with ethanol: (1) sample not washed (as indication of the intensity of the browning); (2): sample not washed (methylene blue absorption); (3) sample washed in water (met. blue); (4) sample washed in ethanol (met. blue).

contain a greater amount of acidic groups. The results showed that brown lines originated in ethanol or acetone were exclusively soluble in the originating solvent (Fig. 4). Such results are consistent with those of Schaffer et al.[9] The degradation products are less polar than those obtained in water. Acidic compounds were soluble in ethanol, they were not covalently bound to the cellulose. The very slight methylene blue absorption together with a residual UV fluorescence after washing in the originating solvent indicated that the cellulose chain itself was degraded to a certain extent. But acidic end-groups attached to the cellulose were minor unlike the case of brown lines originated in water. This result could also be interpreted by considering that UV fluorescence is a more sensitive technique than methylene blue absorption for the detection of degradation products (as the experiment of consecutive drops showed). This experiment shows that the nature of the degradation originated with ethanol and acetone likely is different from the degradation obtained at a water wet/dry interface.

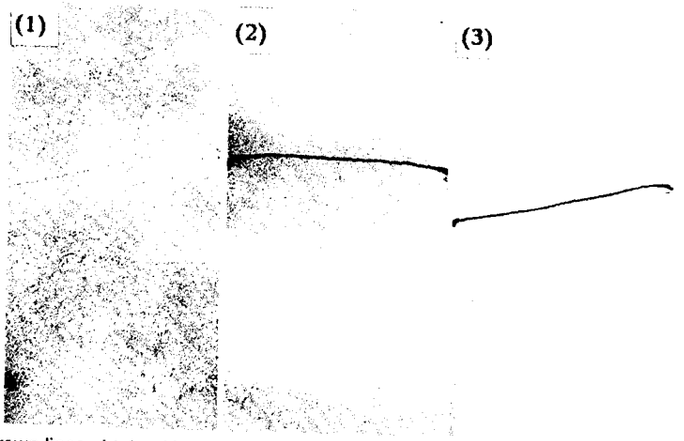

Fig. 5. Brown lines obtained in water: (1) before ageing (as indication to evaluate the extent of the damage after ageing); (2) after ageing with no further treatment; (3) after ageing and further washing in water.

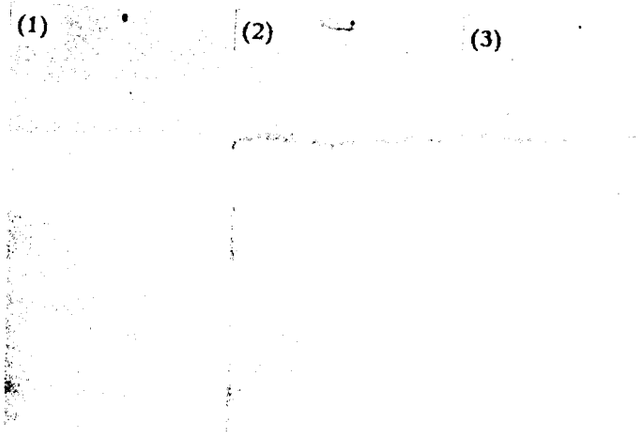

Fig. 6. Brown lines obtained in ethanol: (1) before ageing; (2) after ageing with no further treatment; (3) after ageing and further washing in ethanol.

– Solubility of aged degradation products

The artificial ageing of the brown degradation products formed at the wet/dry interfaces led to a drastic increase of the browning. This result showed an increased concentration of conjugated double bonds. The brown lines obtained with water were the most affected by ageing, turning to a very dark brown color. Brown lines obtained with ethanol and acetone were also dark-

Table 5. Solubility of aged degradation products

Visual observation	Solubility in water of brown lines originated in water after ageing	Solubility in ethanol or acetone of brown lines originated in same solvents after ageing
In daylight	totally insoluble: same color as reference samples (Fig. 5)	partly soluble: slight decrease in color intensity (Fig. 6)
UV fluorescence	same fluorescence as reference samples	slight decrease

ened, although to lesser extent. The results in Table 5 showed that ageing led to a total insolubility of the brown lines originated in water (Fig. 5) and a partial insolubility of the brown lines originated in ethanol or acetone (Fig. 6). We observed a general increase in the UV fluorescence of the artificially aged paper. Washing in water lead to a slight decrease of this general fluorescence of the aged paper, which was therefore partly due to cleaved fragments. The washing in ethanol or acetone had no consequence on the general fluorescence of the aged paper. Degradation products resulted from ageing the cellulose were not soluble in these solvents.

Influence of the chemical condition of the cellulose on the formation of brown lines

The purpose of this experiment was to evaluate the contribution of the chemical condition of the paper (cellulose partly oxidized, versus pure hydroxylated cellulose) in the brown line formation.

– Effect of washing and reduction on unaged paper

The results showed that brown lines formed on all the samples: not washed (1), washed (2), washed and reduced (3). The mechanism of formation of brown line at the wet/dry interface is therefore independent of the extent of oxidation of the cellulose chain. The intensity of the browning observed in daylight, UV fluorescence, and methylene blue absorption of the brown lines are by decreasing order: (1) > (2) > (3). This experiment is consistent with the results of earlier research[1,7,9–13] that the mechanism of the brown line effect is not related to chromatographic migration of impurities in the paper. It proved also that it is not due either to the pre-existence of oxidized groups on the cellulose chain. Although, this experiment showed that both do contribute to increase the quantity of degradation products at the interface and the color intensity of the brown line.

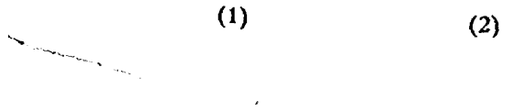

Fig. 7. Brown lines obtained on paper unaged (1) (=reference) and on paper aged (2).

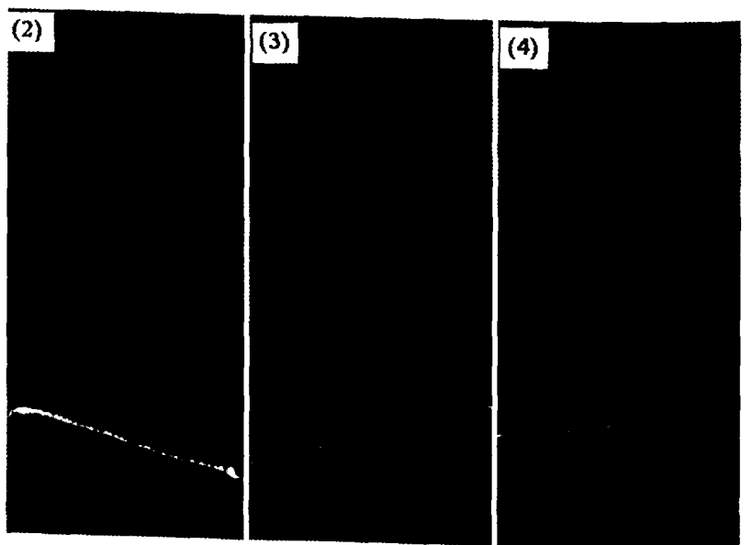

Fig. 8. UV fluorescence of brown lines obtained on paper aged (2), on paper aged then washed in water (3) and on paper aged then washed and reduced in $NaBH_4$ (4).

– Effect of washing and reduction on artificially aged paper

Here again, brown lines formed on all the samples: reference not aged, not washed, not reduced (1), test sample aged (2), test sample aged then washed (3), test sample aged then washed and reduced (4). Fig. 7 shows a brown line obtained on paper aged (2) versus a brown line obtained on paper unaged (1) for comparison of the intensity of the brown lines in daylight.

The colour intensity of brown lines was in decreasing order: (2)>(1)=(3)>(4).

The intensity of UV fluorescence was in decreasing order: (2)>(1)>(3)≥(4) (Fig. 8).

Ageing in a humid oven has been shown to cause preferential hydrolytic scission producing one carbonyl per scission.[14] Cleaved oxidized units were able to migrate with the water and could also be further oxidized, contributing to enhanced browning. The results showed that degraded compounds cleaved from cellulose on ageing did solubilize in the water during washing (comparison of browning and UV fluorescence of samples (1) and (3)). Reduced samples, freed from any oxidized group, showed the less intense brown lines. The cellulose chain was degraded to some extent by the ageing and the oxidized groups attached to the chain of sample (3) (which could not be washed) did participate in the brown line formation.

This experiment simulated the degradation produced by brown lines on an old document. It is likely that at least three processes contribute to paper degradation at the wet/dry interface: (i) the presence of a large number of oxidized end-groups attached to the cellulose chain as a result of the natural ageing process, (ii) the solubilization and migration of cleaved oxidation products by water, and (iii) further oxidation at the wet/dry interface contributes, additively, to the degradation.

The beneficial effect of a simple washing of an old paper document should be emphasized, even if there is no absolute necessity in the conservation treatment. Reduction treatment did not seem to be significantly more beneficial than a simple washing on the amount of degradation products likely to form at the wet/dry interface. However, additional ageing treatment of samples (3) (aged then washed) and (4) (aged then washed and reduced) would be necessary to show if reduction with $NaBH_4$ could somehow "protect" the cellulose from extensive oxidation better than a simple washing or if, on the contrary, it would enhance further degradation.

Table 6. Reduction with $NaBH_4$ of brown lines unaged or aged (Table 2 gives the references used with each test sample)

	Reduction treatment of unaged brown lines		Reduction treatment of aged brown lines	
Visual observation	Brown lines originated in water	Brown lines originated in solvents	Brown lines originated in water	Brown lines originated in solvents
In daylight	less brown	revert to uncolored	no improvement: no color change	slightly less colored
UV fluorescence	less fluorescent	residual	same fluorescence as reference but enhanced as compared with unaged brown lines	lesser as compared with reference but still higher than unaged brown lines

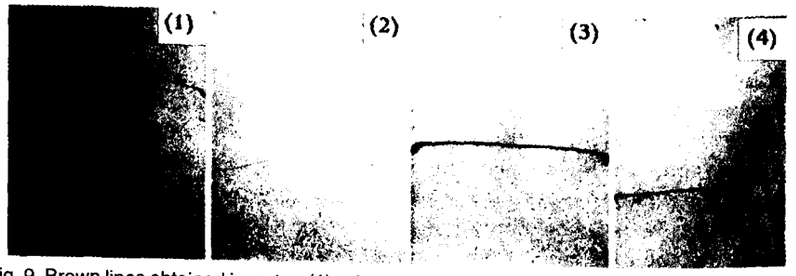

Fig. 9. Brown lines obtained in water: (1) reference sample with brown line not aged; (2) sample with brown line not aged and reduced; (3) reference sample with brown line aged; (4) sample with brown line aged and reduced.

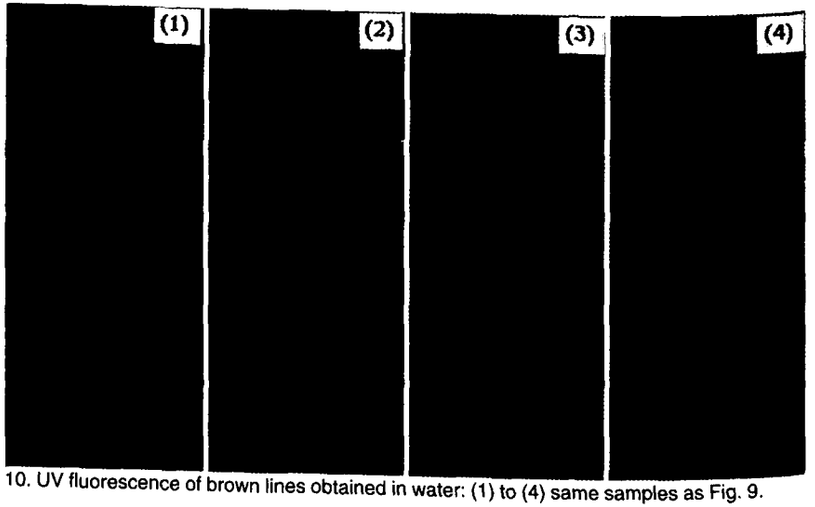

Fig. 10. UV fluorescence of brown lines obtained in water: (1) to (4) same samples as Fig. 9.

Reduction with sodium borohydride of unaged or aged brown lines originated in water, in ethanol or in acetone

Sodium borohydride was chosen because it reduces the carbonyl groups present on the cellulose chain to hydroxyl groups, decreasing the probability of browning, since browning is due to the presence of conjugated double bonds. The results are summarized in Table 6. Results showed that before ageing, brown lines obtained in water were discolored slightly by the borohydride treatment (Fig. 9, 10) while those obtained in solvents reverted to totally uncolored compounds (Fig. 11, 12). This confirmed the different nature of the brown degradation products obtained with organic solvents versus those obtained with water, as mentioned earlier. The former seem to con-

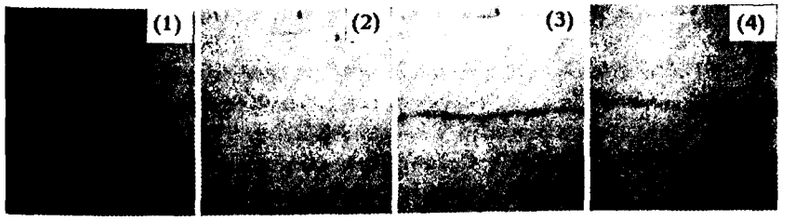

Fig. 11. Brown lines obtained in ethanol: (1) reference sample with brown line not aged; (2) sample with brown line not aged and reduced; (3) reference sample with brown line aged; (4) sample with brown line aged and reduced.

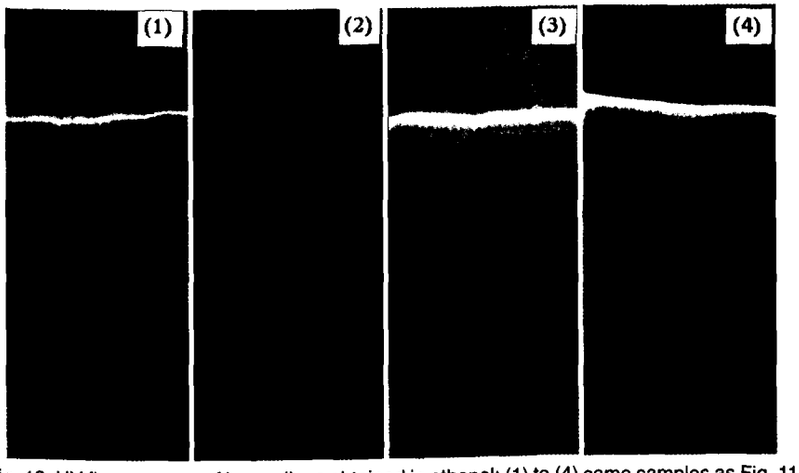

Fig. 12. UV fluorescence of brown lines obtained in ethanol: (1) to (4) same samples as Fig. 11.

tain mostly carbonyl groups. However, the residual UV fluorescence of the samples proved that some degradation products are still present on the cellulose chain. Therefore, those residual fluorescent compounds are not carbonyl-containing compounds. Brown lines formed in water contained colored compounds with relatively less carbonyls than brown lines formed with non-aqueous solvents. These carbonyl-containing compounds produced from the degradation at the wet/dry interface may oxidize further and form, for instance, colored furan derivatives.[2,15–17]

The results showed that reduction with sodium borohydride did not return the cellulose in the brown line area completely to its initial chemical state. Borohydride treatment reduced the carbonyl groups to alcohol groups, thereby decreasing the number of double bonds and reducing the production of colored degradation products.

The same observation was made on the general fluorescence of the samples. As mentioned earlier, the washing in water of brown lines obtained with water also leads to a slight decrease of the overall fluorescence of the paper after ageing. However, results of the present experiment showed that reduction treatment seemed to be more effective. The fragments cleaved from the cellulose contained carbonyl end-groups and were soluble in water; however, there were still oxidized groups on the cellulose chain that were not washed away but that could be reduced by the borohydride.

Formation of oxidized cellulose on the suction table

The purpose of this experiment was to evaluate the eventual oxidative effect of an interface between two different liquids or between two areas with different humidity content in the paper.

The results showed that wet/dry interfaces could appear in a very short time if the paper was not carefully and evenly rewetted during the work on the suction table. This was especially noted when the organic solvents were used. Organic solvents have a drying effect on the cellulose, due to their higher volatility as compared with water: organic molecules replaced water molecules in the paper fibers. In order to avoid a wet/dry interface, the samples were sprayed with water at the end of the work on the suction table, before the drying. In a conservation treatment, after humidification of the document, the borders are usually covered by pieces of mylar on the suction table. The inner part of the document, not covered with mylar, should be regularly rewetted.

As previously seen, during the experiment, samples were carefully kept as evenly damp as possible. Nevertheless, after the treatment, some of the samples showed uneven UV fluorescence with very randomly located patchy bright spots. As the only explanation, these fluorescent small spots were probably due to the presence of neighboring areas which had a significantly different humidity content at a given moment during the experiment. On ageing, some of these fluorescent spotty areas became brownish marks; others, still invisible to the eye, only showed enhanced UV fluorescence. No brown rings were visible in daylight on the samples before ageing at the local treated area. Nevertheless, observation under UV showed circular areas on some of the samples (corresponding to the local drop treatment) which did fluoresce less than the whole surface of the sample (especially the areas which had 5 ml poured through). This was probably because the washing removed part of the fluorescent compounds. On ageing, these "washed" areas did undergo less yellowing than the surrounding paper: they appeared whiter. It was somehow the opposite effect of browning in brown line effect.

It is therefore very important to point out that local treatments should of course avoid any wet/dry interface, but also avoid any boundary created by neighboring areas of different humidity contents. However, we observe that the control of the humidity of the paper while working on the suction table is not easy, and that the chance to undergo degradation which could further develop into brown spots is significant. The conservator must be very careful to always keep the artifact as evenly slightly damp as possible while working on the suction table. Building a humidifying chamber around the suction table with polyethylene plastic sheets, for instance, big enough to be able to work in, may help.

Discussion of foxing

When talking about brown water-stains on paper, foxing comes naturally to the mind of the paper conservator. It seems legitimate to draw a parallel between the two phenomena. Literature on foxing is extensive but its origin remains controversial. Most authors attribute the brown spots either to a development of color from iron particles, or to fungal activity[18,19] or to both mechanisms which could act together or separately.[20] The effect of fluctuating moisture content on a cellulose substrate which does not respond at the same rate or velocity in all of its parts (in a book, for instance, the edges of the pages are more exposed to environmental fluctuations in temperature and humidity than the inner core which reacts more slowly) should be considered as potentially damaging.[21] Bogaty[10] observed that *Aspergillus niger* preferentially grew along a brown line area of cotton than on the rest of the cloth. This suggests that the observed growth could also be a result of spotting rather than a cause. An investigation on foxing stains and discoloration of leaf margins and paper surrounding printing ink supports the view that browning reactions take place in paper at accumulations of moisture caused by local condensation processes in the book.[22]

CONCLUSION

The experiments reported were carried out in order to approximate the nature of the brown degradation products forming on cellulose at the wet/dry boundaries, and to approach the conditions in which a brown line is likely to form in usual paper conservation treatments. Our results are consistent with earlier works carried out on textile, indicating oxidation of the cellulose at the wet/dry interface.[1,7,9–13] However, they are complemented with artificial ageing, sodium borohydride reduction testing, and usual conservation treatments. We focused as much as possible on working in the conditions more

often encountered in wet treatments in paper (and textile) conservation. For instance, organic solvents were chosen because of their frequent use in local treatments for the removal of stains (adhesive tapes, grease marks, etc.). Water-stains are sources as well as consequences of damage to cellulose: browning not only is unsightly, but it also is an indication of oxidation to some extent. Both washing and bleaching with the reduction agent sodium borohydride were found effective to remove or attenuate the browning on brown lines freshly formed. However, it was shown that degradation did not only lead to cleaved compounds from the cellulose chain, but also to oxidized cellulose with new end-groups attached to the macromolecule. Washing and reducing with sodium borohydride could be complementary treatments of the brown lines. Upon ageing, the solubility of the brown degradation products is found to decrease, not to say brown lines become insoluble. Both washing and bleaching with sodium borohydride appear to be more or less ineffective on aged brown lines. It was also found that wet treatments may be potentially harmful to paper artifacts. Any process including local wetting or creation of uneven humidity content of the artifact represents a potential source of oxidation if wet/dry boundaries are allowed to form. From this point of view, the drying of cellulosic material should also be emphasized as a step to follow very closely during a conservation treatment. The conservator must be aware that use of the suction table requires a very accurate control of the humidity content of the artifact. The removal of adhesive tapes, grease stains and other dirt marks as local treatments is also pointed out as susceptible to promote oxidation. UV fluorescence appeared to be very sensitive to detect fluorescent oxidized areas which could further develop brown stains on ageing, and to prevent them by considering a washing or a reduction treatment when possible. Since it is a very handy method, we recommend to use it as much as possible in the paper and textile conservation field, for instance, for evaluation reports of the artifacts before treatment, as well as a tool to follow the course of a treatment. This work does not attempt to answer all the questions on the formation of brown lines. The chemical analysis of the degradation compounds formed at the wet/dry interface is explored elsewhere by the author[8] and gives more information on the nature of the phenomenon of the brown line formation.

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SUMMARIES

Degradation of cellulose at the wet/dry interface. I. The effect of some conservation treatments on brown lines

This article contains results from the study of the formation of brown lines on filter paper at the wet/dry interface with water, ethanol or acetone. The effect of ageing and the effect of the conservation treatments of washing and bleaching with the reduction agent sodium borohydride were investigated. Qualitative evaluation of the degradation of the paper at the location of the brown line is done in daylight, under UV at 366 nm and staining with methylene blue dye. The results showed that any wet/dry interface, even a brief exposure, may be a potential cause of degradation. Ageing resulted in a drastic darkening of the brown line and insolubility of the brown compounds. It was also confirmed that degradation led not only to distinct compounds cleaved from the cellulose chain, but also to oxidized cellulose with new end-groups attached to the macromolecule. The compounds formed at the wet/dry interface were identified as containing carbonyl and acid groups. Reduction with borohydride was found effective to decrease the browning of freshly formed brown lines exclusively. Washing was also found effective only on recent brown lines and had to be done in the liquid that originated the brown line (water or organic solvents). Results showed that conservation processes involving local or global wetting of paper documents are a potential source of browning. Practical recommendations are given for the conservator, such as the frequent observation of paper artifacts under UV wavelengths to detect where browning could appear on ageing.

Degradation de la cellulose à l'interface humide/sec. I. L'effet sur les lignes brunes de quelques traitements de restauration

Le présent article expose les résultats d'une étude sur la formation de lignes brunes sur du papier filtre pure cellulose à l'interface humide/sec, avec de l'eau, de l'éthanol ou de l'acétone. Sont étudiés les effets du vieillissement accéléré et des traitements de restauration tels que le lavage et le blanchiment avec un agent réducteur (borohydrure de sodium). L'évaluation qualitative de la dégradation du papier à l'endroit de la ligne brune est réalisée en lumière du jour, sous UV à 366 nm et par coloration au bleu de méthylène. Les résultats ont montré que toute interface humide/sec, même éphémère, peut être une cause potentielle de dégradation. Le vieillissement accéléré a entraîné un accroissement du brunissement et une insolubilisation des composés bruns. Les résultats ont également confirmé que la dégradation produit non seulement des composés distincts scindés de la chaîne de cellulose, mais également une cellulose oxydée comportant des nouveaux groupements terminaux. Les composés présents à l'interface comportent des groupements carbonyles et acides. La réduction au borohydrure de sodium a pour effet de diminuer la coloration des lignes brunes fraîchement formées. Le lavage est également efficace sur des lignes brunes fraîches s'il est effectué dans le liquide qui les a généré (eau ou solvants organiques). Les résultats montrent que les procédés de restauration mettant en jeu une humidification locale ou globale des documents papier sont une cause potentielle de brunissement. Quelques recommandations pratiques pour le restaurateur sont suggérées, telle que l'observation fréquente des objets sous lumière ultraviolette, qui permet de localiser les endroits du papier où des marques brunes sont susceptibles d'apparaître au vieillissement.

Der Abbau von Cellulose an der Übergangsstelle Naß/Trocken. I. Die Wirkung von konservatorischen Maßnahmen auf die braunen Ränder

Der Aufsatz referiert Ergebnisse einer Untersuchung von braungefärbten Rändern, wie sie an der Stelle des Übergangs Naß-Trocken von Papieren entstehen, die teilweise mit Wasser, Ätha-

nol oder Aceton getränkt werden. Es wurde untersucht, wie diese Ränder auf eine beschleunigte Alterung sowie auf Wässern und auf reduktives Bleichen mit Natriumborhydrid reagieren. Die Ränder wurden bei Tageslicht und unter UV (366 nm) sowie nach Einfärben mit Methylenblau visuell beurteilt. Es zeigte sich, daß jede Übergangsstelle Naß/Trocken, auch kurzzeitige, einen Abbau des Papiers verursachen kann. Beschleunigte Alterung führt zu drastischer Intensivierung der braunen Verfärbung und zu Unlöslichkeit der sie bildenden Celluloseabbauprodukte. Es bestätitgte sich auch, daß Celluloseabbau nicht nur zu bestimmten Produkten führt, die von dem Cellulosemolekül abgespalten werden, sondern auch zu oxidierten Gruppen am Ende des Makromoleküls. In den Abbauprodukten, die die Wasserränder darstellen, wurden Carbonyl- und Carbosylgruppen nachgewiesen. Natriumborhydrid kann nur neugebildete braune Ränder mildern. Auch Wasser kann solche Ränder mildern, sie seien aus Wasser oder aus organischen Lösemitteln entstanden. Insgesamt zeigen die Ergebnisse, daß restauratorische Manahmen, die eine Flüssigkeit einsetzen, sei es lokal oder am ganzen Blatt, möglicherweise eine Verbräunung bewirken können. Es werden praktische Hinweise gegeben, wie unter UV die Neigung eines Papiers, bei entsprechender Behandlung braune Ränder zu entwicklen, erkannt werden kann.

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Creating Buildings for Rare Books and Archival Documents

by ARTHUR DAVID BAYNES-COPE

It is reasonable to consider these two groups of materials as one. Archival documents have a legal and administrative status peculiar to themselves; they are preserved for the evidence which they bear; they are, in effect, irreplaceable and, save for the difference in the nature of the evidence, the same may be said of rare books. The materials of which both are made are, for all practical purposes, identical in their "scientific" properties, that is, the materials are identical chemically, in their physical properties and in their liability to attack by living organisms. Thus, the conservation requirements for materials in either class are identical in both "active" and "passive" systems, for the conservation is based on "scientific" properties. The rarity that leads to certain books being singled out for that description also requires that they be kept with the same degree of security as are archival documents.

It is then reasonable for both rare books and archival documents to be housed comparably, and the provisions of relevant standards, British Standard 5454: 1989, Recommendations for the Storage and Display of Archival Documents", e.g., can be applied to the creation of a rare book library, but, alas, it has not been unusual for those provisions to be overridden in the pursuit of aesthetics. In 1951, R.H. Ellis laid down the Principles of Archival Repair[1], and I advanced modified versions of these in 1994[2] to cover processes of chemical conservation. I noted that the principle advanced by Ellis and myself applied to "active" and not to "passive" conservation: No method of storage or display for archival documents may be used which will wantonly or unneccesarily diminish the evidence they contain or reduce their integrity.

Passive conservation makes a wider demand on the conservator than the immediate care of the book or document. A biological attack may have its origins well away from the object, in a building fault, directly by admitting damp or indirectly by allowing, e.g, dermestids to spread from dead birds in an unsealed loft. That is, not merely the book but the building as a whole is a concern, and Dutch experts would extend the conservator's do-

main to the flora round the building. Passive conservation must then be founded in the design of the building and extend to its management and principles for passive conservation must take account of that, too. The principles of "minimum intervention" may now be introduced, leading to: Both the building and its system of management should offer minimum intervention into the integrity of the contensts.

The "system of management" must surely include the care, maintenance and repair of the structure. This might fairly be said by any householder, but there are deeper concerns in buldings in the class under consideration. A householder builds for his or her own comfort and aesthetic delight, but the rare book librarian or archivist should build primarily for the passive conservation of the collection coupled with its use by readers and the need to house the staff. The passive conservation of this material depends far more upon engineering than upon aesthetics, for engineering expertise and principles govern the properties of all the building materials and equipment, the modes of access to the materials, the comfortable housing of humans and ultimately the internal climate. The householder demands a building beautiful in all he or she sees, usually requiring much more than ascetic simplicity and may choose to allocate money to delight rather than to function while disregarding permanence.

The curator does not have this choice, for the integrity of the material is the primary purpose for which the building is needed, and that purpose is served by "engineering". Much as we may love any beautiful volume or utilitarian archival document, we must admit that their care demands function rather than beauty. But there is a constraint on all who build; the depth of the purse. The householder is very nearly a free agent, but the curator is not and his or her duty is to spend on the integrity of the collection rather than on ornamentation. The word "ornamentation" is used here rather than "beauty" because there are so many beautiful buildings of great simplicity with little, if any, ornament. We hope for the architect who can find a felicity comparable with that of Charles Lamb, by designing for unobtrusive beauty which is discovered only upon reflection. Again, the architect must design for permanence; frequent repairs will risk more than minimum intervention into the material and deny access to the readers for whose use it is preserved.

Is it possible to formulate a set of principles for the creation of a rare book library or archive building? The principles for the repair and conservation of documents cover the reasons for a set of practical actions that can be considered piecemeal, step by step. It is possible to cover passive conservation with the single requirement for minimum intervention into the material, but architect, curator, engineer and scientist alike need guidance in its exegesis. Snorre Sturluson said "First attempts generally leave room for improvement", and it is better to attempt than to fear a fall.

A rare book library or archive repository exists to perserve for use, for the forseeable future, textual material which is either archival in nature or unique and irreplaceable for whatever reason, but especially rarity.

The primary essential purpose of a rare book library or archive repository building is the preservation of the evidence contained in the material with minimum intervention into its integrity.

The secondary essential purpose of a rare book library or archive repository building is to provide access to the material without compromising its integrity.

The building must be designed to reduce to the minimum any intervention into the integrity of the material from physical, mechanical, biological and human sources.

The engineering and scientific factors that contribute to the perservation of the integrity of the material should, and in conditions of financial stringency must, take precedence over aesthetics.

The care, maintenance and management of the building must always be designed and directed, as the priority, to the minimum intervention into the integrity of the material it holds.

There can be no practical objections to these principles, and their implementation would certainly ease the burdens borne by conservators and curators in preserving the world's history, freed from hindrance by costly but often ephemeral fashions.

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Effect of Various Deacidification Solutions on the Stability of Cellulose Pulps

by JANA KOLAR & GABRIJELA NOVAK

INTRODUCTION

It has been recognized for years that acid hydrolysis is the prime cause of degradation of paper. To hinder the degradative effect that acids exert on paper, the latter is usually treated with alkaline aqueous solutions of calcium hydroxide or magnesium bicarbonate.

Although these two solutions have been in use worldwide for more than 50 years, conservation scientists have not yet reached a unanimous conclusion as to which one stabilizes paper to a greater extent. This is primarily due to the following factors:

- most methods used to determine the extent of the degradation give very divergent results;
- measurements are often carried out on real papers, which introduces too many variables into the experiments;
- measurements are usually limited to two or three different paper samples.

For these reasons, some authors prefer the use of calcium hydroxide,[1] while the majority recommend the use of magnesium bicarbonate deacidification solutions.[2-5]

Despite the difficulties in the interpretation of the research results, some facts gathered from the literature indicate that papers treated with magnesium bicarbonate solutions could degrade somewhat faster than those which were treated with the calcium hydroxide solutions, namely:

- papers treated with the calcium hydroxide solutions give better results on dry-oven aging than those treated with the magnesium bicarbonate solutions;[1,4]
- papers treated with magnesium bicarbonate showed poor light stability.[1] Yellowing of magnesium carbonate containing papers after humid acceler-

ated aging was greater than that of the untreated and calcium carbonate-containing papers;[4]
- Deacidification using magnesium bicarbonate in some cases resulted in heavy crystalline deposits on the surface of the paper. This "magnesium carbonate gritting" was converted into dark "foxing" stains after humid oven aging.[6]

As part of the research on the aging stability of cellulose and paper,[7] it was the purpose of this study to determine whether there is a difference in the extent to which calcium hydroxide and magnesium bicarbonate solutions stabilize celluloses of different origins.

To accomplish this, three types of chemical pulps were treated with solutions of calcium hydroxide, magnesium bicarbonate and a non-aqueous solution of carbonated magnesium methoxide (PTS-2). After accelerated aging, the extent of degradation was determined using a modified standard cupri-ethylene diamine viscosity test.

We decided to use viscosity measurements as a prime method to determine the extent of degradation of celluloses with aging, mainly for the following reasons:

1. Viscosity measurement is the simplest, oldest and most widely used method for the determination of degree of polymerization (DP).
2. The change of fiber strength with aging is primarily dependent on the decrease of the average degree of polymerization of cellulose.

The main factors reported to influence the physical strength of cellulose fibers are:

- naturally occurring fibril angle of the S_2 layer;
- defects in fiber wall, caused primarily during defibering of the pulp;[8]
- average degree of polymerization of cellulose.[9]

Of these, only the average degree of polymerization changes during aging of pulp; we can assume, therefore, that the drop of the DP (as determined by viscosity measurements) of the pulp is the main cause of the decrease of fiber strength with aging.

3. Accuracy of viscosity measurements.

Viscosity measurements are much more accurate than measurements of mechanical properties of fibers where the inhomogeneity of paper itself, among other factors, is known to cause very disperse results.[10]

EXPERIMENTAL

The following pulps were used in the experiments:

1. Vallvik, Ncb AB, VaDja, S; ECF, northern bleached softwood kraft, pH 6.3 (Tappi 529), [η]=795.0 (SCAN-CM 15:88)
2. MoDocrown, Mo och Domsjö, Örnskldsvik, S; ECF, bleached two stage sulfite softwood, pH 6.5, [η]=1093.8
3. CBB, Videm, Krško, SLO – unbleached magnefite hardwood, pH 6.4, [η]=1088.8; 1.12% of acid insoluble lignin (Tappi, T 222 om-83)

Paper sheets were made according to ISO 5269-1 standard.

Samples were deacidified[4] using 0.01 M $Ca(OH)_2$ and 0.04 M $Mg(HCO_3)$ solutions. Immersion time was 30 minutes. In the case of non-aqueous treatment, samples were immersed into PTS-2 (Archival Aids) solution for 10 min. After treatment, the samples were air dried. Samples were artificially aged for 28 days at 80°C and 65% relative humidity.

The procedure was repeated to obtain comparative results.

Viscosities were measured according to SCAN-CM 15:88 method using fresh cupri-ethylene diamine (CED) solvent (Carlo-Erba). The temperature of a Schott GeraDte CT150 thermostat was controlled to ±0.015°C using a Beckmann thermometer. Results are an average of two measurements, the difference between which was typically 0.4% and in no case more than 1.1%.

Prior to the measurements, celluloses were reduced with 0.01M aqueous solution of sodium borohydride[11] for 24 h at room temperature.

Aqueous solutions of sodium borohydride decompose according to the equation:

$$NaBH_4+2H_2O=NaBO_2+H_2$$

Due to the formation of sodium(III) borate, the pH of the solution gradually increases during the reduction treatment. Alkaline pH can cause partial degradation of unreduced cellulose as well as dissolution of low Mw portions of the sample. Loss of this material, which contributes to the mass, but not to the viscosity of the solution, could cause erroneous results. To avoid this problem, samples were weighed prior to the reduction. After borohydride treatment, samples were washed with 0.01 M acetic acid, followed by subsequent thorough washing with distilled water. Viscosities of the reduced samples were then determined.

Surface pH measurements (Tappi T529 0m-82) were performed using a combination flat-head electrode (Beckmann 39507) and a Beckmann pH meter. The values represent an average of three measurements.

Table 1. Calcium and magnesium content of deacidified pulps (duplicate)

	$Ca(OH)_2$ mmol Ca/kg paper	$Mg(HCO_3)$ mmol Mg/KG paper	PTS mmol Mg/paper
sulfate	135.2	182.4	289.3
sulfite	167.5	250.7	283.4
magnefite	116.4	233.3	332.8

ISO brightness (ISO 2470) values were determined using an Elrepho 2000 apparatus. Results are an average of seven measurements. Atomic absorption measurements were taken according to Tappi T266 om-88 standard on a Thermo Jarell Ash instrument.

Results and Discussion

Magnesium and calcium contents in treated papers (duplicate), as determined by atomic absorption spectroscopy, are summarized in Table 1. Treatments with magnesium-based alkali solutions resulted in higher alkali-earth content of the pulp than those treated with calcium hydroxide solutions.

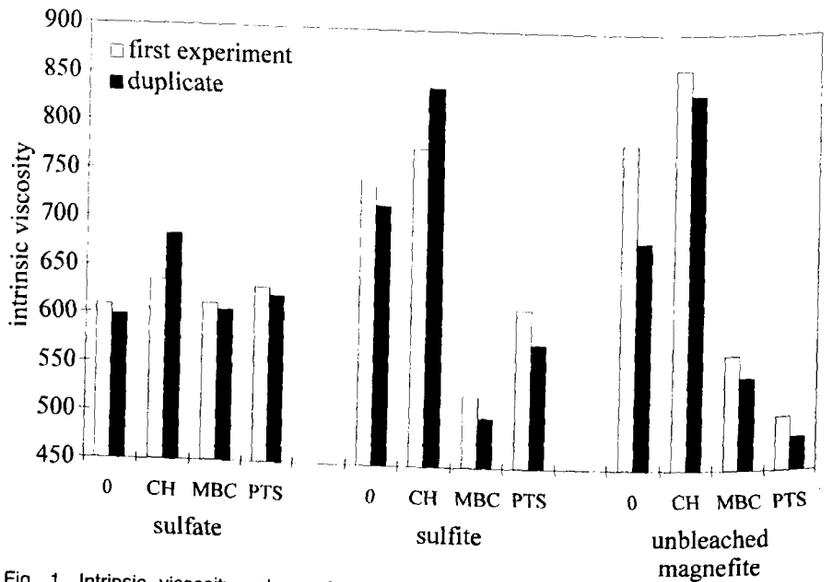

Fig. 1. Intrinsic viscosity values after deacidification and aging of sulfate, sulfite and unbleached magnefite pulps treated with: O) untreated, CH) calcium hydroxide, MBC) magnesium bicarbonate and PTS) PTS-2 solutions. Results of duplicate experiments are also shown.

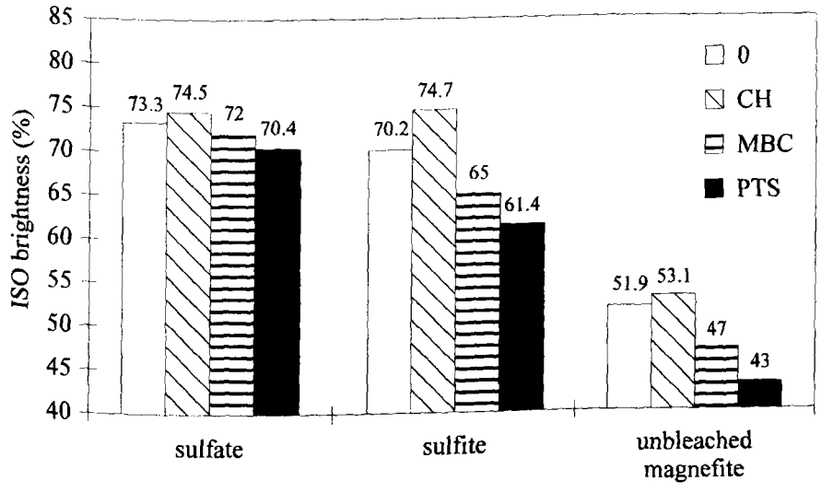

Fig. 2. ISO Brightness after deacidification and aging of sulfate, sulfite and unbleached magnefite pulps treated with: O) untreated, CH) calcium hydroxide, MBC) magnesium bicarbonate and PTS) PTS-2 solutions.

Surface pH values of all artificially aged papers were still alkaline after aging. Calcium hydroxide-treated papers had a pH of 8.5 0.1 while magnesium bicarbonate and PTS-treated samples had a pH of 9.9 0.1. The pH values of the untreated aged sulfate, sulfite and magnefite pulps were 5.9, 5.5, and 5.3 respectively.

Results of intrinsic viscosity determinations of the two comparative aging experiments are shown in Fig. 1. It can be seen that, while there are some obvious differences between the two comparative aging experiments, the behavior of the treated samples follows the same pattern.

It is obvious that the aging of sulfate pulp is the slowest. Intrinsic viscosity of the untreated sample decreased by 24.6% during accelerated aging as compared to a 34.4% and a 37.1% decrease in cases of sulfite and unbleached magnefite pulp, respectively. Consequently, the differences in the intrinsic viscosities of the alkali treated samples were also the smallest for sulfate pulp. Nevertheless, it is seen that the stability of the pulp decreases in the order: calcium hydroxide>carbonated magnesium methoxide>magnesium bicarbonate and untreated control.

Similar behavior is observed in the case of sulfite pulp, with the more pronounced differences between differently treated samples. Here, both magnesium-containing treatments destabilized the paper compared to the untreated control. The differences are largest for unbleached magnefite pulp. While the calcium hydroxide-treated sample is again the most stable,

both magnesium-based solutions destabilized the paper. Unlike the case of the two bleached pulps, here PTS solution gave the least stable paper.m m

The results of % ISO brightness are summarized in Fig. 2. Again, the smallest differences are observed for sulfate pulp. Nevertheless, it is seen that while brightness retention of the calcium hydroxide treated papers is better than that of the untreated control, loss of brightness for both magnesium-containing papers was larger. A more pronounced trend was observable also for sulfite and unbleached magnefite pulp.

Conclusion

Viscosity measurements proved to be an adequate method for the determination of aging stabilities of deacidified pulps. Results of the present research show that three different types of calcium hydroxide-treated chemical cellulose samples during accelerated aging degrade more slowly than those containing magnesium-based alkalis and untreated controls. Also, brightness retention of the calcium hydroxide-treated papers is the largest.

To generalize the above conclusions, more experiments on various types of cellulose pulps are necessary. This work is in progress.

Summaries

Effect of various deacidification techniques an the stability of cellulose pulps

The effects of calcium hydroxide, magnesium bicarbonate and non-aqueous carbonated magnesium methoxide solutions on the aging stability of three types of chemical pulps were evaluated. The modified cupri-ethylene diamine viscosity test was used to determine the extent of the degradation of samples after accelerated aging. Results show that for given pulps, calcium hydroxide treated celluloses degrade more slowly than those containing magnesium based alkalis.

Effet de différents traitements de désacidification sur la stabilité de la cellulose

On a évalué les effets d'hydroxyde de calcium et de bicarbonate de magnésium (deux traitements aqueux) ainsi que de méthoxyde de magnésium (traitement non-aqueux) sur le comportement de trois types de pâtes chimiques. On a mesuré la viscosité (avec la méthode à base de cuprié thylène diamine) pour évaluer la dégradation des échantillons après vieillissement accéléré. Les résultats montrent que, pour les pâtes testées, les celluloses traitées avec de l'hydroxyde de calcium se dégradent plus lentement que celles contenant des alcalis à base de magnésium.

Die Wirkung verschiedener Entsäuerungsmethoden auf die Stabilität von Zellstoff

Es wurde untersucht, welchen Einfluß eine Behandlung mit Calciumhydroxid, Magnesiumhydrogencarbonat (wäßrige Lösungen) und Magnesiummethoxid (nichtwäßrige Lösung) auf drei

verschiedene Zellstofftypen hat. Eine Viskositätsmessung (Kupferäthylendiamin) gab Auskunft, in welchem Maß der Polymerisationsgrad der Proben als Folge einer beschleunigten Alterung zurückgeht. Die Ergebnisse zeigen, daß – für die untersuchten Zellstoffarten – die Behandlung mit Calciumhydroxid eine langsamere Alterung bewirkt als die Behandlung mit magnesiumhaltigen Alkalinen.

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Paper Splitting at the German Library in Leipzig – Development from Craftmanship to Full Mechanisation

by W. WÄCHTER, J. LIERS & E. BECKER

Introduction

The idea of restoring weak and damaged leaves by splitting the paper and stabilising it in the centre of the leaf is very old. The London restorer Baldwin reported on this for the first time in 1848.

Today paper splitting is an excellent method for restoring paper in an object that contains an extreme amount of damage. The damage can have been caused by various factors, mechanical, chemical (e.g. acid deterioration or ink corrosion) or biological (e.g. damage by microbes or mildew).

For 30 years the University and State Library in Jena and the German Library in Leipzig have worked with paper splitting. Their work has involved the development of paper splitting methods from a craft to partial mechanisation. This meant an improvement by which a very high-risk method became a routine process.

In the summer of 1994 the German Library in Leipzig was able to take the next step: paper splitting equipment was put into operation, and the process of paper splitting thus became completely mechanised.

Complex Process of Paper Restoration

At the Centre of Preservation and Conservation at the German Library paper splitting is a part of the complex process of paper restoration. This process includes wet treatment, leaf casting and paper splitting. Conventionally, wet treatment is the first step in the paper restoration process; leaf casting is the second step; and paper splitting is the final treatment. But in practice, the decision regarding which of the individual processes to be used depends on the specific damage to and the composition of the object.

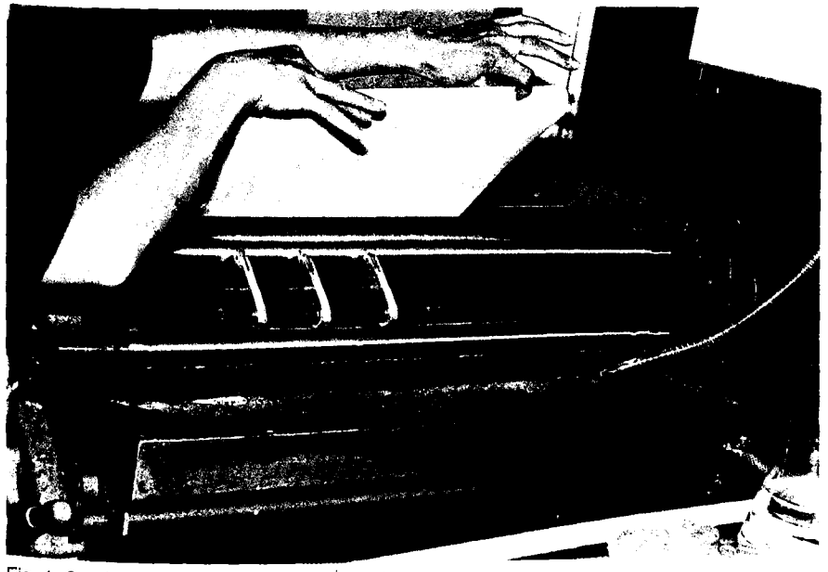

Fig. 1. Coating the carrying paper with gelatine.

Wet treatment

The equipment for wet treatment comprises 6 heatable basins with a volume of 220 l each and equipment for water desalination and preparation of a satured solution of $Ca/Mg(HCO_3)_2$. The paper to be treated is put into baskets that allow the leaves to be submerged vertically. We use a crab to transport the baskets among the different basins.

This equipment allows for different working steps in the wet treatment process. Depending on the specific damage, possibilities include cleaning, oxidising, reducing, conservation resizing or deacidification baths.

Leaf casting

We use two different leaf casting machines made by Laursen.[4] One machine is only able to treat single pages, but the other one works continuously.

The process of leaf casting enables us to replace missing parts of the leaves and to give the page a new format by bordering the treated page with a margin. The margin protects the treated paper and is also useful in binding the book later.

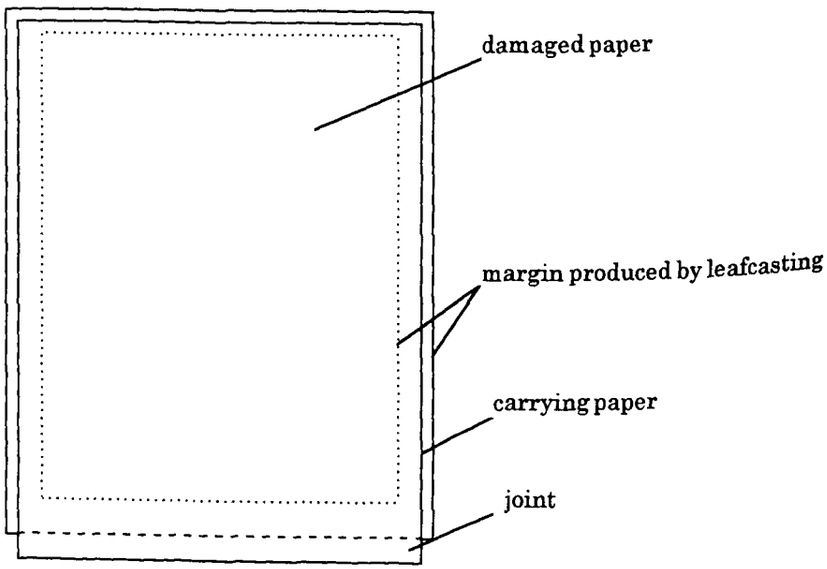

Fig. 2. Diagram of the embedded paper.

Paper Splitting

Partially mechanised paper splitting process

Detailed reports on the technology of paper splitting were given by Müller,[1] Wächter[2] and Gast[4]. Therefore this article is limited to a description of some of the technological specialities of the Centre of Preservation and Conservation at the German Library.

The first step in paper splitting is to cover the leaves with carrying paper. The carrying paper used is wet-strength filter paper with a weight of 90 g/m^2. First the carrying paper is coated with gelatine as an adhesive. We use edible gelatine with a bloom-grade of 220. To ensure an appropriate viscosity in the adhesive and a regular gelatine-film on the paper, the gelatine is thermostated to about 60°C and coated by means of gluing rollers (Fig. 1). A bookbinder's glue applicator is used for this work.

Then the damaged object is embedded between two leaves of coated carrying paper. It is very important that at one edge the two leaves of carrying paper overlap up to 3 cm (Fig. 2). At this edge the two pages of carrying paper stick together and do not open during the splitting process. This edge acts as a joint and allows for an exact recombination of the split paper. At the other three edges the fibres produced by leaf casting overlap the carrying paper by some millimetres. In this way it is possible to "open" the covered paper later in the splitting process. After covering, the leaves are pressed between cardboard sheets overnight.

Fig. 3. Splitting the paper.

When the adhesive has set, the actual splitting takes place. Starting at one end, the carrying papers are quickly and evenly pulled apart. The intact sheet is kept vertical, and the two halves already separated are pulled at an angle of 90 degrees to the vertical position (Fig. 3). The paper sticks to the two support papers and splits down its centre. The splitting takes place in the centre of the paper because only 1/3 of each side of the leaf has been penetrated by the gelatine, so that the centre thus remains free of adhesive.

The inner surface of the split paper is now exposed: it is coated with glue as an adhesive for the core material. A similar device as for coating the carrying paper is used. Then the new core material is inserted and the split paper is pressed down lightly (Fig. 4).

To prepare this adhesive 150 g methyl cellulose, 150 g carboxy methyl cellulose, 20 g $CaCO_3$, 20 g $MgCO_3$ and 100 ml polyacrylate (Acrymul^T) are dissolved in 10 l water. The carbonates are needed as an alkaline buffer for the paper, while the acrylate improves the resistance to water.

The core material (produced by Feinpapierfabrik Bad Muskau GmbH, Germany) is unsized paper which contains 100% pure cotton fibre and 5% $CaCO_3$ as an alkaline buffer. The weight of the paper is about 12 g/m^2.

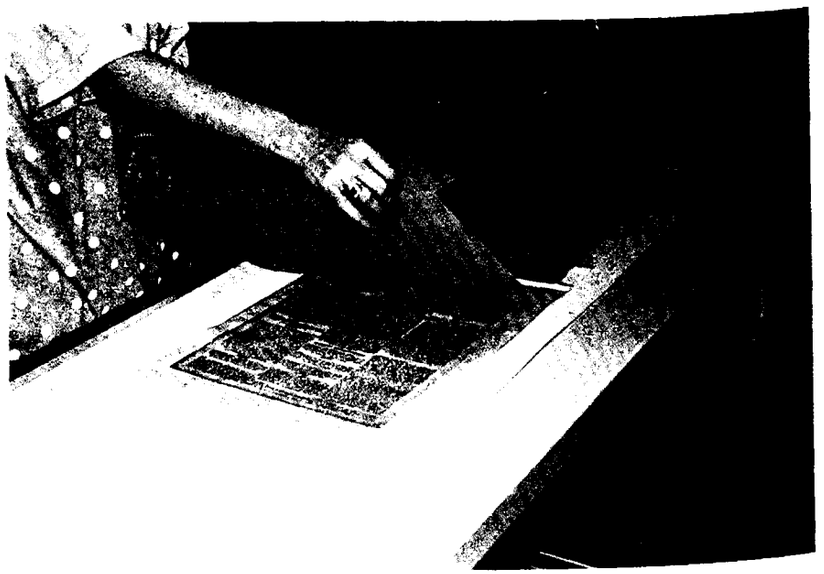

Fig. 4. Inserting the core material.

After insertion of the core material, the stabilised leaves are stacked between sheets of cardboard and weighted down. Heavy pressure must be avoided in order to prevent the core adhesive from diffusing onto the carrying paper and mixing with the gelatine.

When the core adhesive is completely dry, the glue of the carrying paper is dissolved in a water bath containing enzymes. The basins of the wet treatment are used for this procedure. A proteolytic enzyme (coralase AF) with a concentration of 0.02 Vol.-% is used. The temperature is about 55°–60°C.

Exposure time is 15 minutes. The baskets with the paper are then moved to a water bath with a temperature of 70°C. This kills the enzymes. After 15 minutes the paper is removed from the water bath. The wet sheets of paper are couched between sheets of felt. In this process most of the water, together with pollutants from the paper, is transported from the centre of the split leaf via the carrying paper to the felt. If soluble ink is present it runs towards the support material as well. Another advantage of the couching is that the glue of the core material diffuses to the surface of the paper and fixes it.

After couching the leaves contain a modest amount of moisture. The carrying material is now removed and the split leaves are pressed with light pressure between sheets of felt and cardboard for about two days. This procedure preserves the texture of the original.

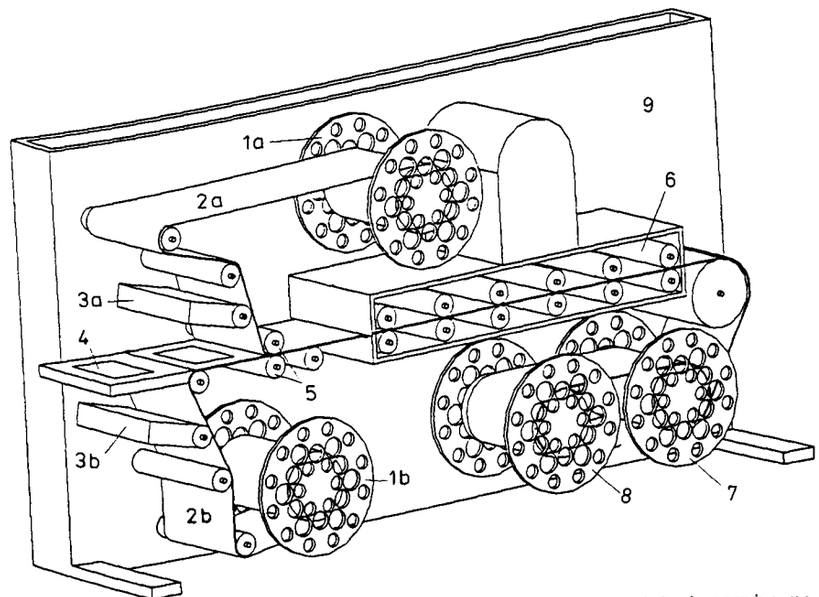

Fig. 5. Diagram of the lining machine. 1 a,b: cylinders for carrying material. 2 a,b: carrying material. 3 a,b: glue applicator with glue pot. 4: loading point for the leaves to be treated. 5: drying section with a forced air system. 6: cylinder for the coated material. 7: cylinder for separating material. 8: frame of machine.

The technology of paper splitting described here gives only the general treatment. Variations of the process are both possible and necessary according to the damage and kind of material. Descriptions of such variations have been published.[1,2,3]

The Completely Mechanised Paper Splitting Process

The Centre of Preservation and Conservation at the German Library uses the partially mechanised technology of paper splitting to treat about 20,000 leaves a year. But to restore documents on a larger scale, as for an entire library, a new kind of technology is required.

For as long as 20 years a completely mechanised paper splitting process has been in developed at the German Library. In 1992 the Becker Preservotec GmbH was engaged to construct paper splitting equipment. In June 1994 the first parts of the equipment, the lining and the splitting machines, were put into operation.

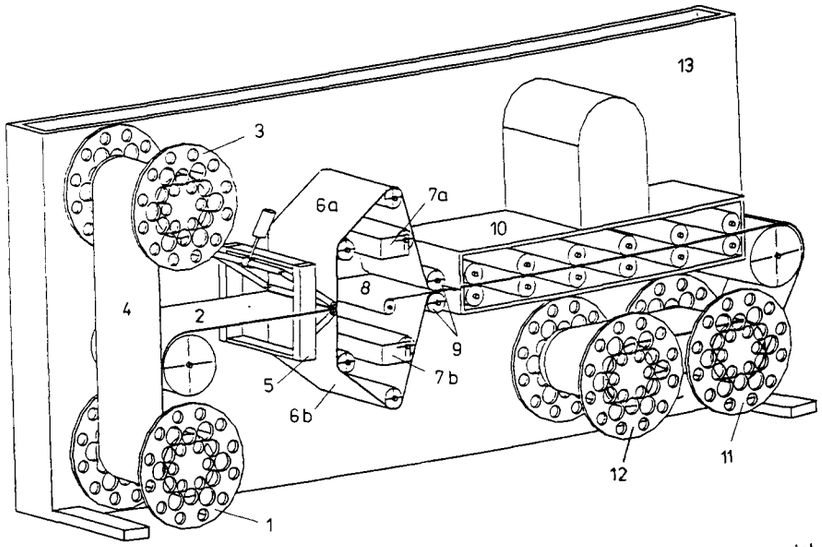

Fig. 6. Diagram of the splitting machine. 1: cylinder for the coated material. 2: coated material. 3: cylinder for separating material. 4: separating material. 5: device for splitting. 6 a,b: upper and lower half of the split coated leaves. 7 a,b: glue applicator with glue pot. 8: cylinder with core paper. 9: drying section with forced air system. 10: cylinder with the restored coated leaves. 11: cylinder for separating material. 12: frame of machine.

The lining machine

Fig. 5 is a diagram of the lining machine. As opposed to the manual treatment, the machine does not work with single sheets but with lengths of paper or cloth. Cylinders for the lining cloth (1), the coated material (6) and the separating cloth (7) are used to handle the lengths.

A cylinder system is used to drive the lengths. The construction of this system guarantees an exact position control and a tight guide for the lengths.

To coat the carrying material with gelatine a glue applicator is used. The temperature of the glue pot, the pipes and the gluing rollers can be controlled and the thickness of the adhesive film can be regulated as well.

A drying section with a forced air system (5) is used to press and dry the lined material.

The process control of the machine takes place via a stored program controller. The controller allows for automatic and manual control of the machine.

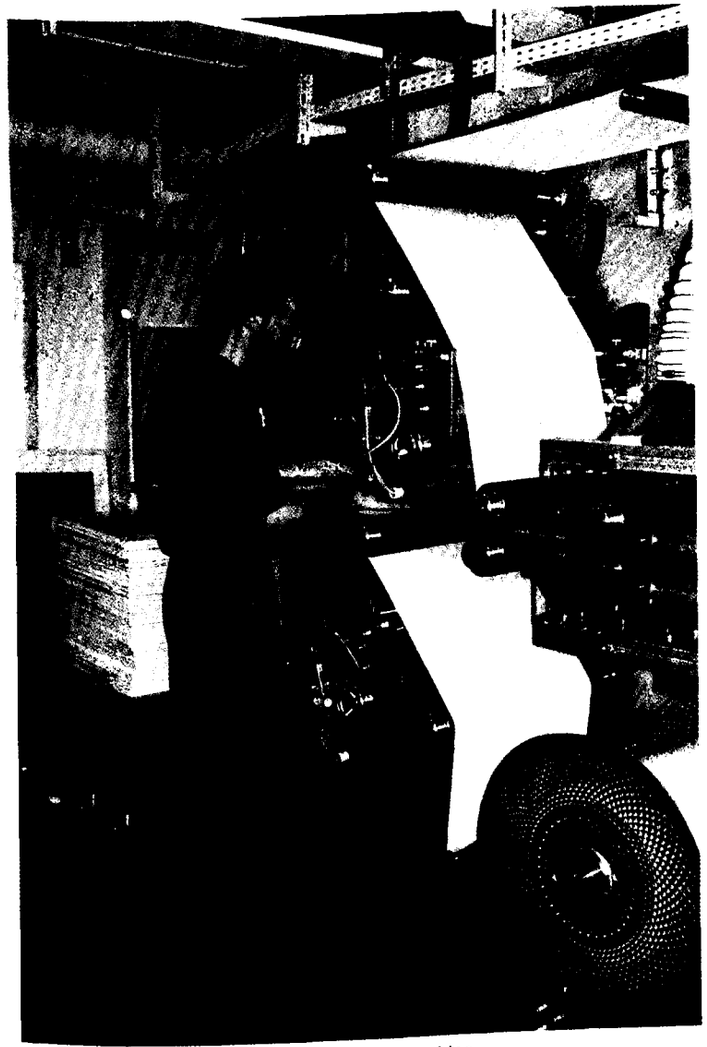

Fig. 7. Inserting the damaged leaves in the splitting machine.

The splitting machine

Fig. 6 is a diagram of the splitting machine. The frame of machine, the cylinders, the glue applicator, the drying section and the controller are similar to that of the lining machine.

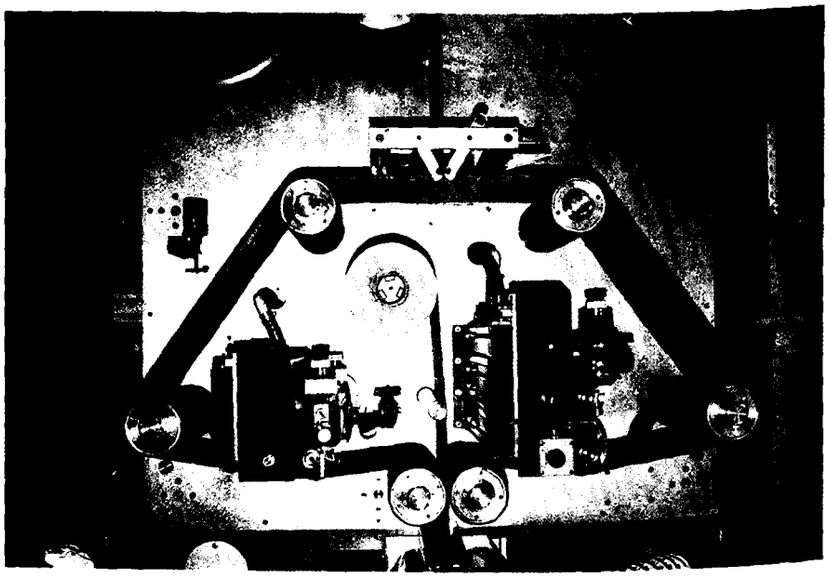

Fig. 8. Splitting the paper and inserting the core material in the paper splitting machine.

But with the splitting machine there is the problem of putting both halves of the split leaves exactly together again. This is solved by a special positional control system that positions the strips to within 1/10 mm.

At present both machines are operated separately but a coupling of the two is planned for the future.

Splitting materials used with paper splitting equipment

The carrying and core paper and the adhesives used on the equipment are similar to the materials used in the traditional process.

When we bring an additional removing machine into use it will be possible to work with carrying material made of polymeric cloth. This carrying material will be reusable.

The Treatment

The lining process

The carrying material (Fig. 5, 2a,b) is unwound from the cylinders (1a,b) and coated with gelatine with the aid of the glue applicators (3a,b).

As Fig. 7 shows, the paper to be split is placed by hand on the lower strip of coated carrying material (Fig. 5, 4). Using the cylinder system the upper length of the carrying material is placed on these and the three layers are pressed and dried in the drying section (Fig. 5, 5).

Then the coated material is rolled up on a cylinder (6). To prevent sticking a separating cloth can be placed inbetween the lengths of coated paper (7).

The splitting process

The material, now rolled up on a cylinder in the lining machine, is suspended in the splitting machine (Fig. 6, 1).

The length of coated paper is unwound and fed into the device for splitting (5). The separating cloth between the layers of coated paper is rolled up on a cylinder (3) and can be reused.

In the splitting device the damaged paper is split by pulling apart the length of the support material at an angle of 90 degrees (Fig. 8). Then the inner surface of the split paper is coated with glue using a glue applicator (7a,b). In the next step the core material (8) is inserted between the two lengths of the split, coated material.

The length with restored, coated leaves is pressed and dried in the drying section (9) and rolled up. It is possible to insert a separating cloth (11) between the strips.

Finally the material, which is still coated, is cut and the carrying paper is removed in the conventional way as described earlier.

Discussion

This equipment offers a completely mechanised process for coating the damaged paper, splitting it and inserting core material. The last step of removing the support paper, must still be performed in the conventional way. The construction of the third part of the equipment, the removing machine, is planned for the near future.

When the three parts of the equipment are combined our department will have a paper splitting facility with a capacity of about 2,000 leaves per day. This will drastically reduce the costs of paper splitting and the process may be accorded a completely new status in paper restoration.

However, the high capacity of the paper splitting equipment demands a similar capacity in the preparatory steps of paper splitting – the wet treatment and leaf casting. Therefore the next steps must be the mechanisation and automatisation of the wet treatment and leaf casting processes.

ACKNOWLEDGEMENTS

The project of developing the paper splitting machine was funded by the German Federal Ministry of Research and Technology (BMFT), for which we hereby express our thanks. The authors are solely responsible for the content of the article. Patents have been applied for to cover the new developments arising from this research.

SUMMARIES

Paper splitting at the German Library in Leipzig – development from craftsmanship to full mechanisation

The equipment for paper splitting was developed in cooperation between the German Library in Leipzig and the company Becker Verfahrenstechnik GmbH. In June 1994 the paper splitting machine was put into operation in the German Library, Leipzig. With full mechanisation, the old process of paper splitting may be accorded a completely new status in paper restoration.

Le fendage du papier à la Deutschen Bücherei à Leipzig – Développement d'un artisanat jusqu'à une mécanisation complète

Une machine pour le "paper splitting" (fendage du papier) a été développée en collaboration entre la Deutsche Bibliothek à Leipzig et la Société Becker Verfahrenstechnik GmbH. Elle a été mise en activité en juin 1994 à la Deutsche Bibliothek à Leipzig. On peut considérer qu'avec une mécanisation complète, l'ancien système de "paper splitting" a reçu un tout nouveau statut dans le domaine de la restauration du papier.

Papierspalten in der Deutschen Bücherei Leipzig – Entwicklung von einer handwerklichen Methode zu einem vollständig mechanisierten Verfahren

Als Gemeinschaftsunternehmen der Deutschen Bücherei Leipzig und der Becker Verfahrenstechnik GmbH wurde eine Anlage zum Papierspalten entwickelt. Im Juni 1994 wurde die Anlage in Leipzig Betrieb genommen. Nach vollständiger Mechanisierung kann das alte Verfahren des Papierspaltens einen neuen Platz in der Papierrestaurierung finden.

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The Feasibility of Using Modified Atmospheres to Control Insect Pests in Museums

by MICHAEL K. RUST, VINOD DANIEL, JAMES R. DRUZIK & FRANK D. PREUSSER

INTRODUCTION

Surveys of natural history and art museums indicate that beetles belonging to the families Anobiidae and Dermestidae and moths belonging to the family Tineidae are major pests.[1] Schrock has provided a list of commonly damaged materials in museums and their associated pests.[2] Other groups such as termites and silverfish may also be extremely important, especially in southeast Asia.[3] The future of fumigation in museums with conventional chemicals is uncertain. The more we learn about many of them, the more questionable their use becomes to operators (ethylene oxide) and to the environment (methyl bromide). In addition to the need to train museum personnel to use these insecticides, there is always the potential for damage to rare antiquities and artifacts.[4,5] Preslock[6] has provided an annotated bibliography of literature pertaining to pest control in museums.

The primary objectives of our study were to determine whether controlled or modified atmospheres were lethal to insects and the minimum time required to provide 100% kill of all developmental stages of insects likely to infest materials, objects and artifacts in museums.

Considerable research has been conducted with the use of modified atmospheres (MA) or controlled atmopsheres (CA) to manage insect pests of stored grains and food. In most studies the lowest range of O_2 concentrations tested were 0.6–0.9%.

Marzke et al.[7] found that, as O_2 concentrations decreased from 21.0% to 0.6%, the mortality of adults and larvae of *Trogoderma glabrum* (Herbst) increased. Mortality also increased with increasing temperature. Three-day exposures at 0.5% O_2 at 26.7°C resulted in 100% kill of adults and larvae. Adults were more susceptible than larvae. Navarro[8] found that exposure time was the critical factor for certain species, such as rice weevil *Sitophilus oryzae* (L.), being almost independent of O_2 concentrations below 3%.

However, as O_2 concentrations decreased, the time required to kill the red flour beetle *Tribolium castaneum* (Herbst) also decreased.

Jay et al.[9] found that, as the relative humidity decreased, the mortality of three stored-product insects exposed to low O_2 atmospheres (0.8–0.97%) increased. Jay & Cuff[10] found that mortality and water loss with *T. castaneum* was low at 97% N_2 and 3% O_2 but high at 99% N_2 and 1% O_2, suggesting that water loss is the major cause of death at high N_2 atmospheres.

In studies with insect pests frequently encountered in museums, Gilberg found that 7-day exposures at 30°C and 65-70% relative humidity (RH) to 0.421% O_2 in nitrogen killed webbing clothes moths, cigarette beetles, drugstore beetles, carpet beetles and powderpost beetles.[11] The same insects exposed for 3 weeks in plastic bags were also killed.[12] Preliminary studies by Valentin[13] showed that exposures to 1.0% O_2 atmospheres for 20 days killed deathwatch and powderpost beetles. Valentin & Preusser[14] found that 30-hour exposures to 0.5% O_2 and 99.5% N_2 atmospheres produced 100% mortality in fruit flies. Exposure time decreased as the temperature at which the exposures were conducted increased. Exposures of 5 days to 80% CO_2 atmospheres provided complete kill of West Indian drywood termites, *Cryptotermes brevis* (Walker), inside pieces of infested wood.[15]

Experimental

Phase I: test system

In the current study controlled atmospheres (CA) were achieved by purging the chambers with pre-purified nitrogen. The test system consisted of 12 acrylic chambers each with a volume of 38 liters that could be independently flushed with nitrogen and sealed to provide stable low oxygen atmospheres. A controllable humidifying apparatus for adjusting relative humidity and nitrogen flow was inserted between the pre-purified nitrogen cylinder (99.999% N_2, <20 ppm O_2) and the input manifold to the chambers. For analytical sampling of the atmosphere in any given chamber without opening it, a gas chromatography septum was installed.

The chambers, constructed of 0.63-cm-thick methacrylate (35.6 cm × 45.7 cm × 26.7 cm), had a 14.6-cm diameter opening that could be quickly closed and sealed. A door fitted with a neoprene o-ring was placed over the opening and tightened to the chamber with 6 capscrews. Although each chamber was connected to the common nitrogen supply line with 0.63-cm copper tubing and an exhaust line, each of the inlet and outlet ports for the chambers was controlled by Whitey valves (Swagelok), making each chamber an independent experimental unit.

The schematic of the relative humidity conditioning unit is shown in Fig. 1. To humidify the nitrogen before flushing the chambers, the nitrogen after passing through the initial on/off valve, was split into two streams; one (controlled by the "wet" metering valve) bubbling through the first bottle (A), and the other to a T-tube where it joined the "wet" nitrogen stream leaving the water bottle. The ratio of wet to dry nitrogen was varied with the two metering valves. The combined flow of nitrogen entered a mixing bottle (B), fitted with a septum through which air samples were obtained for analysis. From the mixing bottle, the nitrogen passed to a third bottle (C) equipped with a relative humidity sensor. The nitrogen then passed to the chambers.

To analyze the amount of oxygen in the mixing bottle or the chambers, a Teledyne Oxygen Analyzer (model 316) was used. The Teledyne Analyzer was standardized by calibrating it with air and zeroing it with samples from the nitrogen mixing bottle. The needle was then inserted through the septum into the chambers and an oxygen reading determined. If the reading was >0.1% above the nitrogen zero, the chamber was reflushed with nitrogen.

To determine the relative humidity of the mixed nitrogen flow, the relative humidity sensor was plugged into a Shinyei temperature and humidity transmitter and LCD digital multimeter (Micronata). The accuracy was about ±1%.

Procedure

Mortality studies were done in two different series of experiments phases or stages. a) Each life stage of the various pests studied was exposed to a nitrogen atmosphere in open containers; the procedure and results are given under testing phase II. b) To mimic an infested object, non-wood-boring insects were placed in vials, and submerged in 0.9-liter jars covered with 10–13 cm of packed flour. Wood-boring insects such as the powderpost beetle and the

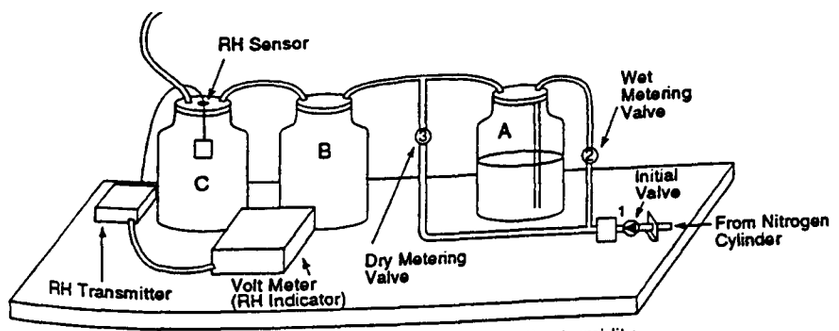

Fig. 1. Apparatus for humidifying the nitrogen flow. RH=relative humidity.

western drywood termites were placed in glass vials covered with a piece of screen to permit air exchange. The vials were placed inside 8 × 8 × 14 cm wooden blocks. The procedure and results are tabulated under testing phase III.

Testing phase II

The vials containing insects or eggs to be tested were transferred to the chambers. The relative humidity inside the chamber was maintained at 55% with 25 ml of a saturated solution of magensium nitrate in a small plastic box. Excess magnesium nitrate (25 g) was added to the saturated solution so that any excess moisture in the chamber was absorbed. Two packets (7 g) of Z-1000 Ageless™ were placed in each chamber. Ageless™ is an oxygen scavenger prepared from moist powdered iron oxide and alkali metal salts (Mitsubishi Gas Chemical Co.).[16] After transferring all insects to the test chamber, the chamber door was loosely sealed. The chamber was flooded for 30 minutes with 99.999% pure nitrogen preconditioned to 55% RH. The chamber was tightly sealed and the flow of nitrogen discontinued.

If the oxygen content inside the chamber was greater than 0.1%, the chamber was flushed again for an additional 5 to 10 minutes. The oxygen content was again analyzed. Every morning the chambers were analyzed for oxygen content. Whenever the oxygen level was greater than 0.1%, the chamber was flushed as described above.

Phase III testing for non-wood-boring insects

The procedure for sorting and preparing the insects was identical to those in phase II except the vials were placed in 0.9-liter glass jars and covered with 10 to 13 cm of flour to simulate conditions where the insects might be buried underneath articles or items.

Phase III testing for wood-boring insects

A simple wooden holding block was designed to confine the beetles deep inside the blocks during the exposure. Pieces of wood (8 cm × 8 cm × 14 cm) were cut from a post of Douglas fir. Each block was cut in half, and the center of each block hollowed to hold a 10-ml glass vial, leaving 1.27 to 2.54 cm of solid wood surrounding each insect vial. Two holes were drilled through the two blocks so that bolts could pass through both blocks. A sheet of parafilm was placed on either block so that when pressing the two halves firmly together, the blocks were sealed. The blocks were held with 6.35-cm bolts and wing nuts and 6 blocks were placed in each chamber for each test.

Mortality evaluation

The insects were transferred to a petri dish to be counted with the aid of a microscope. Adults and larvae were individually probed with a pair of soft forceps. If they moved, they were scored as alive. All larvae that pupated or adults that emerged from cocoons were scored as alive. The remaining cocoons were opened. If they moved, they were scored as alive. The eggs were scored as alive if the egg had hatched and a larvae could be found near the egg shell.

Description of insects tested

A brief description of the various insects tested as well as the exposure times and number of insects tested are detailed below. The cockroach, firebrats and termites have incomplete metamorphosis and lack a pupal stage. For all the species tested, the experiments were replicated 3–5 times on 3–5 different dates. A detailed report can be requested from The Getty Conservation Institute, 4503 Glencoe Avenue, Marina Del Rey, CA 90292, USA.

The webbing clothes moth

The webbing clothes moth, *Tineola bisselliella* (Hummel), is the most common clothes moth found in the United States. In museum storage, it is not uncommon to find active infestations inside acid-free boxes, Hollinger boxes, textile storage boxes and even dressers and closets.[17,18]

The five different exposure periods selected for testing were 3, 24, 48, 72 and 96 hours. The number of insects tested varied with each exposure because of the difficulty in obtaining certain stages. In the untreated control, all stages were held in the 55% RH holding box on top of the testing chamber during exposures. Approximately 350 pupae, 650 larvae, and 80 eggs were tested in phase II, plus controls.

The three exposure times tested in phase III were 48, 72 and 96 hours. Approximately 540 pupae, 400 larvae and 1270 eggs pupae were tested in phase III, plus controls.

The furniture carpet beetle

The furniture carpet beetle, *Anthrenus flavipes* (LeConte), is destructive to a wide variety of household and museum articles made of animal products. In particular, they attack upholstered furniture, hair, feathers, natural brushes, and carpets. Other materials damaged include wool, fur, leather bindings of books and glue of book bindings. Fabrics such as silk, and cotton may be attacked if they are contaminated with perspiration, blood or urine.

The typical life cycle of the furniture carpet beetle at optimal rearing conditions from egg to adult is about 3 to 4 months.

Five different exposure periods tested with all life stages were 6, 16, 24, 48 and 72 hours. Each test chamber contained four vials of adults, pupae, and larvae with 20 insects per vial totalling approximately 240 insects per test plus the control insects in phase II.

The only exposure time tested in phase III was 72 hours, which was the minimum time required to produce 100% mortality in phase II. Approximately 630 adults, 190 pupae, 650 larvae and 200 eggs were tested in phase III, plus control insects.

The firebrat

The firebrat, *Thermobia domestica* (Packard), is a primitive wingless group of insects belonging to the order Thysanura. Firebrats feed on numerous items found in museums and libraries, especially those made with starch, paste, glue (as in bookbinding), and starched cotton, linen, rayon or lisle. They are pests of paper, especially those with a glaze or sizings consisting of starch, dextrin, casein, gum or glue. Occasionally, synthetic items will be attacked if they are coated with sidings or paste.[19] The typical life cycle of firebrats at optimal rearing conditions (37–39°C) is about 1.5–3.5 months.

In phase II, nymphs and adults were exposed for 0.5, 1, 2, 3, 16 and 24 hours. Eggs were exposed for 3, 16 and 24 hours. To determine whether the exposures were lethal, the contents of each vial were placed into a petri dish. Nymphs and adults were examined 24 and 168 hours after the exposure. Eggs were inspected at 24, 48 and 168 hours after exposure. The eggs were held for an additional 9 weeks before a final count was made. Approximately 1040 nymphs, 750 adults and 1500 eggs were tested in phase II.

In phase III the only exposure time tested was 48 hours because it equalled the minimum time required to produce 100% mortality in phase II plus 24 hours. Approximately 150 nymphs, 250 adults and 120 eggs were tested.

The cabinet beetle

The larvae of the cabinet beetle, *Trogoderma inclusum* (LeConte) damage insect collections, hides, skins, wool and feathers. The larvae are more likely to be a pest of processed dry foods, animal feeds and storage facilities than a serious pest of stored grains. The distribution of *T. inclusum* is influenced by climate, being encountered in areas with the relative humidity in excess of 35%.[20] The typical life cycle of cabinet beetles under normal rearing conditions is about 5.5 to 7 months.

In phase II, the five different exposure periods selected for testing with the pupal, larval, and egg stages were 24, 48, 72, 96 and 120 hours. Approximately 290 adults, 670 pupae, 1500 larvae and 1640 eggs were tested in phase II, plus controls.

The two exposure times tested in phase III were 96 hours and 120 hours (the minimum time required to produce 100% mortality determined in phase II). The tests were replicated three times. Approximately 270 adults, 530 pupae, 1150 larvae and 740 eggs were tested in phase III, plus controls.

The larder beetle

The larder beetle, *Dermestes lardarius* L., feeds on ham, bacon, dried beef or fish, cheese, hair, horn, feathers, fur and carcasses. With the discontinuance of curing meats at home, the larder beetle has become less important in recent years. However, the presence of the larder beetle may indicate rodent or bird carcasses in buildings. The typical life cycle from egg to adult is 3 to 4 months.

Seven different exposure periods were selected for testing in phase II: 6, 18, 21, 24, 48, 72 and 96 hours. Approximately 650 adults, 320 pupae, 650 larvae and 750 eggs were tested in phase II, plus controls.

The only exposure time tested in phase III was 96 hours. Approximately 100 adults, 200 pupae, 560 larvae, and 500 eggs were tested in phase III, plus controls.

The cigarette beetle

The cigarette beetle, *Lasioderma serricorne* (F.), is the most destructive pest found in stored tobacco but will attack a variety of stored products. It also causes minor to serious damage to the binding and leaves of books while in storage or on shelves of libraries. The larvae feed on upholstered furniture, particularly stuffing. Other items it feeds on are seeds, paper, spices, drugs, grain, cereal products, botanical specimens, insect specimens, silk, rodent bait and dried plants.[17] It is an important pest of books, damaging the binding and leaves.[14] The life cycle (egg to adult) is 7 to 14 weeks.

In phase II, the five different exposure periods selected for testing with the adult, pupal, and larval life stages were 48, 72, 120, 144 and 168 hours. In addition, the egg stage was exposed for 192 hours. Cocoons containing pupae were exposed for 168 hours only. Most exposures were replicated 2–6 times, all on different dates.

Adults, larvae and cocoons were inspected for mortality 3 weeks after exposure to low oxygen atmospheres. Eggs were inspected at 5 weeks. Approximately 920 adults, 1050 pupae, 1590 larvae, 3000 eggs and 60 g of cocoons were tested.

The only exposure time tested in phase III was 192 hours because it equalled the minimum time required to produce 100% mortality of phase II, plus 24 hours. The tests were replicated twice on different dates.

The confused flour beetle

The confused flour beetle, *Tribolium confusum* Jacqulin du Val, is considered to be one of the most important pests of stored food. Confused flour beetles feed on broken grains, beans, nuts, spices, drugs, and herbarium and museum specimens. They are unable to feed on unbroken grains, but readily attack processed food.

The typical life cycle of *T. confusum* in heated warehouses or structures is about 3 months, with 4 to 5 generations of beetles yearly.

In phase II, the six different exposure periods selected for testing with all life stages were 6, 18, 21, 24, 48 and 72 hours. Three to four open dishes (20 insects per dish) of each life stage were tested per replicate. The only exposure time tested in phase III was 72 hours.

The American cockroach, brownbanded cockroach and German cockroach

The American cockroach, *Periplaneta americana* L., is the largest of the common structural infesting cockroaches, being 38 mm long with fully developed reddish-brown wings. The American cockroach is found most commonly in restaurants, grocery stores and bakeries, wherever food is prepared and stored. They are also attracted to fermenting liquid. They are occasionally found in museums in north America and commonly found in museums in southeast Asia.[3] In museums they feed on starchy materials, sugary or fermented foods, leather, and parchment. In addition to sighting live insects, they can be detected by feeding damage, excrement and egg cases. Fifty to 60 adult males, adult females without oothecae (egg capsules), small nymphs (6 mm long), large nymphs (20 mm long) and oothecae were tested at each exposure period, totalling approximately 250 to 500 cockroaches, including controls.

The brownbanded cockroach, *Supella longipalpa* (F.), is a cosmopolitan cockroach pest, occurring both outdoors and indoors. In Egypt, this species is often referred to as the furniture cockroach. The brownbanded cockroach is tan to brown with light yellow crossbands on the dorsal side, especially prominent in nymphs. The adult is small, up to 12.5 mm long, active and flies readily when disturbed. It prefers warm temperatures and is found in areas of the structure where the temperatures exceed 26.5°C for most of the year. It prefers high locations such as shelves, behind picture moldings, etc. The damaging stages are the nymphs and adults. In museums they feed on starch materials, sugary or fermented foods, leather

and parchment. The complete life cycle takes an average of 5.5 months. Fifteen to 20 adult male, adult female without oothecae, small nymphs (3 mm long), large nymphs (6 mm long) and oothecae were selected for each low oxygen exposure. Four hundred to 500 cockroaches, including controls, were tested.

The German cockroach, *Blattella germanica* (L.), is a cosmopolitan species occurring primarily indoors in areas where food is prepared or served. Adult German cockroaches are about 16 mm in length, brown in color, with two dark longitudinal streaks on the pronotum. They breed throughout the year indoors, especially in a humid environment averaging approximately 25°C. The life cycle (egg to adult) is approximately 2 months. The selection procedure was identical to that described for brownbanded cockroaches, with the exception of one additional adult stage. Since the German female carries the oothecae until 1–2 hours before it is ready to hatch, females with oothecae were also selected.

In phase II, the five different exposure periods selected for testing with adults and nymphs of *P. americana* were 1, 4, 6, 8 and 24 hours. Egg capsules of American cockroaches were also exposed for 92 and 120 hours. For brownbanded cockroaches, five different exposure periods, 1, 2, 3, 6, and 24 hours, were selected for testing with all nymphs and adults. Two additional exposure periods, 96 and 120 hours, were tested against the egg capsules. Four exposure periods, 1, 3, 6, 1 and 24 hours, were selected for testing with all life stages of *B. germanica.*

Only the oothecae of the American cockroach were tested in phase III because it was the most tolerant stage. Three different exposure periods, 72, 96 and 120 hours, were selected for testing. Four replicates were tested at the 120-hour exposure.

Only the egg capsules of the brownbanded cockroach were tested in phase III, with two different exposure periods of 96 and 120 hours. The oothecae were the most tolerant stage of brownbanded cockroach examined in phase II. Exposures were replicated 2 times.

In phase III, 70 female and male adult German cockroaches were exposed for 48 hours. Females with oothecae and large and small nymphs were tested with 10 to 20 insects per life stage per chamber. The tests were replicated 5 times.

The powderpost beetle

Beetles belonging to the family Lyctidae are collectively referred to as true powderpost beetles. The larval stage of powderpost beetles limit their feeding to hard woods such as ash, oak, hickory, mahogany, walnut, wild cherry, locust, poplar, sycamore, orange, eucalyptus and other open grained woods. Articles made of bamboo are also frequently infested. Infestations are com-

monly found in hardwood floors, furniture, antiques, tool handles, gunstocks, picture frames, packing crates and ornamental pieces such as grape canes and figurines.[17] The entire life cycle of powderpost beetles range from 3 months to a year or longer.

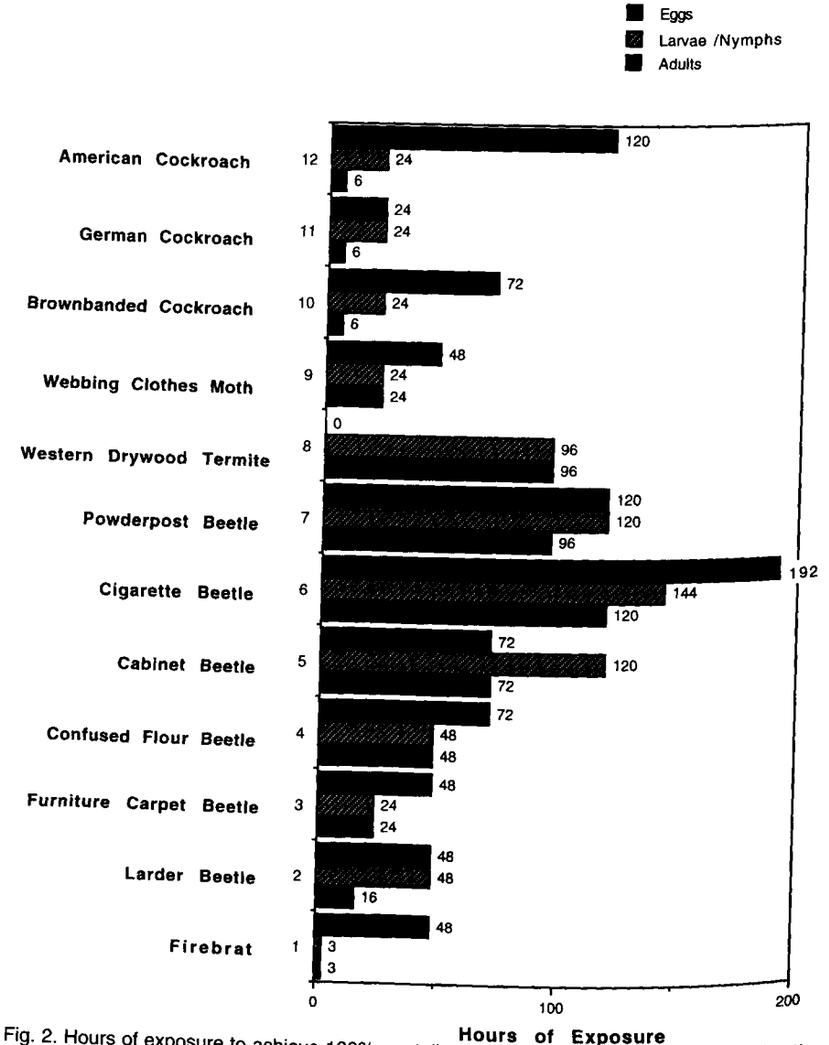

Fig. 2. Hours of exposure to achieve 100% mortality for ten commonly found insect pests exposed to nitrogen (<0.1% oxygen) in open containers at 25.5°C and 55% RH.

Three species used in the tests were *Lyctus brunneus* (Stephens), *Lyctus linearis* (Goeze) and *Trogoxylon prostomoides* (Gorham). *L. brunneus* and *L. linearis* are cosmopolitan species, found in a wide variety of hardwoods. *T. prostomoides* has been found infesting toys, furniture, herbwood and bamboo.

Three different exposure periods tested with adult *T. prostomoides* were 48-, 96- and 120-hour exposures. Adult *L. brunneus* were exposed for 24, 120 and 144 hours.

Approximately 50 adult *T. prostomoides* were tested in phase II. About 50 adults, 20 larvae and 20 pupae of the *L. brunneus* were tested.

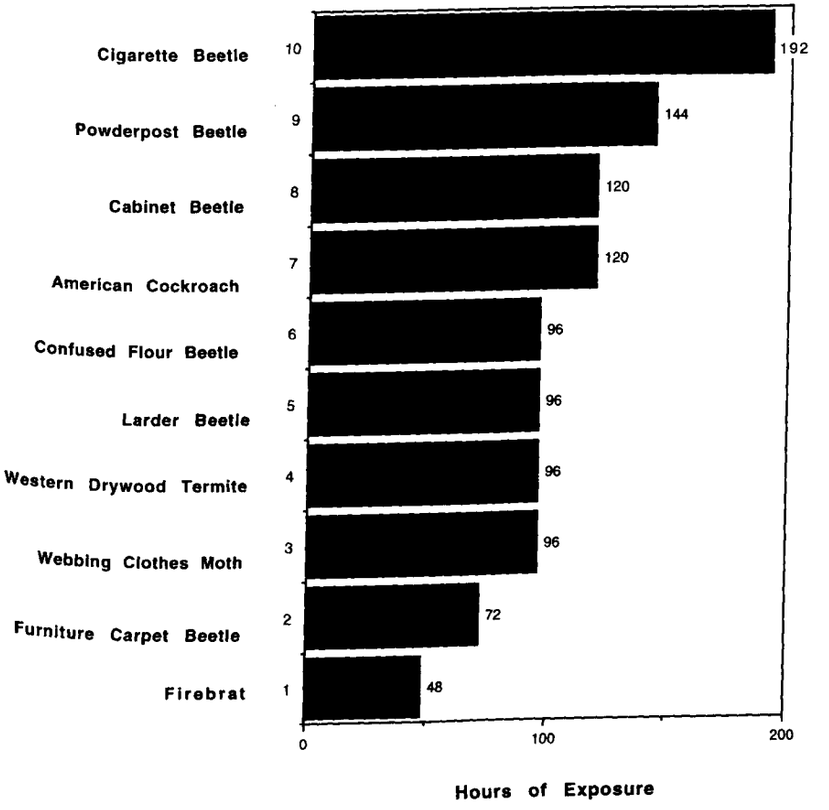

Fig. 3. Hours of exposure to achieve 100% mortality for the most tolerant stage of ten commonly found insect pests exposed to nitrogen (<0.1% oxygen) in closed containers at 25.5°C and 55% RH.

The western drywood termite

The western drywood termite, *Incisitermes minor* (Hagen), is the most destructive drywood termite in the United States. The drywood termites are aptly named because they establish themselves in wood that is not decayed or in contact with ground moisture. They frequently attack softwoods used in framing structures which is perfectly dry, but they occasionally infest hardwoods used in furniture construction.[17]

In phase II, five exposure periods were selected: 15, 24, 48, 72 and 96 hours. Approximately 1400 nymphs were tested in this phase, plus controls.

Three exposure periods of 48, 72 and 96 hours were tested in the next phase. Approximately 1650 nymphs were tested in phase III, plus controls.

Results and Discussion

The exposure times for 100% mortality of all life stages of pests studied at 55% RH and 25.5°C are tabulated in Fig. 2 for phase II and Fig. 3 for phase III. A brief discussion of the results for all the insects tested are given below.

Webbing clothes moth

In phase II, the larvae and cocoons (containing resting larvae, and pupae) were readily killed when exposed to the low oxygen atmospheres for 24 hours. Three-hour exposures killed 71–75% of the larvae and cocoons. A 48-hour exposure produced 100% kill of the eggs.

The 48-hour exposures resulted in 100% kill of all stages tested in phase III, but only 98.7% of the cocoons were killed with a 72-hour exposure. All stages were killed with a 96-hour exposure.

The furniture carpet beetle

In phase II, exposure for 24 hours produced 100% kill of adult carpet beetles. The adults are short-lived, 25% being dead at day 7 in the untreated controls. The egg was the most tolerant stage, only 50% being killed with a 24-hour exposure. Exposures for 48 hours were required to produce 100% kill of the eggs and pupae. Larvae were the most susceptible stage, requiring only a 24-hour exposure to give 100% kill.

In phase III, exposure of 72 hours produced 100% mortality. The use of 72-hour exposure should provide a sufficient margin of error to ensure complete kill of all life stages.

The firebrat

In phase II, firebrat nymphs and adults were readily killed when exposed to the low oxygen atmospheres. As short as a 3-hour exposure killed all the stages within 24 hours. Eggs were the most resistant life stage, requiring exposures of 29.8 hours to provide complete kill.

Brief exposures of 0.5 or 1 hour provided significant latent mortality when firebrats were examined after 168 hours. The mode of action is unknown.

In phase III, the 48-hour exposure produced 100% kill of all stages. Oxygen was quickly displaced from the flour and replaced with nitrogen. The use of 48-hour exposure should provide sufficient margin of error to ensure complete kill of all stages.

The cabinet beetle

The cabinet beetle was the only species tested in which the larvae was the most tolerant stage to low oxygen atmospheres. In phase II, larvae required 120-hour exposures to produce 100% mortality, compared with 48 hours for pupae and 72 hours for the eggs and adults.

In phase III, the 120-hour exposures provided 100% kill. The flour did not increase the exposure time required to completely kill larvae.

The larder beetle

The adults were the most susceptible life stage tested with the low oxygen atmosphere. In phase II, 16-hour exposure resulting in 100% kill. The pupae were the most tolerant stage in that 24-hour exposure resulted in 70.1% mortality compared with 98.9% kill of larvae and complete kill of eggs and adults. All stages were killed with 48- or 72-hour exposures.

In phase III, 96-hour exposures killed 100% of all stages buried in the flour.

Cigarette beetle

Adult cigarette beetles were killed with 120-hour exposure. All of the adult and pulpal cigarette beetles were killed with 144-hour exposure in phase II. Control mortality was extremely high at 3 weeks (>97%). Larvae required exposure of 144 hours, the egg stage was the most tolerant stage tested, requiring 192 hours to produce 100% kill.

All stages of the cigarettes beetle were killed with 192-hour exposure in phase III.

The confused flour beetle

The adults and larvae were completely killed with 48-hour exposures in phase II. All developmental stages were killed with a 72-hour exposure. The reason for the significant increase in mortality of larvae and pupae between 7 and 21 days after exposure is unknown.

In phase III, all stages were killed with 96-hour exposure to low oxygen atmopsheres.

It is extremely unlikely that *T. confusum* will develop resistance to low O_2 treatments as reported by Donahaye.[21] He exposed red flour beetles to 0.5% O_2 for 40 generations at 95% RH. The lethal times increased from 36 hours in the second generation to 190 hours in generation 26. It is unlikely that this degree of selection would ever be achieved under practical conditions.

The American cockroach, brownbanded cockroach and German cockroach

Adult cockroaches are the most susceptible stage to low oxygen atmospheres, requiring 6-hour exposure to produced 100% kill of all 3 species tested in phase II. The nymphal cockroaches of all 3 species are somewhat more tolerant of low oxygen atmospheres, requiring 8–24 hours to kill 100%.

The oothecae are the most tolerant life stage. Exposures of 120, 72 and 24 hours were required to kill 100% of the developing nymphs of *P. americana, S. longipalpa* and *B. germanica,* respectively.

In phase III, exposure of 120 hours was necessary to kill 100% of the *P. americana* oothecae. There was no apparent effect of burying the capsules in the flour.

The powderpost beetle

In phase II, 48-hour exposure produced 97% kill of adult beetles, 96-hour or longer exposure produced 100% mortality and 90% kill of the *Lyctus* larvae within 24 hours was achieved, all other life stages being completely killed. At least a 96-hour exposure in phase II with *T. prostomoides* was necessary to provide 100% kill. In phase II, 120-hour exposure produced only a 90% kill of the *Lyctus* with the larval stage, indicating a need for a longer exposure period to achieve 100% mortality.

The colonies were too small and thus it was not possible to test sufficient replicates. Phase III provided final results for *Lyctus* larvae.

In phase III, the only exposure period tested for adult beetles was 144 hours, which provided 100% kill. Two exposures were tested for *Lyctus* larvae, 120 and 144 hours, all resulting in 100% kill.

The western drywood termite

Exposure for 96 hours resulted in a 100% kill of nymphs within 24 hours in phase II. A 72-hour exposure killed 100% of the nymphs within 14 days after the exposure.

When termites were exposed for 15, 24 or 48 hours, there was a significant increase in mortality between day 1 and day 7. The exposure to the low oxygen atmospheres produced some latent effects.

In phase III, 48-, 72- and 96-hour exposures produced 100% kill within 14 days. The wooden block was not a barrier to displacement of oxygen by nitrogen. The 96-hour exposure produced a 100% kill within 24 hours.

CONCLUSION

The use of low-oxygen atmospheres to control insect pests in museums looks extremely promising. It was possible to maintain low-oxygen atmospheres (<0.1%) for at least 8–10 days with only an occasional flushing of pre/purified N_2 and several packets of Ageless™ oxygen scavenger. The results showed that the time required to kill 100% of the insects varied between species and even between the developmental stages of a given species. For most insects tested, exposure of less than 96 hours was required to ensure complete kill. Certain stages such as eggs of cigarette beetles may require up to 8-day exposure to ensure complete kill. Preliminary tests indicated that the addition of CO_2 to the nitrogen slightly decreased the exposure time required to kill the insects. It is likely that the exposure time in the low-oxygen atmosphere would be dramatically decreased by increasing the temperature above 25.5°C and lowering the relative humidity below 55%. However, the upper temperature limits and lower relative humidity limits would depend on the nature of the object.

The time required to kill the most resistant stages of each insect tested did not substantially increase in phase III testing. The oxygen was quickly displaced and removed by the Ageless™, killing the insects buried deep in the wood or flour. Consequently, it will probably not be necessary to specially prepare or stack items for treatment.

The Getty Conservation Institute and the J. Paul Getty Museum have developed special bags capable of enclosing larger items such as furniture and paintings and still maintaing the low-O_2 atmosphere.[22–24] Hence the use of low oxygen atmospheres can replace the current use of insecticide sprays and fumigants effectively.

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SUPPLIERS OF MATERIALS

Swagelok tubing fittings and valves: Swagelok Co., 31400 Aurora Road, Solon, OH 44139, USA

Ageless™: Conservation Materials, P.O. Box 2884, Sparks, NV 89432, USA

Teledyne Model 316: Teledyne Analytical Instruments, P.O. Box 1580, City of Industry, CA 91749, USA

Shinyei Temperature and Relative Humidity Transmitter: Shinyei Kaisha, 1-10-7, Shinbashi, Minato-ku, Tokyo, Japan.

SUMMARIES

The feasibility of using modified atmospheres to control insect pests in museums

The mortality of all life stages of pexts commonly found in museums was evaluated at 55% relative humidity and 25.5 °C in a nitrogen atmosphere (less than 0.1% oxygen). The insects studied were webbing clothes moths, furniture carpet beetles, firebrats, cabinet beetles, larder beetles, cigarette beetles, confused flour beetles, American cockroach, brownbanded cockroach, German cockroach, powderpost beetles and western drywood termites. The time required for 100% kill ranged from 3 hours for the adult firebrats to 192 hours for the eggs of the cigarette beetles.

Possibilité d'utilisation d'atmosphères modifiées pour contrôler les insectes dans les musées

La mortalité à tous les stades de croissance d'insectes habituellement rencontrés dans des musées a été évaluée à 55% HR et 25.5°C dans une atmosphère d'azote (moins de 0.1% d'oxygène). Les insectes étudiés ont été: les teignes des vêtements (mites communes), les anthrènes des tapis, les thermobies, les trogodermes des conservatoires, les dermestes du lard, les lasiodermes du tabac, la blatte américaine (coquerelle des caves), la blatte à bandes brunes, la blatte germanique, les lyctes et les termites du bois sec. Le temps nécessaire pour obtenir une élimination 100% a varié de 3 heures pour les thermobies adultes à 192 heures pour les œufs des lasiodermes du tabac.

Über die Möglichkeit, Insektenbefall in Museen durch modifizierte Umluft zu bekämpfen

Es wurde die Sterblichkeit aller Stadien von Schadinsekten, die in Museen begegnen, bei 25,5°C 55% rF in Stickstoff-Atmosphäre (<0,1% Sauerstoff) untersucht. Gegenstand der Untersuchung waren Kleidermotten, Teppichkäfer, Ofenfischchen, Kabinettkäfer, Speckkäfer, Amerikanischer Reismehlkäfer, Amerikanische Schabe, Braunbandschabe, Hausschabe, Splintkäfer und "Kleine Trockenholzkalotermite" (Incisitermes minor). Die Zeit bis zum vollständigen Abtöten betrug zwischen drei Stunden für entwickelte Ofenfischchen und 192 Stunden für die Eier des Tabakkäfers.

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