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The Influence of Light on Ageing of Newsprint Paper

by VLADIMÍR BUKOVSKÝ

INTRODUCTION

History has shown that paper is a most convenient and useful support for keeping and communicating linguistic and pictorial information. Its importance throughout history to the present is undisputed. There is no problem with the lifetime of handmade rag book paper, if it is stored in appropriate conditions. Groundwood paper, however, which has been produced since the 2nd half of the last century, is expected to have a short life. The problem of preserving this type of paper is very topical and concentrated efforts towards achieving this will be intensified during the next decades[1].

Several factors influence the degradation of groundwood paper. There is a vast amount of knowledge about the course of degradation reactions in cellulose and hemicellulose[2–5]. It is certain that besides acid hydrolysis, which may be caused for instance by improper storage or a polluted atmosphere, UV radiation is the crucial negative factor because it carries sufficient energy for the breakdown of chemical bonds[4]. On the other hand, there is less information about the course of degradation reactions of lignin, which is the 2nd most important component of paper, during the ageing of groundwood papers. This lack of information has to do with the very complicated structure of lignin[5–6].

In the main, light induced oxidation reactions have significant degradation influence on the lignin molecule. Under the influence of UV radiation and also of visible light, groundwood paper yellows[6, 8], the complicated structure of lignin changes and consequently, various low-molecular weight degradation products with chromophoric properties split off[9, 10]. These degradation products remain in the paper and significantly influence the usability and longevity of groundwood paper. The presence of free phenolic hydroxyl groups and C-α-carbonyl groups is needed for light induced oxidation radical reactions on lignin[5]. The reaction of methoxy magnesium with phenolic hydroxyl groups occurs with the deacidification of paper with methyl methoxymagnesium carbonate (MMMC). The first re-

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action reduces the amount of free phenolic hydroxyl groups and thus a significant inhibition of light induced oxidation reactions can take place.

Other important factors of lignin degradation are hydrolytic reactions in an acid or alkaline medium. In our preceding work[11] we tried to describe the influence of an acid medium (alum) on the longevity of groundwood paper and to assess the influence of thermo-oxidation on the loss of mechanical properties in the conditions of dry accelerated ageing before and after deacidification. The course of ageing was modelled as corresponding to 100 years[12]. In the follow-up work, presented here, we observed, on the same paper samples, the influence of sunlight on the mechanical properties of paper under conditions, which most resemble the realistic use of documents in libraries and archives (study, exhibitions etc.). Comparing the results from the preceding work we tried to evaluate both the main degradation factors of groundwood paper: hydrolysis and light induced oxidation, and their share in shortening the lifetime of this paper.

METHOD

Paper samples

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

- No 1: Modern newsprint 1996, manufacturer: Jihočeské papírny a.s. Větrní, Czech Republic.
  ca. 66% bleached groundwood, ca. 24% unbleached sulfite
  7–8% kaolin
  no sizing
  produced in an acid medium; retention of aluminum sulfate and polyethylendiamin; grammage 48,8 g/m^2.
- No 2: Modern newsprint 1996, manufacturer: Norske Skog, Štetí, Czech Republic;
  ca. 50% classic groundwood bleached by hydrogen sulfide; ca. 15% half-bleached sulfate pulp; 35% recycled material consisting of newspaper/magazine mixture (1:1)
  all fillers supplied by the recycled material
  no sizing
  made in a slightly acid medium: pH ca. 6,8; retention of filler by NALCO 74508*, a product on polyacryl amide base; a little amount of aluminum sulfate
  grammage 48,8 g/m^2.

- No 3: the *Hlas našej dediny* newspaper, 1956, Slovak Republic
- No 4: the *Neue Ordnung* newspaper, 1942, Croatia
- No 5: the *Pesti Hirlap* newspaper, 1881
- W1: Chromatographic paper Whatman 1 manufactured from the pure cellulose.

Samples 6x1 cm were cut out of the modern newsprint in the machine direction. Other samples were cut out of the rest of the newspapers also in machine direction from the outer margin (at least 1 cm from the page margin), always from the same issue or from consecutive issues. Chromatographic paper W1 samples were cut out in the machine direction.

Preparation of samples

The papers were divided into 2 groups:

- Controls (C). Soaked for 5 minutes in 50 ml pure methanol. With the historic newspaper samples yellow degradation products migrated into the methanol.
- Deacidified papers (D). Neutralized for 5 minutes in 4% methanol solution of methyl methoxy magnesium carbonate: $(CH_3\text{-}O\text{-})_2MgCO_2$: MMMC. Coloured degradation products migrate into the MMMC solution in methanol during neutralisation.

The alkaline reserve ($MgCO_3$) formed from MMMC of the D-paper after evaporation of methanol over 48 hours was determined as a difference of weight between the C and D samples after 48 hours of conditioning.

The average alkaline reserve of all samples of individual newsprint papers used in the experiment is given in Table 1. The actual alkaline reserve determined by titration is lower, about 20–35% according to the type of paper[13]. Deacidification of W1 and newsprint papers with 4% MMMC provided such a high alkaline reserve that there was no significant decrease of pH during light ageing.

Table. 1: Alkaline reserve (%) after deacidification.

Paper No	1	2	3	4	5	W1
Alkaline reserve (%)	5.75 ±0.88	3.62 ±1.52	3.30 ±0.75	6.14 ±1.54	2.08 ±1.36	4.23 ±1.06

Sample exposure

Paper samples were placed on the windowsill in a room on the south side of the building. The sun shone on all samples directly through two glazed windows during the period May 15th to October 11th 1998, i.e. 156 days. We assume that a substantial portion of UV radiation was filtered out by the window[14]. The position of the samples on the windowsill was changed every seven days. The dynamics of the degradation processes were evaluated on the 15th, 32nd, 48th, 77th, 115th and 156th day (periods I–VI) of light exposure. The intensity of irradiation was dependent on the height of the sun in the given period (Table 2) and on atmospheric conditions (Table 3). It is stated as a percentage share of sunny and cloudy days. The intensity of radiation was observed at 10:00 a.m. and 2:00 p.m.; the results are average figures of these observations.

Table 2: The amount of energy falling on the surface of the earth in our latitude depending on the height of sun[15].

Day	Energy (Jm-2s-1)	Day	Energy (Jm-2s-1)	Day	Energy (Jm-2s-1)
1.5.	382	1.7.	414	1.9.	352
15.5.	398	15.7.	409	15.9.	324
1.6.	410	1.8.	396	1.10.	287
15.6.	415	15.8.	380	15.10.	253

Table 3: Intensity of the irradiation of paper samples by sunlight in the course of observed intervals as a percentage of individual days. A: cloudless – B: almost cloudless – C: partly cloudy – D: almost cloudy – E: overcast – F: overcast, dark sky.

Irradiation in individual intervals (%)								Whole irradiation (%)						
Interval	Day	A	B	C	D	E	F	Interval	Day	A	B	C	D	E	F
I	15	6	3	27	29	18	17								
II	17	24	12	12	24	13	15	I–II	32	13	6	26	26	16	13
III	16	3	16	50	16	12	3	I–III	48	11	10	26	30	12	10
IV	29	10	12	16	12	28	22	I–IV	77	11	16	22	18	22	11
V	42	11	22	23	22	12	10	I–V	119	10	19	26	16	19	10
VI	37	7	7	6	15	34	31	I–VI	156	10	16	22	16	21	15

Thermal regime during exposure

To judge the influence of temperature on the course of hydrolytic and thermo-oxidation reactions we measured the topical temperature of a sample placed at

10:00 a.m. and 2:00 p.m. (Table 4). The results coincide with theintensity of the falling light (Table 2–3). The most energy fell on the paper in the intervals V and II, less in the intervals III, IV, I and VI, where in the interval VI the room was already heated. The high intensity of irradiation in the interval V was manifested, for instance, by the creation of carbonyls (Fig. 7). The results are average values of the temperature from both measurements, and maximum and minimum temperatures in the observed interval.

Table 4: Temperature of the samples during sunlight irradiating in the course of individual intervals (average ± standard deviation) .

Temperature in individual intervals					Whole temperature				
Interval	Day	oC	Max.	Min.	Interval	Day	oC	Max.	Min.
I	15	25.8 ±3.6	31.5	19.0					
II	17	29.0±3.3	35.0	24.0	I–II	32	27.3±3.6	35.0	19.0
III	16	27.9±3.0	33.0	19.0	I–III	48	27.6±2.8	35.0	19.0
IV	29	27.8±5.1	36.0	19.0	I–IV	77	27.6±3.5	36.0	19.0
V	42	29.5±4.9	39.5	22.0	I–V	119	28.0±4.0	39.5	19.0
VI	37	26.3±4.9	38.0	18.0	I–VI	156	27.8±4.1	39.5	18.0

Measurements

The following parameters were measured:

- Double folds. After conditioning the samples were tested for the number of double folds according to Schopper[16]. Induced tension was 10 N in the samples 1, 2 and 6 and 2,5 N in the samples 3, 4 and 5. There were 10 measurements and an average is given for 8 measurements; the two most extreme values were excluded.
- Brightness. The brightness (reflectance) of samples was measured, as determined in our preceding work, at 457 nm[6]. We did this on both the irradiated and on the reverse sides of the paper. An average of 10 measurements is given.
- Acidity. The 6 x 1 cm samples were extracted in 2 ml of deionized water (pH 7) at 100°C for 1 hour. Acidity in the extract was determined using a pH-meter M-120 Mikrotechna (Czech Republic). The average of 5 measurements is given.
- Extractable agents. Light absorbance (optical density) of the extract was measured at 457 nm by the photocolorimeter Specol 11 (Carl Zeiss, Jena, Germany) before determining the pH. An average of 5 measurements is given.

Sample preparation for both C-samples (soaked in methanol) and D-samples (deacidified in MMMC) removed original degradation products. Extractable agents detected are therefore considered to have been formed during irradiation. It is certain that, besides coloured degradation products, a small amount of colourless extractable degradation products are formed. Their proportions were not determined.

- Carbonyl content in individual samples was determined by the hydrazine photocolorimetric method according to Albertsson and Samuelson[17]. An average is of 5 measurements is given.
- Carboxyl content was determined by the photocolorimetric reaction with methylene blue (MB) according to the method T-237 su-63[18] with modification for the low weight samples. An average is of 4 measurements is given.
- Lignin content. So-called Klason's lignin in the samples of each newsprint paper was determined according to the method of König and Rump[19]. The amount is expressed as a weight percentage of lignin in the dry paper sample. The average is of 3 measurements is given.

Table 5: The amount of lignin observed in paper samples[11].

Paper No	1	2	3	4	5	W1
Lignin (g/100 g dry paper)	18.5	17.5	17.0	21.3	15.0	0

RESULTS AND DISCUSSION

For basic characteristics of selected types of groundwood papers[11] and chromatographic paper W1 before and after 156 days of exposure on light and the same paper samples after deacidification see Fig. 1. Compared to the groundwood papers 1–5 the following most basic characteristics of chromatographic paper W1 were observed; these are therefore the characteristics of cellulose and the degradation reactions of cellulose:

- The paper is neutral, with a very small amount of aqueous extractable agents;
- it has very low carbonyls and carboxyls content (even the carbonyl/carboxyl proportion) similar to groundwood paper of the sample 5.

These differences enable us at least partially to recognize light induced oxidation reactions in the cellulose and lignin molecules of groundwood papers.

The alkalinity of papers after deacidification measured in an aqueous extract is increased to values around pH 9; only in W1 it is higher. This value is impor-

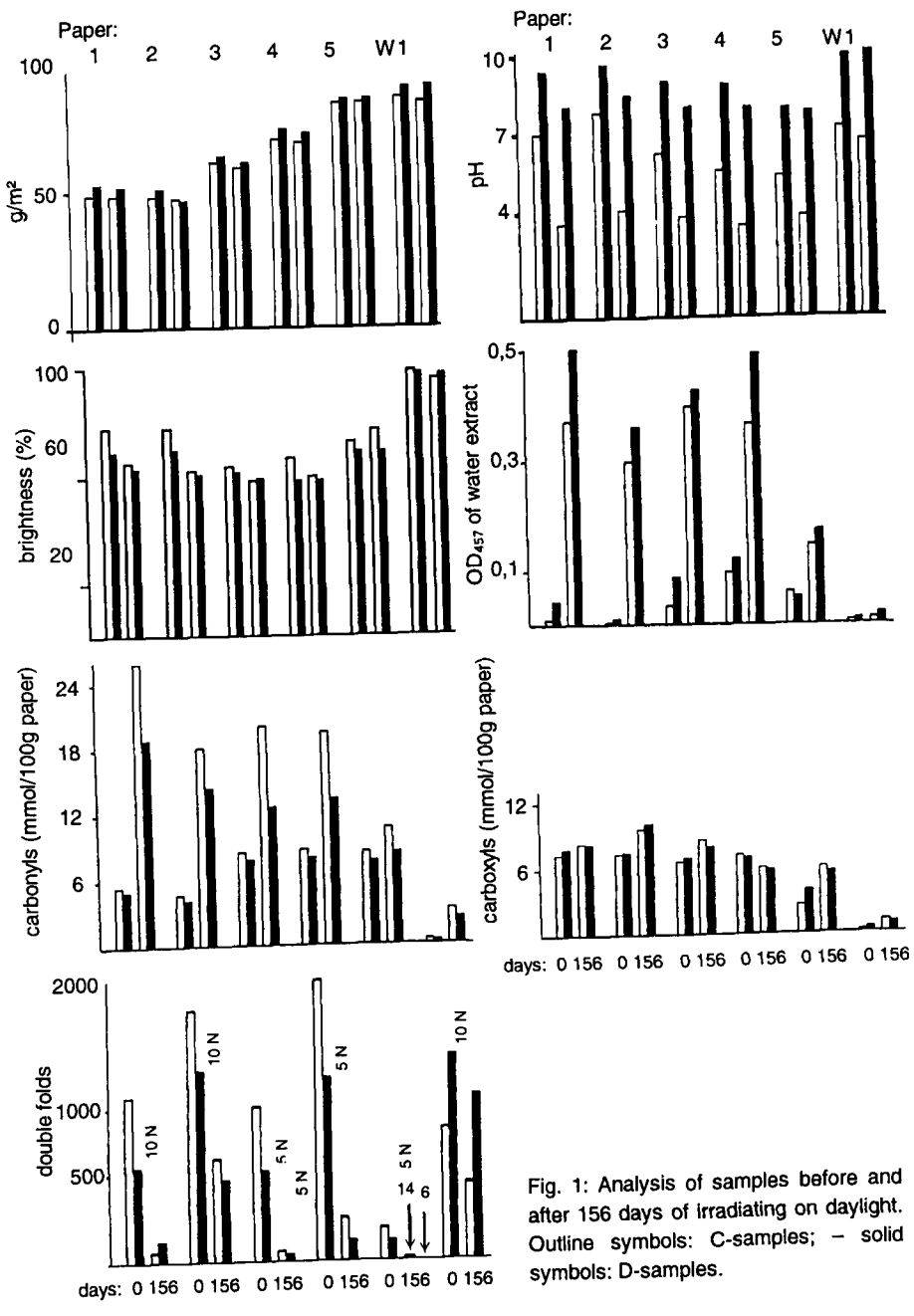

Fig. 1: Analysis of samples before and after 156 days of irradiating on daylight. Outline symbols: C-samples; – solid symbols: D-samples.

tant to judge the influence of the alkaline medium on the course of auto-oxidation reactions of cellulose[2–4, 8]. Generally, there is a significant increase of the extractable agents after deacidification in groundwood papers, coinciding, to some extent, with a decrease in brightness. With W1 the increase of extractable agents caused by deacidification is distinctly less there is virtually no change in brightness at all. This reflects the crucial role of lignin in the creation of coloured products in the alkaline medium of $MgCO_3$ formed from the MMMC, as well as its direct reaction with lignin molecules[6]. It seems that the content of carbonyls and carboxyls in groundwood papers as well as in W1 is not changed by deacidification.

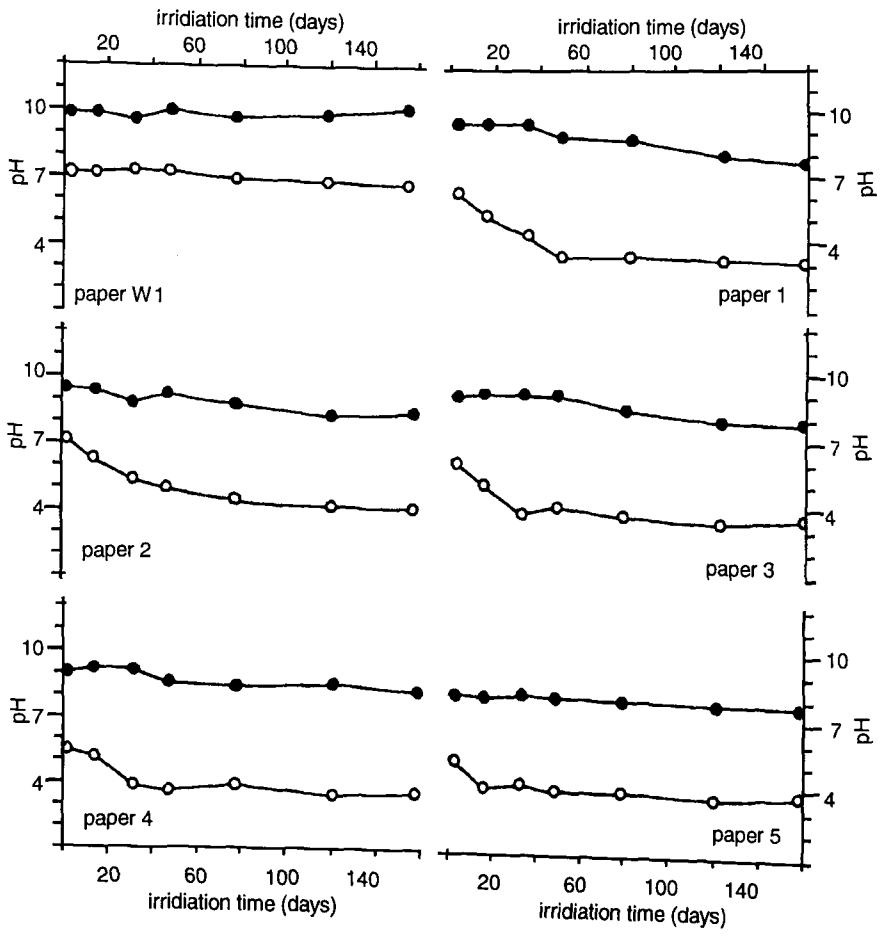

Fig. 2: Acidity and alkalinity of the W1 paper and newsprints during irradiating on light. Outline symbols: C-samples; – solid symbols: D-samples.

The folding endurance of groundwood paper after deacidification is lower, which may be due in part to a corresponding augmentation of grammage from the alkaline reserve, in effect by providing additional filler. The folding endurance of W1 paper, however, is increased by deacidification[13]. We ascribe this phenomenon to the reaction of MMMC with the hydroxyl groups of cellulose. In this way bonds of CH_3-O-Mg-O-R or R_1-O-Mg-O-R type may be formed. This will have to be proved by further research.

Irradiating groundwood paper has a significant influence on the basic qualities of paper, which change as a consequence of light induced oxidation reactions on lignin. The changes that take place during light ageing irradiating can be divided according to their dynamics, into both the changes occurring shortly after irradiation has begun and the changes provoked by long-term exposure to light

Acidity and alkalinity (Fig. 2)

Even short-term irradiation of groundwood papers has significant influence on the increase of paper acidity: the pH decreases. Regardless of its initial state, the pH decreases to 4–3,5. This decrease is more significant in modern newsprint than in historic newsprint papers, which are already considerably acidic. As far as the acidity measured in an aqueous extract is concerned, we assume that the decrease of pH is caused mainly by low-molecular water-soluble agents, i.e. organic acids created as degradation products of lignin or cellulose[5]. The decrease of pH is very rapid for the first 48 days of exposure. After this time the decrease is considerably slower.

Deacidification raises the pH of the extract to 9–10. After irradiation the value gradually decreases approximately by 1. In W1 and Paper 5 the pH is not changed.

Compared to dry accelerated ageing, where the crucial process of degradation is an acid catalysed hydrolysis, the decrease of pH of groundwood paper, after irradiation is much quicker. We assume that the temperature at which the light induced oxidation takes place (cf. Table 4) does not significantly influence the speed of hydrolytic reactions.

Folding endurance (Fig. 3)

Changes in paper strength are the result of the changes in all paper components that take place during thermal ageing, irradiation and whatever other conditions a paper is exposed to. Folding endurance of modern newsprint rapidly decreases immediately after irradiation up to the 48th day of exposure, Sample 1 having

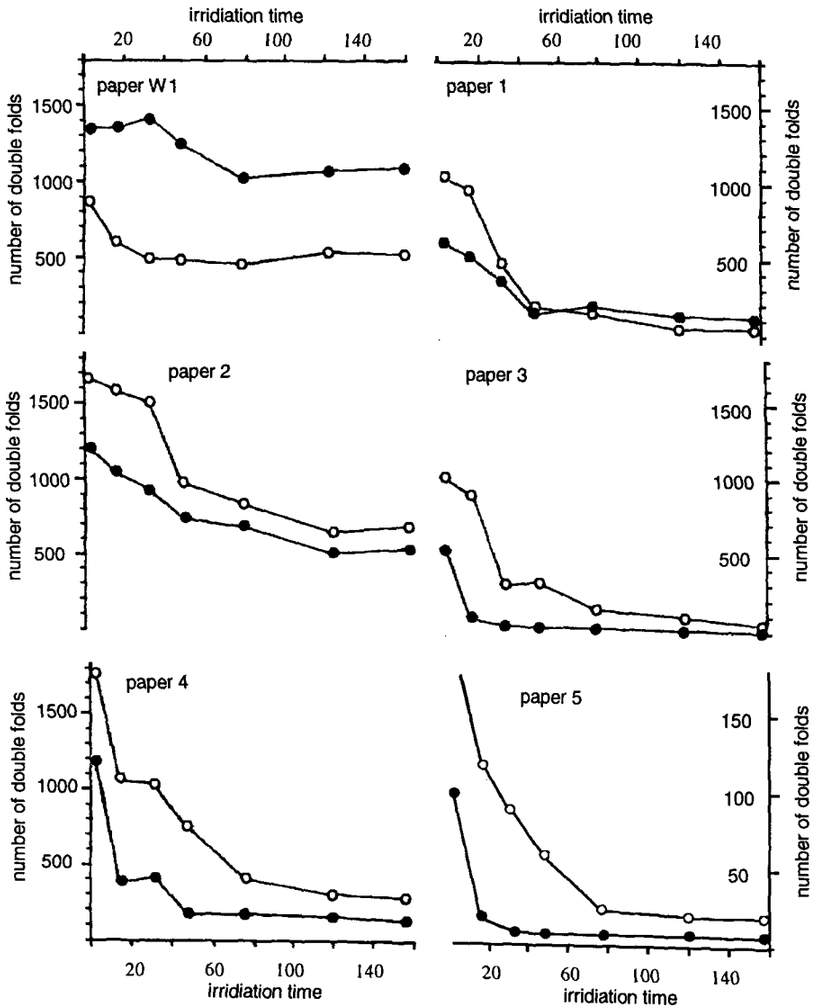

Fig. 3: Folding endurance of the W1 and newsprints during irradiating on light. Outline symbols: C-samples; – solid symbols: D-samples.

considerably worse mechanical qualities than Sample 2. The decrease in historic papers is rapid, but equable. The strength of Samples 3 and 5 after 156 days of irradiating is very low. In W1 there are two stages in the decrease of strength: immediately after irradiation, and up to approximately 30 days, when there is a

significant and rapid decrease. After that period the strength is not changed by further irradiation. The pH does not change, during either the first or during the second period.

Deacidified modern newsprint papers already have lower folding endurance before being light aged. They lose further strength during light ageing, as, to a lesser extent, do C-samples and after 156 days the strength of the deacidified samples is similar to that of samples, which have not been deacidified. The course of light-induced ageing in historic newspapers after deacidification is different. The papers lose their strength very rapidly; they are already weak by the 15th day. The next stage in the decrease of strength is slower, but faster than in C-samples. After 77 days the strength of C-, and also of D- samples is very low and there are no significant further changes. On W1 the favourable influence of deacidification is also manifested during irradiating; this paper keeps its increased strength during the whole course of this treatment.

Comparing the results with those of dry accelerated ageing we can state that the loss of strength of groundwood papers after irradiation, is significantly higher and that it has a different course within a time frame. During dry accelerated ageing of groundwood paper a favourable influence of deacidification can be observed. This is not supported by our observations in the course of irradiation, i.e. light ageing.

Brightness (Fig. 4 and 5)

The brightness of groundwood paper rapidly decreases up to about 30 days after irradiation, except with Sample 5. This decrease is more rapid in modern newsprint papers even considering their higher initial brightness. The decrease in historic papers is smaller. Further irradiation does not significantly change the colour of all samples. The brightness of the Sample 5 is not decreased during light ageing; it even increases after approximately 77 days. We assume that there is a bleaching effect of light[20]. – The brightness of W1 is not changed.

Deacidificationcauses significant yellowing of groundwood papers[6]. During irradiating we observed a further decrease of brightness. After the 30th day of irradiation no more change took place. The difference between C-samples and deacidified papers was minimal.

Compared to dry accelerated ageing, the change of brightness during irradiation is completely different for both the deacidified samples and those which were not deacidified. The decrease during dry accelerated ageing is not significant, but it is equable and slow; the considerable initial difference between D- and C-samples was not significantly changed.

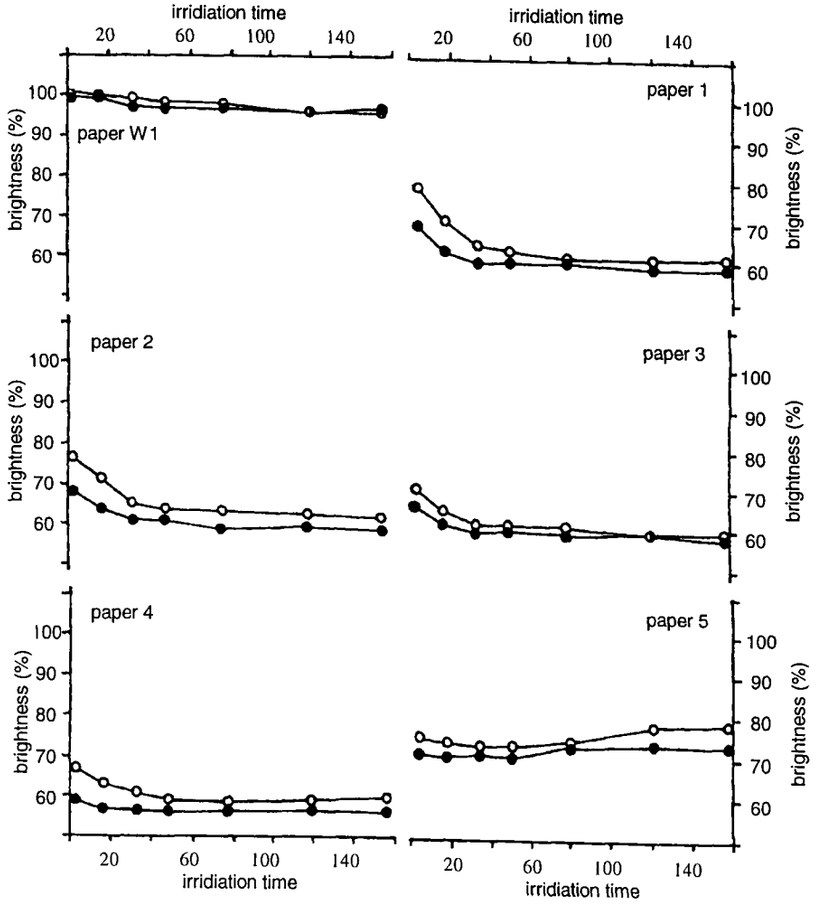

Fig. 4: Brightness of the W1 and newsprints after irradiation by daylight on the irradiated side. Outline symbols: C-samples; – solid symbols: D-samples.

The course of yellowing of the reverse sides of irradiated papers, C- as well as D-samples, is significantly different from the irradiated sides. In modern newsprints the decrease of brightness on the reverse side is slow and equal during the whole course of irradiating, even if the brightness on the illuminated side does not change further after its initial sharp decrease. We attribute this phenomenon to diffusion of colour degradation products from the irradiated side to the reverse one. In historic papers the decrease is even slower and the difference between

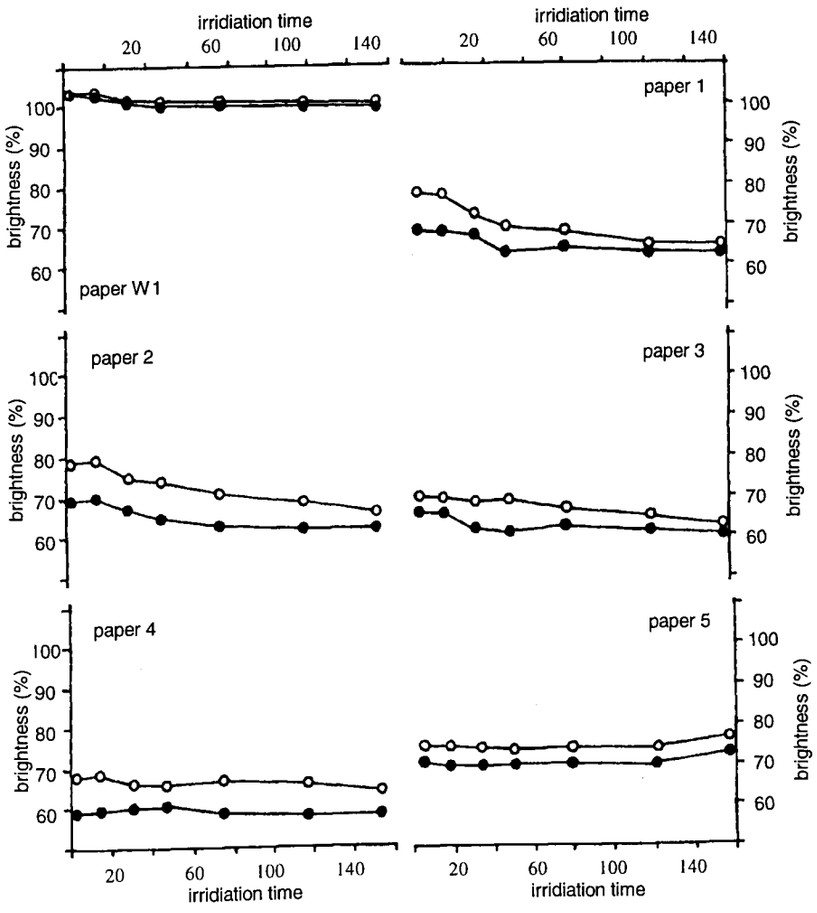

Fig. 5: Brightness of reverse side of the W1 and newsprints after irradiation by daylight on the irradiated side. Outline symbols: C-samples; – solid symbols: D-samples.

the initial and final values is very small. The brightness of Sample 5 does not change. The bleaching effect of light observed on the iradiated side of Sample 5 can also be observed on the reverse side.

The reverse sides of deacidified papers yellow in a similar way as in the C-samples, but the initial difference in brightness between C- and D-samples gradually lessens in the course of irradiation. The brightness of W1 essentially stays the same.

Water extractable agents (Fig. 6)

Regarding water extractable agents there is little difference between modern and historic newsprints, neither in their amount nor in the course of being formed during prolonged irradiation. There is one exception: In Sample 5 about 50% less extractable agents are formed. The pure cellulose paper W1 contains very little of these agents, and their amount does not change significantly during ir radiating. In three of the five groundwood papers chosen for the experiment

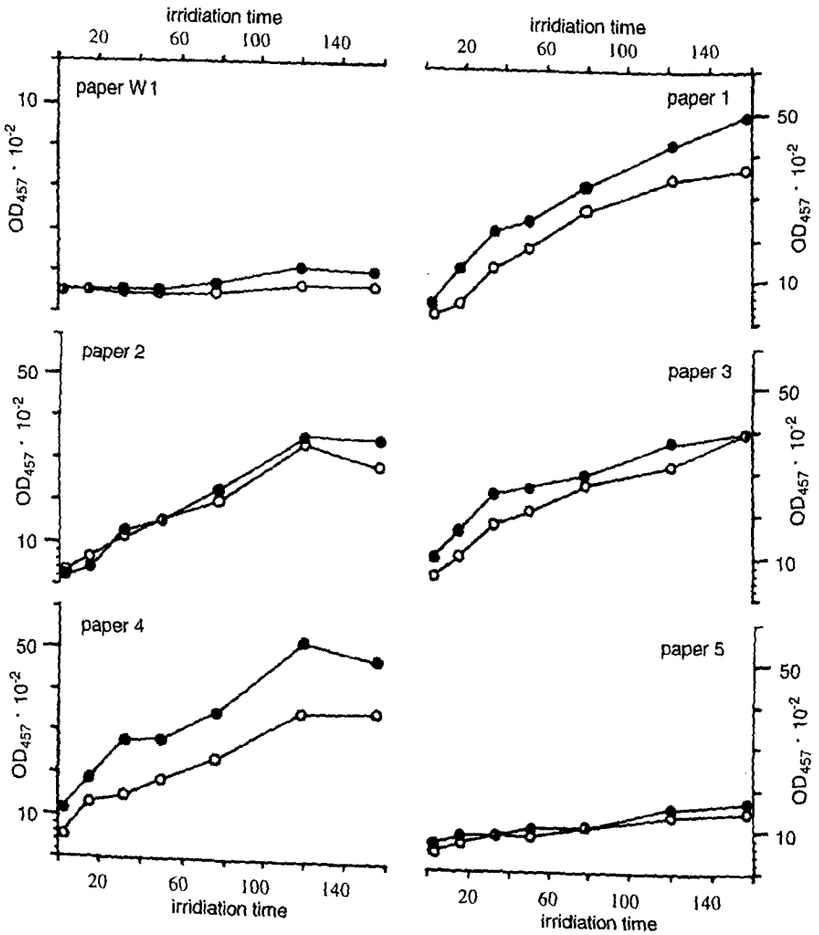

Fig. 6: The amount of water extractable agents originating during irradiating. Outline symbols: C-samples; – solid symbols: D-samples.

(Sample 1, 3 and 4) deacidification caused an increase formation of these agents; there was no significant differences between C- and D-samples for the samples 2, 5 and W1.

If we compare the creation of water extractable agents during irradiation and during dry accelerated ageing, we can see that in the first case much more of them are formed (with the exception of Sample 5). The amount of these agents is increased about 8–10 times in modern and about 4 times in historic newsprints, while with the Sample 5 the increase rate is about 1,5. From alkaline papers (D-samples), compared to neutral or acid ones, there are significantly more agents extracted than from the acidic C-samples. There seem to be light-induced processes on lignin finally resulting in water-extractable compounds, which take place in an alkaline environment to a significantly higher degree than in an acidic one. Since these compounds are the final products of degradation, their analysis could help to understand the detailed course of such a complicated process as the ageing of historic groundwood paper[20, 21].

Carbonyls (Fig. 7)

A determination of these groups is giving information on oxidative degradation taking place in the macromolecules of cellulose and lignin in presence of oxygen after light ageing.

Within very short time after irradiation (32–48 days) there is a high increase of carbonyls in newsprint papers. This indicates that this paper is very sensitive to light. After longer irradiating of modern papers the amount of carbonyls is increased further, even if not as intensely as in the beginning. The maximum amount of carbonyls in historic papers (samples 3 and 4) is reached on approximately the 48th day at the value of about 20 mmol/100g. This refers to the difference between light induced oxidation of modern and historic papers. In Sample 5 the carbonyl content increases significantly more slowly, with a peak at about 13 mmol/100g after 120 days of irradiation followed by a decrease. This phenomenon – a decrease after prolonged irradiation – can also be observed with Sample 2, 3 and 4. In cellulose (Sample W1) light induced oxidation resulting in carbonyl increase also takes place, even if in a much smaller amount; there is a peak at 3–4 mmol/100g after the longest period of irradiation.

Deacidification of groundwood papers, i.e. adding Mg-ions[23], significantly inhibits the creation of carbonyls[6]. The trend of their increase during irradiating is similar to that of the C-samples, but their amount is lower: in modern newsprint about 23–27%, in historic papers about 22–43%. The Mg-caused inhibition of light induced oxidation can be observed even in the pure cellulose paper W1.

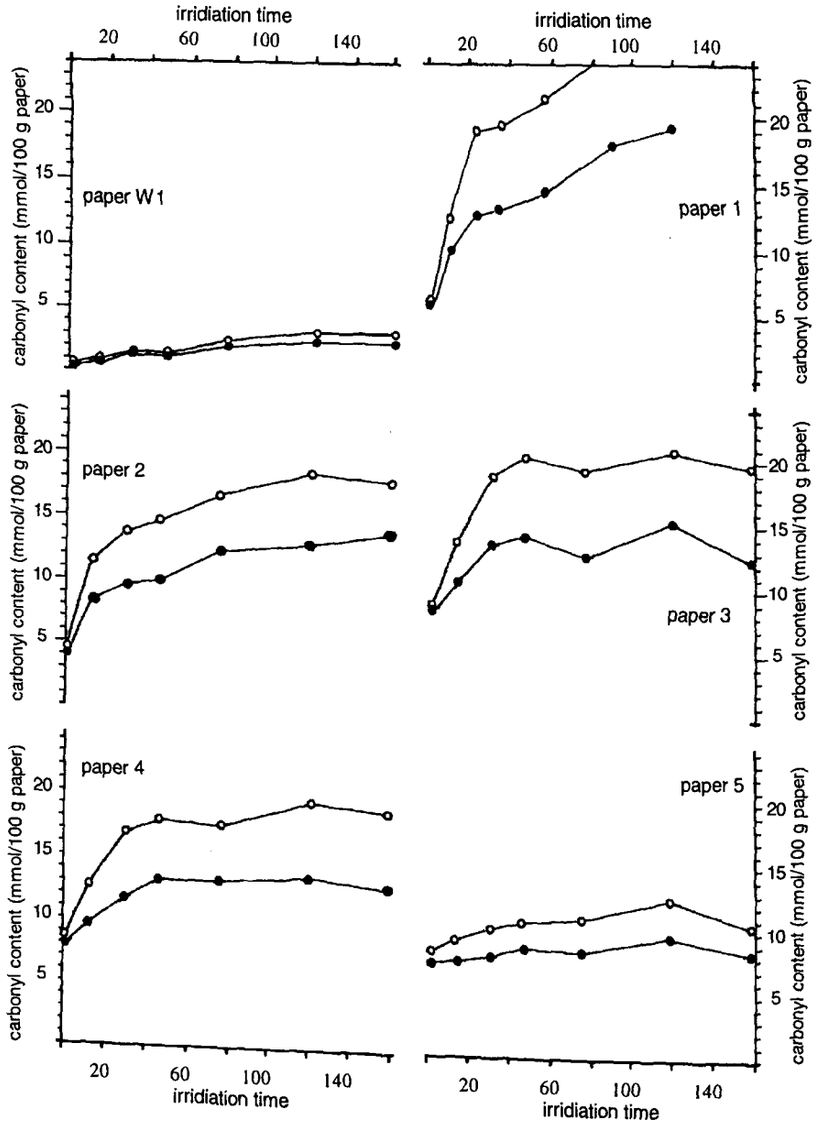

Fig. 7: Amount of carbonyls during irradiating of the W1 and newsprints on light. Outline symbols: C-samples; – solid symbols: D-samples.

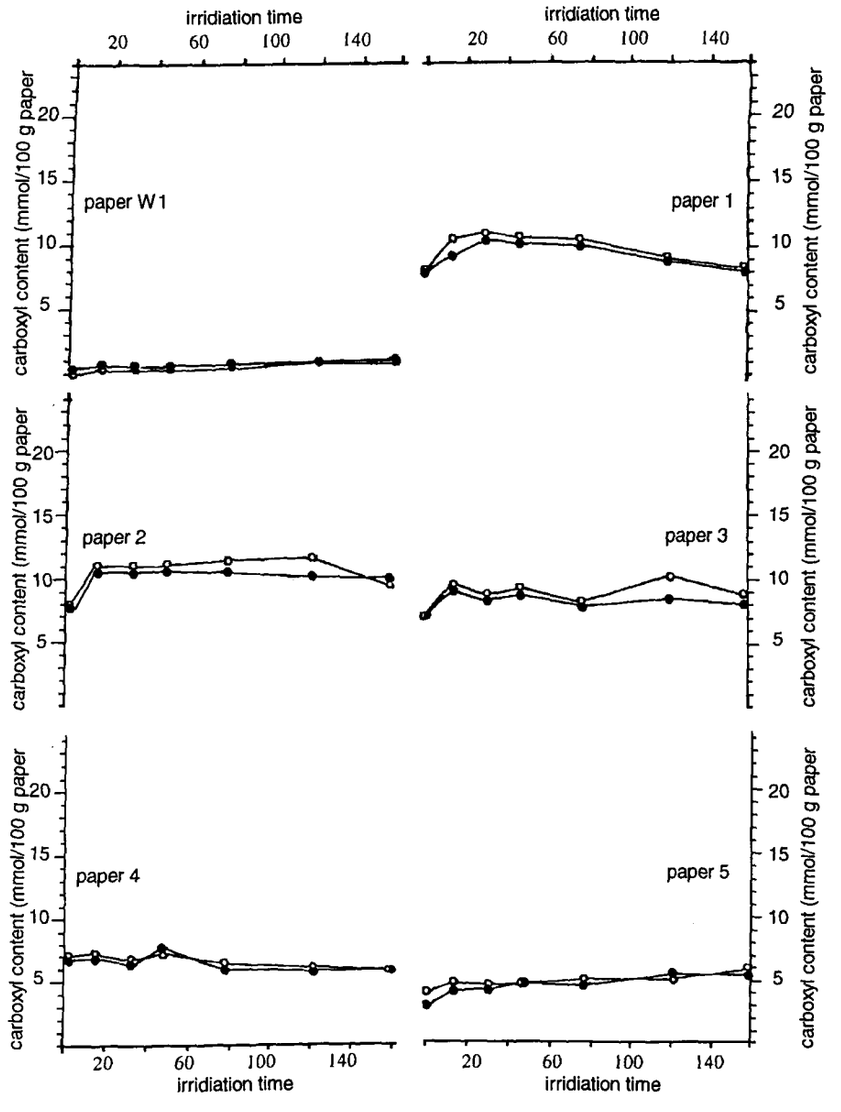

Fig. 8: Amount of carboxyls during irradiating of the W1 and newsprints on light. Outline symbols: C-samples; – solid symbols: D-samples.

Comparing these observations with dry accelerated ageing it can be stated that oxidation reactions in the degradation of modern and historic papers, as it is evaluated by the amount of carbonyls during dry accelerated ageing, is very low and that there is further possibility for oxidation in the paper under research, mainly on its lignin. The amount of carbonyls during degradation of paper stabilises quickly at a certain value and then it does not change.

Carboxyls (Fig. 8).

The formation of carboxyls are another intermediate stage of oxidative decomposition in the macromolecular structures of cellulose and lignin and in forming low-molecular water soluble agents. A determination of their additional amount provoked by deacidification with MMMC and the interpretation of the results are complicated and do not significantly help to explain the course of ageing, of mainly of groundwood papers[18].

The amount of carboxyls formed during light induced oxidation in modern newspapers, which have considerably high carboxyl content already before irradiation, is increased up to the 32nd day. Further irradiating does not result in a further increase of carboxyls; on the contrary: despite the increased amount of carbonyls and water soluble degradation products, a slight decrease of carboxyls is recognised. A similar situation applies for historic newspapers. The amount of carboxyls in W1 is much lower, but we observed a slight, regular increase during the whole course of paper irradiating, similar to the increase of carbonyls in this paper. This course of light induced oxidation indicates that, on cellulose the change of carbonyls into carboxyls is very slow, and it is shown also in the considerably low amount of coloured water-extractable agents and the course of their creation in this paper during irradiating.

The deacidification of samples was not significantly contributory to in the amount of carboxyls formed during the whole course irradiation.

The course of carboxyl forming during irradiation is similar to that during accelerated ageing.

Conclusion

Pure cellulose paper

- Despite the very low UV content in the light used for irradiating, the light induced oxidation reactions take place even on cellulose, at least to a small degree.

- pH is not changed during irradiation.
- The amount of light absorbing agents is very low, which again confirms the low reactivity of cellulose towards light.
- The brightness of this paper does not significantly change during irradiating.
- Pure cellulose paper has a low carbonyl and carboxyl content.
- After deacidification, there is an inhibition of the creation of carbonyls. This inhibition is probably caused, to a considerable extent by the antioxidative effect of Mg.
- Deacidification with MMMC has a very positive influence on the strength of paper made from pure cellulose.
- When evaluating the results regarding Sample W1, it must be taken into account that the cellulose of this paper was produced under different conditions from those used to prepare cellulose for modern and mainly historic newsprint and also that its stage of degradation is different.

Groundwood papers

- We assume that the share of cellulose in degradation reactions of groundwood papers is low and that the observations we made give a picture of mainly lignin degradation.
- After irradiation the papers become acid very quickly. Acid degradation products can be extracted from the paper and light induced oxidation takes place.
- The paper significantly yellows right from the beginning of irradiating. The diffusion of degradation products deeper into the paper slows down the yellowing in the course of further irradiating.
- In some types of paper long-term irradiating by daylight can have a bleaching effect.
- Light induced oxidation is manifest by the significant creation of carbonyls; the carboxyl content does not have a considerable parallel change into the degradation products.
- Intense deterioration of the mechanical qualities takes place after only brief irradiation and this deterioration is crucial for the usability of paper. It is mainly the light induced oxidation reactions of lignin, rather than the hydrolytic reactions of cellulose and lignin, which share in the deterioration.
- An alkaline reserve created by deacidification suffices to secure the alkaline reaction of paper, i.e. to neutralize acid degradation products.

- The alkaline medium inhibits the creation of carbonyls in the process of light induced oxidation of lignin, but increases the share of hydrolysis reactions in the degradation of paper. In this way a different composition of degradation products is to be expected.
- An inhibition effect on the course of light induced oxidation of lignin is probably caused by the presence of Mg ions in paper, and also by the neutralising agent bound to phenolic hydroxyl groups, which hinders their change into the reactive phenolic radicals.
- Deacidification with Mg increases the yellowing of paper, but the difference between original and deacidified papers is lessened during long-term irradiating.
- Deacidification has a significantly unfavourable influence on the mechanical qualities of modern and historic groundwood papers evev soon after irradiation. Acidity elimination has no favourable influence on the actual strength of groundwood papers.

The unfavourable influence of light on the life of groundwood papers is considerably greaterr than we expected. Therefore suitable light conditions, when exposing books and documentary exhibits made from groundwood paper, are highly recommended. It seems that deacidification of groundwood papers results in a good condition for their storage in dark rooms, but limits their utility for presentations in museums, galleries, libraries and archives.

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SUMMARIES

The Influence of Light on Ageing of Newsprint Paper

Irradiating of groundwood paper (newsprint) by modified sunlight has a considerably high degradation effect which is manifested by yellowing, increased acidity and loss of mechanical qualities. It is shown that the lignin component of such paper is most sensitive to light. Light induced oxidation reactions are of crucial importance in the degradation of lignin. Deacidification of groundwood papers with MMMC significantly inhibits the course of light induced oxidation reactions, but increases certain processes which result in a greater amount of water extractable degradation products and in lower folding endurance. Deacidified papers are very sensitive to light radiation, which significantly limits their utility for exhibition purposes. The cellulose component of groundwood paper is resistant to the degradative effect of light.

L'influence de la lumière sur le vieillissement du papier à base de pâte mécanique

L'irradiation du papier à base de pâte mécanique (papier journal) par une lumière solaire modifiée a un effet considérable de dégradation qui se manifeste par le jaunissement, par un accroissement de la teneur en acide et par la perte de résistance mécanique. On a démontré que la lignine contenue dans ce papier est très sensible à la lumière du soleil. Les réactions d'oxydation induites par la lumière ont une importance cruciale dans la dégradation de la lignine. La désacidification du papier contenant du bois (pâte mécanique) au moyen de carbonate de magnésium méthoxyméthylique (MMMC) inhibe significativement le cours des réactions d'oxydation induites par la lumière mais accroît le nombre des produits de dégradation extractibles par l'eau et réduit la résistance au pliage. Le papier désacidifié de cette façon est très sensible au rayonnement de la lumière, ce qui limite significativement sa capacité à être utilisé pour des expositions. La cellulose contenue dans le papier-bois résiste à l'effet de dégradation de la lumière.

Die Beeinflussung des Alterns von Holzschliffpapier durch Licht

Die Bestrahlung von Holzschliff- (=Zeitungs-) Papier mit modifiziertem Sonnenlicht bewirkt dessen Abbau in bemerkenswertem Ausmaß, was sehr bald in Vergilbung, zunehmendem Säuregehalt und Rückgang der mechanischen Festigkeit Ausdruck findet. Es wird gezeigt, daß das in diesem Papier enthaltene Lignin besonders empfindlich gegen Sonnenlicht ist. Eine Neutralisierung des Holzschliffpapiers mit Methylmethoxymagnesiumcarbonat (MMMC) verringert deutlich den Ablauf der lichtinduzierten Oxidation, hat jedoch einen Anstieg der mit Wasser extrahierbaren Abbahprodukte und einen Rückgang der Falzzahl zur Folge. Derart neutralisiertes Papier ist sehr empfindlich gegen Lichteinstrahlung, was seine Eignung für Ausstellungen deutlich einschränkt. Die in Holzschliffpapier enthaltene Cellulose ist unempfindlich gegen die abbaufördernde Wirkung des Lichtes.

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

Part 1: Acid Migration at 90° C

by HENRY CARTER, PAUL BÉGIN & DAVID GRATTAN

INTRODUCTION

The discolouration of paper that is in contact with acidic materials has often been attributed to acid migration[1]. An example is the browning of paper in contact with an adjacent sheet containing acidic printing inks[2] The extent of this migration, of non-volatile acids from one paper, does not seem to occur at a significant rate beyond the adjacent sheet of paper[1]. However, it has been suggested that volatile acids would be able to migrate through paper much faster than non-volatile acids[1].

According to Shahani[3,4], the accelerated ageing of papers in stacks generates volatile, acidic degradation products that accumulate in the paper and are unable to escape into the environment. This "stacking effect" produces the following results:

- Stacks of 100 sheets of paper age faster than individual sheets. That is, the migration of volatile acidic products creates an autocatalytic effect on the degradation of paper, resulting in an enhanced ageing of paper in stacks. Hendriks[5] also observed that the accelerated ageing of paper within paper stacks occurs at a faster rate than does the ageing of single sheets.
- Following accelerated ageing, the stacks of paper have an odour similar to that observed in old books, while the single sheets do not.
- Compared to single sheets, accelerated ageing leaves the pH of paper stacks about 0.5 units lower.
- During accelerated ageing, single sheets that are encapsulated in 4 mil (0.0254 mm) polyethylene terephthalate (PET) become brittle twice as fast as sheets that were not encapsulated. However, if the sheets are deacidified with aqueous magnesium bicarbonate prior to encapsulation, the lifetime of the sheets

is extended dramatically. In addition, if the sheets are encapsulated along with alkaline paper, the lifetime of the sheets is extended significantly. Presumably, the alkaline sheets neutralize the volatile acidic degradation products.

Following the premise that volatile acidic degradation products escape from single sheets during accelerated ageing, but remain trapped inside stacks of sheets, an experiment was designed to observe the migration of volatile acidic products through stacks of sheets.

Previous experiments have involved either the accelerated ageing of stacks of sheets, placed between glass plates and exposed to the atmosphere of the oven[6], or accelerated ageing of paper within sealed enclosures[3,4]. This experiment involves the accelerated ageing of a stack of 30 sheets with a glass plate at the bottom and a 1 inch plexiglass frame at the top of the stack. The plexiglass frame, while holding the stack of papers in place, prevents volatile acidic products from escaping where it makes contact with the paper. At the same time, volatile acidic products escape through the larger section of the stack where the frame does not make contact with the paper. Following accelerated ageing, both sections of the paper were tested.

Experimental

Samples

A commercial alum-rosin sized, fully bleached, kraft paper (pH = 4.66; grammage = 115 g/m^2) was used.

Accelerated ageing

A stack of 30 sheets was aged at 90°C and 69% relative humidity. The stack was prepared by placing 30 sheets of paper between a glass plate at the bottom and a 1 inch (2.54 cm) plexiglass frame (¾ inch thickness) at the top of the stack. The plexiglass frame measured 11 x 8 ½ inches to fit perfectly over the paper.

Tests

Tristimulus colour measurements were made using a Minolta CR-300 chroma meter with a D65 light source. In particular, CIE b* values, that represent the yellow-blue component of colour perception and are a reflection of the degree of

yellowing of paper, were recorded. Measurements were made across the middle of each page not covered by the plexiglass frame and averaged. Measurements were also made on the edges of the paper that had been covered by the plexiglass frame.

Dry zero-span tensile strength measurements were made using the Pulmac apparatus[7]. The dry zero-span tensile strength is considered to be a good measure of the strength of fibres in the dry state[8]. Before zero-span measurements were made, the paper was preconditioned by drying at 40°C for 4 hours and allowing to equilibrate overnight.

The cold extraction pH of the paper was measured in both deionized water (CPPA standard G.25P[9]) and in a 0.1 M sodium chloride solution[10] using an Orion EA 940 pH meter. Obtaining the cold extraction pH using deionized water does not account for hydrogen ions that remain located in the interior of the cellulose fibre wall. These hydrogen ions can be released to the exterior solution where the pH is measured through ion exchange using a sodium chloride solution.

Results and Discussion

Following accelerated ageing of the stack of 30 papers at 90°C and 69% relative humidity for 7 days, the region of paper covered by the 1 inch plexiglass frame was noticeably darker than the paper open to the oven atmosphere for the first few sheets at the top of the stack. The difference in colour between the open section and the section covered by the plexiglass frame could be visually observed for the first seven pages at the top of the stack. For the first page, the average value for b* was 11.19 at the edge covered by the plexiglass during accelerated ageing and 8.59 for the paper open to the atmosphere of the oven. As one goes past the first seven sheets and further into the aged stack, the darkness of the paper appears more uniform and the colour of the paper covered by the 1 inch border of the frame and the paper exposed to the atmosphere of the oven appears the same.

The CIE b* values for the pages of the stack of 30 papers following ageing are shown in Table 1. To observe trends, b* values were consistently measured across the middle of each page from left to right, and the values for the paper in the frame opening were averaged. Colour measurements were made for the edges covered by the frames, but only the b* values for the left middle edges are shown in Table 1. As can be seen, the b* values for the edges vary only slightly and range from 11.10 to 11.48. Here, noticeable degradation of the paper has occurred where the volatile acidic products are prevented from escaping by the plexiglass frame.

Table 1: Data of pages of a stack of 30 papers from top to bottom following ageing at 90° C and 69% RH for 7 days

	b* values		Zero Span Tensile Strength			pH		
page	not covered	covered	km /15 mm	km	g/m²	H2O	0,1 M NaCl	°C
control	5.11	5.11	19.9	11.5	114.9	4.66	4.56	23.0
1	8.59	11.19	12.8	7.36	115.9	4.85	4.48	23.0
2	9.19	11.10	11.4	6.48	117.4	4.60	4.39	23.1
3	9.58	11.19	10.1	5.72	117.8	4.50	4.34	23.1
4	9.84	11.26	9.38	5.26	118.9	4.48	4.33	23.0
5	10.17	11.28	9.16	5.15	118.6	4.41	4.30	23.5
6	10.45	11.37	8.83	5.11	115.1	4.37	4.26	23.0
7	10.63	11.47	8.91	4.99	119.0	4.36	4.26	23.0
10	10.74	11.26	8.35	4.86	114.5	4.32	4.26	23.1
12	10.96	11.48	8.32	4.72	117.6	4.26	4.23	23.0
15	11.07	11.37	8.06	4.54	118.3	4.24	4.20	23.0
20	11.00	11.15	8.02	4.53	118.1	4.32	4.25	23.7
25	11.08	11.22	8.02	4.51	118.5	4.27	4.24	23.0
30	11.09	11.21	7.73	4.48	115.0	4.21	4.19	23.0
1-edge			7.91	4.55	116.0	4.30	4.25	23.5

In contrast, a dramatic difference is found for the paper in the frame opening. As seen in Table 1 and in Fig. 1, the b* values rise quickly from page 1 at the top of the stack to page 7 and then taper off to approximately the values found for the edges of the paper covered by the plexiglass frame. The observed trend suggests migration of volatile acidic products from the bottom of the stack to the top and out through the open window of the frame. The b* value is lowest for page 1 at the top of the stack where the volatile acidic degradation products can readily escape and highest for the middle of the stack and beyond where the acidic products are hindered from escaping.

Zero-span tensile strength measurements in the machine direction are shown in Table 1. Zero-span tensile strength values were converted to zero-span breaking length values and plotted versus page number in Fig. 2. Again, similar trends are observed. The zero-span breaking length is highest at 7.36 km for page 1 in the open window of the frame at the top of the stack. Fibre strength decreases going from the top to the middle of the stack where the zero-span breaking length of 4.54 km becomes similar to that of the edge of page 1 at 4.55 km.

pH measurements for samples in both deionized and 0.1 M NaCl are shown in Table 1. Both series of measurements show a downward trend going from

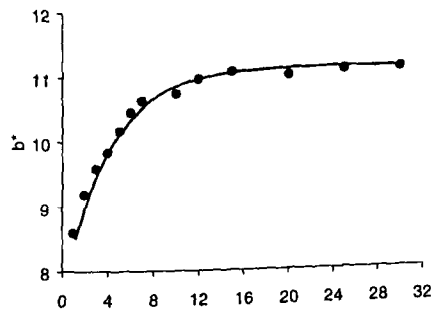

Fig. 1: Average b* values for the middle row of the page plotted versus pages of a stack of 30 papers from top to bottom following ageing at 90°C and 69% RH for 7 days.

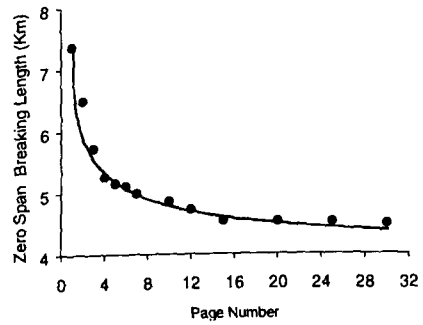

Fig. 2: Zero-span breaking length (km) plotted versus pages of a stack of 30 papers from top to bottom following ageing at 90°C and 69% RH for 7 days.

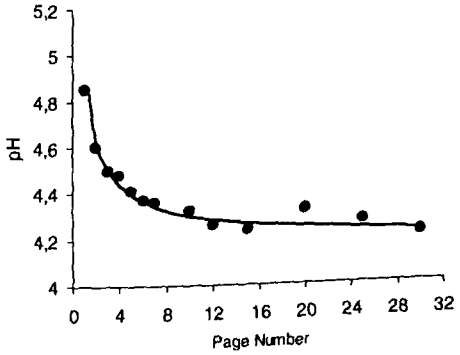

Fig. 3: pH plotted versus pages of a stack of 30 papers from top to bottom following ageing at 90°C and 69%RH for 7 days.

page 1 to about the middle of the stack where the pH tapers off to a value (4.24 for deionized water) close to that for the edge of the paper (about 4.30 for deionized water) covered by the plexiglass frame. This is again consistent with acid migration through the stack. As expected, the pH values obtained in 0.1 M NaCl are lower than the corresponding values in deionized water. However, the pH range for the pages in the stack is broader and more pronounced for the deionized water compared to 0.1 M NaCl. A plot of the pH values obtained in deionized water versus page number is shown in Fig. 3. The pH value of 4.85 for page 1 is quite noteworthy in that it exceeds the value of 4.66 for the unaged paper. This would suggest that the migration of volatile, acidic products through the frame opening has left the page at the top of the stack less acidic.

Conclusion

Evidence for the "stacking effect" at high temperatures has been found from colour, pH and zero-span tensile strength measurements on a stack of 30 sheets of commercial alum-rosin sized, fully bleached kraft paper. Under conditions of accelerated ageing at 90°C and 69% relative humidity, acid migration takes place through a stack of acidic paper. If the top of the stack is open to the atmosphere of the oven while the bottom of the stack rests on a glass plate, the migration of volatile acidic degradation products occurs towards the top of the stack.

Whether or not the same extent of acid migration naturally occurs over a period of time in books under ambient conditions is yet to be determined. In fact, it is difficult to extrapolate to room temperature conditions information obtained at high temperature[11], where the relative importance of competing mechanisms for the ageing of paper may be different[12–13]. In addition, diffusion rates of volatile acidic products are not expected to keep pace with the formation and reactions of degradation products as the temperature is increased[14]. It may well be that the "stacking effect" and acid migration are artifacts of accelerated ageing.

In the meantime, it will be interesting to study acid migration through stacks of paper at different temperatures at selected time intervals. This work is currently in progress.

Summaries

Migration of Volatile Compounds through Stacked Sheets of Paper during Accelerated Ageing. Part 1: Acid Migration at 90° C

The effect of accelerated ageing at 90°C and 69% relative humidity on a stack of 30 sheets of commercial alum-rosin sized, fully bleached kraft paper was studied. Colour (CIE b*), zero-span tensile strength and pH measurements were used to test the stack that was contained by a glass plate at the bottom and a 1 inch plexiglass open frame at the top. All three types of measurements indicated migration of volatile acidic degradation products within the stack and out through the open plexiglass window.

La migration de composés volatils à travers les piles de papier lors du vieillissement accéléré. 1ère partie : La migration acide à 90°C

On a analysé l'effet du vieillissement accéléré à 90°C et 69% d'humidité relative sur une pile de 30 feuilles de papier ordinaire vendu dans le commerce (cellulose au sulfate fortement décolorée, collage à la résine). La pile a été placée entre une plaque de verre au-dessous et un cadre en plexiglas de 1 pouce (=2,54 cm) au-dessus. Les paramètres utilisés pour décrire les variations de la pile sont : le jaunissement (CIE b*), la force nulle de résistance à la traction et le pH (potentiel d'hydrogène). Les trois types de mesure ont indiqué qu'une migration volatile de produits d'une dégradation acide avait lieu tant à l'intérieur de la pile que vers l'extérieur par l'ouverture du cadre en plexiglas.

Die Wanderung von flüchtigen Bestandteilen durch Papierstapel bei der beschleunigten Alterung I: Die Säurewanderung bei 90°C

Es wurde die Wirkung einer beschleunigten Alterung bei 90°C und 69% rF auf einen Stapel von 30 Blatt handelsüblichen Papiers (hochgebleichter Sulfat-Zellstoff, Harzleimung) untersucht. Die Stapel wurden zwischen einer unten liegenden Glasplatte und einem oben liegenden Plexiglasrahmen von 1 Zoll (2,54 cm) Innenraum gehalten. Parameter zur Beschreibung der auftretenden Veränderungen waren Vergilbung (CIE b*), Nullbruchkraft und pH. Alle drei wiesen auf die Wanderung flüchtiger saurer Abbauprodukte innerhalb des Stapels und nach außen durch die Öffnung des Plaxiglasrahmens hin.

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Foxing

A New Approach to an Old Problem

by N.L. REBRIKOVA & N.V. MANTUROVSKAYA

INTRODUCTION

Foxing spots, or brown stains, can be considered as a widespread damage of drawings, engravings, manuscripts, books, archival documents, and cotton fabrics. They appear usually as stains of various dimensions: from small to relatively large. The paper affected by foxing stains is weaker, more acidic and friable than the unaffected, uncoloured one.

APPEARANCE

The stereo-binocular microscopic examination of affected paper showed that the foxing stains look like as if they were slightly pressed into the surface of the substratum. As distinct from pigment fungal stains similar to foxing stains, the colouring of the latter is more homogenous. Their colouring varies from lemon yellow to dark-brown. Dark foxing stains are characteristic for those on high-quality paper. The most light coloured ones, having a citric shade, are found on low-grade paper like newsprint. Foxing spots in books, having the center of development on one leaf, affect the neighbouring ones; their intensity decreases with increasing distance from the center of infestation. Rigid fragile formations like crystals are occasionally seen in the center of foxing stains.

The number of foxing stains in a book, on a drawing or an engraving gradually increases with ongoing time. There are cases where, after some lapse of time, they appear again after bleaching treatment to remove them.

Foxing stains show intensive luminescence in UV-light at the initial phase of formation, when they are practically unseen in visible light. In the formed foxing stains detectable at common illumination the peripheral zone only shows luminescence. Sometimes fluorescence of fully formed foxing spots is absent.

Foxing

Foxing stains can be seen on different kinds of paper dating from the beginning of 16th-century to 50's, 60's of our century. It is well known that they appear on paper after a certain period of natural ageing. Their presence frequently serves as one of the attributes of authenticity of drawings, engravings, and archival documents for experts and researchers. Inspections conducted in museum funds and libraries have shown that the number of books, art works, and documents affected by foxing increased relatively to unaffected ones with the reduction in the age of paper[1]. Foxing stains are mostly widespread on paper produced in the end of the 18th up to the beginning of 20th century. Frequency of foxing appearance increase with development of paper manufacture: grinding instead of beating the pulp, what results in deeper fragmentation; application of different strong bleachers. It is well known that the development of industrial paper production has rendered a negative effect on the long-term stability of the product. On the basis of observations made during examination collections of drawings, rare books and manuscripts, it is possible to contend that the appearance of brown stains depends also on the history of their shelf life and use. Formation of foxing spots is promoted by dust and various pollution, long exposure in light, increased moisture, fluctuations of temperature and humidity.

RESEARCH IN FOXING

The history of research in the nature of foxing dates back to the 1930's. Two versions of the origin of foxing stains have arisen simultaneously. One of them explains their formation by oxidation of iron. The other accounts their appearance as result of development of microorganisms.

So far the problem is under discussion. It is interesting to note that research in the foxing problem both via direct microscopic observations in visible light and via scanning electronic microscopy has revealed only infrequent separate spores and fragments of fungal hyphae, but not the accumulation of cells indicating colony formation in the stain area. Attempts to obtain fungal isolates from paper samples affected by foxing often led to unsuccessful results. Isolating fungi from foxing areas, some researchers obtained different fungal strains present on paper in dormant state. Usually there is a certain quantity of fungal spores and fragments of mycelium on paper. Using these fungal isolates it was impossible to reproduce foxing spots in the laboratory. Iron found in foxing stains was only a trifle over that in the ambient areas. It was found mainly in the center of the foxing stains. Such small amount of iron was insufficient to cause the formation of stains like rust stains from the contact with metal objects. Therefore it stands to reason that not the iron compounds are provoking the colouring of foxing stains. So neither

"iron" or the "microbiological" hypothesis gave an answer to the all-arising questions. Both opinions did not explain the nature of foxing luminescence. Certain researchers – microbiologists – consider the phenomenon of luminescence of foxing stains as the evidence of their biological origin. But molecules of organic and inorganic substances composing the living or nonliving systems show fluorescence.

On the basis of experiments Arai[2, 3] came to the conclusion on the fungal etiology of foxing. In his opinion, locations of micro-colonies of xerophylic fungi could be the areas of foxing formation and the appearance of foxing stains is not connected to fungal pigments dyeing of paper (fungal pigment stains). The coloured products emerge in the process of interaction of oligosaccharides with amino acids. The amino-carbonyl reaction is also named as the Maillard reaction. Oligosaccharides are formed upon partial cellulose hydrolysis by fungal organic acids. Amino acids are liberated as a result of the fungal cells breakdown.

However, fungal isolates from fungal colonies on foxing stains have been obtained only after incubation of the paper samples in a chamber providing a humidity level of about 80%. In this high humidity fungal colonies that were allocated in cultures began to develop on the paper samples. The primary fungi development in foxing stains can be explained by the fact that at their locations small hollows are formed where dormant spores as well as mycelium fragments can accumulate. The laboratory reproduction of brown stains was carried out not as a result of infection of paper samples by allocated fungal cultures, but applying the drops of organic substance (carbohydrates and amino acids) solutions on the paper. Found in the foxing area mono- and dicarbonic organic acids had been assigned to the metabolic products of mould [3]. However, organic acids could also be the products of cellulose destruction, for instance as a result of oxidation. Thus, in our opinion, the version of fungal etiology of foxing appears to be insufficiently convincing.

Italian scientists also have conducted investigation in foxing in order to find proofs for the hypothesis of their biological origin. They studied foxing stains by scanning electronic microscopy. They also tried to isolate microbial agents of the disease and to reproduce the observable damage of paper by inoculating it with them[4]. As a result of isolation on nutrient media relatively few fungal isolates were obtained in relation to the number of made sowings. The results of isolation of microorganisms fitted well with the electron microscopy picture of areas on paper damaged by foxing. Microscopy examination revealed some infrequent spore and hyphae that are always present, particularly in old papers, and no signs of developing fungal colonies were found. Only two fungal isolates – *Chaetomium spinosum* and *Aspergillus terreus* – were able to reproduce the yellow and brown stains on the paper. Therewith, the medium with the submerged

strips of paper contained $FeCl_3$ (between 25 and 400 mg/l), and the obtained stains showed no fluorescence. A. Strzelczyk has experimentally received the stains similar by their colour to foxing by inoculating the paper with cultures of actinomycetes[1]. However, she considered that foxing spots could appear both as a result of development of microorganisms and as a consequence of chemical processes. All the microbiologists who investigated foxing spots concurred that in the stain area clusters of cells of microorganisms were lacking. The results of microbe isolation on artificial nutrient media are frequently negative. The investigators have isolated different fungal species. Concurrence in the published lists is rare enough. The microscopy of foxing stains, the results of isolation of microorganisms and analysis of microclimate parameters where they are formed, as well as attempts of experimental reproduction of foxing in the laboratory via paper infection by microorganisms do not permit to make the conclusions on microbial etiology of foxing spots.

The French scientists conducted an interesting research on foxing. They examined foxing stains applying the fluorescent analysis and infrared spectroscopy. The measurement of foxing stain fluorescence with the aid of a spectrofluorimeter has shown that the luminescence intensity was on the average twice or three times higher than that of surrounding paper (rag paper with gelatinous sizing). The maximum of excitation for the luminous foxing stains was marked at wavelength of 395 nm, maximum of emission at wavelength of 460 nm. Analysis of foxing by infrared spectroscopy has shown the presence of compounds containing carbonyl groups, unsaturated compounds with double bonds =C, =N, C=O, diene type ones with conjugated double bonds X=C=Y (where X is C or N and Y is C, N or O) bound with sugars[5]. All mentioned compounds can be formed during the process of cellulose oxidation. Besides, they can be formed as a result of condensation reactions in the act of interaction of products of cellulose oxidation with nitrogen-containing compounds. The products of cellulose oxidation impart a peculiar colour to the stains, yellow for the double bond compounds, and brown for those containing nitrogen.

FURTHER RESULTS

Inspection of museum and library collections

We have conducted an inspection of rare book collections and graphic collections in museums and libraries. The results of our observation of foxing development in books and works of graphic art can be summarized as follows:

The foxing appearance depends on:

- Technology of the paper production.
  Most frequently they are found on paper made between the end of 18th and the beginning of the 20th centuries (application of bleaching agents, increasing of number of fine fibre fractions). Paper with high content of lignin intending to rapid oxidation is not favourable for foxing appearance.

- Level of light exposure during storage.
  Foxing spots begin to develop on the edges of books, on parts of single sheets that are projecting from the book block or from a pile of paper, on the upper sheets of such a pile and on cardboard bookbinding. They also tend to appear on drawings, engravings, single sheets of books, manuscripts and objects of cotton materials, that were exposed for a long time.

- Level of dust and dirt on books and graphic arts.
  Foxing stains are located mostly on the front and back fly leaves, on margins of leafs, on the edges of books, in deformed parts of book blocks, on the illustrated pages. Such appearance is consistent with ways of penetration of dust into the book block. Obviously, these parts of the book block are subjects to the most profound oxidative damage. Sometimes we observed the formation of foxing in books and museum textiles on sections that were polluted in the process of use. There are also cases, when in process of conservation treatment of cotton fabrics, water polluted by iron compounds was used and this factor provoked foxing formation.

- The microclimate conditions, –
  the environment of place where the papers were stored. Foxing formation is connected with increasing humidity of paper or substantial change in humidity throughout the year that facilitates diffusion. Though the increased moisture of paper or its variations promote foxing formation, it should be mentioned that they appear on the paper having a water content insufficient for development of microscopic fungi. Objects affected simultaneously by fungal discolouration and foxing spots could be relatively rarely met in museum stores. Foxing damage is considerably more widespread in museum and library funds than fungal discolouration (Fig. 1–4).

Laboratory research investigations

We have conducted investigations on samples of the foxed rag paper of the 19th century. The pH of paper within the stains and outside was checked in cold

extract (1 hour; 0,5g paper in 35ml). Microbiological sowings were made from the paper samples with foxing. Foxing spots were dyed with yellow blood salt (potassium hexacyanoferratum (II) three hydrate $K_4[Fe(CN)_6]\cdot 3H_2O$ for determination of Fe^{3+}.

No fungal or other microbe cells indicating colony formation were observed during microscopic analysis of the paper. However, separate fungal spores and mycelium scraps occasionally came to the view. The microscopic observations were confirmed by the results of microbiological sowings.

The positive results on the presence of Fe(III) in the center of the stain were obtained upon dyeing foxing stains with an pronounced center. Comparative pH determination of the foxing area and of paper section around it has shown that the paper in the foxing zone was always more acidic. The difference of pH varied from 0,86 to 0,10; it seems to depend on the kind of paper and the stages of foxing formation. The most significant pH difference was observed in the initial stage of the stain development (Table 1). An unusual high pH of thin rag paper used for interleaving albums is connected with its filler. A considerable amount of such elements as Zn and Ti were found by spectral analysis in the samples of this paper. Havermans and Dufour point out that if paper contains components like ZnO or TiO_2, the sensitivity towards oxidative deterioration can be enhanced. These compounds can promote free-radical oxidation of cellulose under neutral and alkaline conditions[6].

Table 1: Paper acidity in the places of foxing formations

Sample no.	Paper	Thickness (mm)	pH
1	Old thick cartography rag paper, section without foxings; the map printed in 1846 year	0,19	6,53
2	The same leaf; foxing stains poorly coloured, showing intensive luminescence		5,67
3	Cartography rag paper, section without foxings; Atlas of the second part of the 19th century	0,08	5,72
4	The same leaf; brown foxing stains show no luminescence		5,53
5	The leaf of thinner rag paper from the same Atlas of the second part of 19th century, section without foxings	0,06	5,50
6	The same leaf; brown foxing stains show no luminescence		5,40
7	Thin interleaving rag paper from the same Atlas; weakly luminescence	0,02	7,03
8	The same leaf; areas with intensive luminescence		6,62

The foxing fluorescence during UV illumination was noted previously. On investigation of manuscripts, printed books, engraves, cotton fabrics under the UV we have drawn attention to the fact that foxing spots show the strongest luminescence at the initial developmental stage (Fig. 5, 6). It is known that luminescence can appear as a result of free radical oxidation of the natural organic substances. The free radicals are formed from molecules under ionizing radiation, on heating in the presence of catalysts, in the course of oxidising-reducing reactions. The source of free radicals can be the transition metal ions. First of all, this refers to Fe(II) ions, which could act as a radical forming center. In biological systems this was demonstrated about twenty years ago. Transition metals can overcome the spin restriction on oxidation by O_2 due to their ability to accept and donate single electrons. They are found in the active site of many oxidases and oxygenases[7]. Neevel and Reisland suppose that Fe(II) ions catalyse the oxidation of cellulose by converting oxygen into more reactive particles, i.e. oxygen radicals[8].

We have assumed that free radicals could be source of fluorescence in the areas of foxing development. The free radicals are formed as a result of cellulose oxidation catalysed by transition metal ions, for instance, iron and copper ones. In this case, copper ions can be more effective catalysts than iron ones but, as a rule, copper amount detectable in paper notably gives way to iron.

The direct method of free radicals detection is the ESR-spectroscopy. We investigated the samples of foxing paper by this technique, what has not been done before. Two kinds of rag paper of the middle of 19th century were investigated: a dense cartography paper and thin used as interleaves in albums and atlases. In the samples of paper both from the foxing areas as well as from the sections visually seeming not attacked free radicals were revealed. However, in the samples of dense paper, where foxing areas were hardly discernible in ordinary light, while showing heavy luminescence under the UV, there were twice as much of free radicals in the border areas of the stains than outside (Fig. 7). In samples of thin paper where a large area was covered with stains showing luminescence, there was nearly the same amount of free radicals in the stain zones and the ambient paper. The amount of free radicals in thin paper controls was much higher than in samples of dense paper. Besides, with help of ESR-spectroscopy much more Fe(III), and Cu(II) ions were observed in areas of foxing formation on dense paper. Based on the obtained results, it can be assumed that in the foxing areas the chemical processes of paper ageing are accelerated, and moreover it may be assumed that one of these mechanisms is free radical cellulose oxidation catalysed by transition metals.

CONCLUSION AND RECOMMENDATIONS

In samples of dust, collected from library depositories, sufficient quantity of iron was found by x-ray disperse analysis, namely ca. 15% of the inorganic part of dust[9]. Paper in contact with oxygen of the air is oxidized in the course of natural ageing. One of the mechanisms that result in increased acidification is the rise in number of carbonyl and carboxyl groups as a result of hydroxyl groups oxidation in cellulose molecules. Acidification rate depends on the technology of paper preparation, intensity of light, durability of exposure in light, pollution of environment, and microclimate in museums, libraries and archives. Oxidation of organic substances, including cellulose, by molecular oxygen is resulting in formation of hydrogen peroxide and peroxide radicals. In the acidic medium hydrogen peroxide can reduce Fe(III) that is usually present in dust or other pollution, to Fe(II). Fe(III) compounds are practically insoluble except for chloride $FeCl_3$. Fe(II) compounds are much more soluble, especially in the acidic medium; Fe(II) can diffuse on certain distance (depending on their moisture) in ambient cotton fibres during the change of moisture content:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2^- + H^+$$

In parallel, Fe^{2+} ions are oxidized by the air oxygen at acidic pH, forming hydroperoxide radicals. Chain reactions of free radical cellulose oxidation speed up this reaction:

$$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + HO_2^-$$

The hydroperoxide radical can react with a cellulose molecule. A new radical is formed as a result:

$$RH + HO_2^- \rightarrow H_2O_2 + R^\cdot$$

In the presence of oxygen this new radical meets the oxygen molecule to form an extra peroxide radical:

$$R^\cdot + O_2 \rightarrow ROO^\cdot$$

Disproportionation (simultaneous self-oxidation and self-reduction) of peroxide radicals results in producing molecules with carbonyl groups that are emitting light. The evolved products of cellulose oxidation can enter an amino carbonyl reaction with nitrogen-containing compounds inherent in paper or present in pollution. The result of the reaction is the formation of melanoidin type coloured compounds which are called *age pigments*. These products have stable bonds; hence they almost do not disrupt and accumulate with time. The reactions of condensation can be initiated by transition metals. They are reactions leading to formation of coloured compounds which are universal; they occur in ageing processes of the living organisms and natural polymers.

The examination of manuscripts under UV has shown that halos around the letters written in iron gall ink that did not yet acquire its brownish hue, showed fluorescence, especially visible at the verso side of paper. Upon further ageing, these halos turn brown. In rare books printed by iron gall typographical paste the lines of text and engravings have passed are imprinted onto the surface of neighbouring interleaf and opposite sheets during natural ageing. These imprints, coloured in brown shades, show yellow luminescence under UV; the weakly coloured or almost uncoloured imprints (initial stage of forming brown by-products) show white luminescence under UV (Fig. 8).

In the course of research in ink corrosion it was found that most iron gall inks contain an excess of iron which is not bound in the complex forming compound of the ink. Some of the Fe(II) ions are oxidized to form insoluble Fe(III) oxihydroxide (rust), which is catalytically inactive. Paper and iron gall ink, however, contain many reducing substances, e.g. products of the acid hydrolysis of cellulose[8]. Fe(II) ions from ink can migrate on a small distance into the surrounding area and catalyse the oxidation of cellulose.

The colour of the haloes (brown discolouration) around ink, the colour of imprints of the text and engravings in rare books, and the colour of foxing are similar, even if the luminescence of each of them in initial stage is different. It is reasonable to assume that this phenomenon is of the same nature: a local accelerated oxidative ageing of paper in comparison with surrounding areas of paper. The local increase of oxidative ageing is triggered by Fe(II) ions or other transition metals, for instance Cu. Their visible appearance as a consequence of reducing Fe(III) and diffusion of the Fe(II) ions is connected to the rate of paper ageing, its acidification in particular. Zn or Ti compounds promote free-radical oxidation of cellulose in the neutral and alkaline medium. Storage of manuscripts, rare books, engravings and cotton textiles at low illumination, minimal fluctuations in humidity as well as in temperature, limited amount of dust in the air and regular dust cleaning will prevent the appearance of foxing. An acid free cardboard of high quality is needed for the mounting of drawings and engravings. Foxing spots in an early stage, when they are still invisible, can be diagnosed by examining of the suspected objects under UV. It is possible to inhibit the further development of foxing detected in an early stage by

- Washing the damaged paper in distilled water or in water-alcohol mixture
- Impregnating the paper with a weak solutions of gelatine, which, due to its high buffer capacity, slows down further acidification of the treated paper.

The use of antioxidants, in particular compounds forming complexes with transition metals seems to be useful, too, but this calls for further investigation.

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SUMMARIES

Foxing. A New Approach to an Old Problem

An investigation was conducted to elucidate the nature of foxings. A connection has been found between foxing formation and paper production, duration of its exposing to light, level of its dusting and storage conditions. UV investigations revealed that foxings show heavy fluorescence at the initial stage of development; luminescence decreases as the colour intensity increases. ESR-spectroscopic technique has revealed the presence of peroxide radicals in the area of foxings. In the initial stage of formation, their amount in stains was the double of that in the surrounding areas. In some fox spots a little bit more iron and copper is found than out of them. Fe(III) exists usually as slightly soluble oxides in dust and impurities. Cellulose oxidation by air O_2 is resulting in the formation of peroxide radicals that are able to reduce Fe(III) to Fe(II) in acid media. Fe^{2+} containing compounds are much more soluble, therefore they can diffuse from dust particles and impurities into the surrounding fibres. The oxidation process increases in the area of Fe(II) diffusion, as the ions of Fe^{2+} are the radical forming centers. The products of cellulose oxidation can undergo reactions of condensation with compounds that contain nitrogen, thus forming brown-coloured products.

Taches de moisissure. Une nouvelle approche pour aborder un vieux problème

Une nouvelle analyse a été réalisée afin d'élucider la nature des taches de moisissure. A cette occasion on a constaté qu'il existe une relation entre les taches de moisissure et la production du papier, la durée à laquelle le papier a été exposé à la lumière, le degré de poussière contenue dans l'air et les conditions de stockage en général. L'observation sous rayonnement ultra-violet a mis en évidence que les taches de moisissure ont à un stade initial de leur développement une forte fluorescence, la luminescence décroît en même temps que l'intensité de la couleur croît. La spectroscopie EPR (résonance paramagnétique électronique) a révélé l'existence de radicaux péroxydes autour des taches de moisissure. A un stade initial de leur formation deux fois plus qu'à la périphérie. Dans quelques unes on a trouvé davantage de fer et de cuivre qu'à l'extérieur. On trouve des combinaisons Fe(III) normalement sous forme d'oxydes légèrement solubles dans la poussière et les impuretés. L'oxydation de la cellulose par l'oxygène de l'air O_2 provient de la formation de radicaux péroxydes qui sont capables de réduire Fe(III) en un acide médium Fe(II). Les composés contenant Fe^{2+} sont beaucoup plus solubles, c'est pourquoi ils peuvent diffuser davantage des particules de poussière et d'impuretés vers les fibres voisines. Le processus d'oxydation sera renforcé dans les endroits où les ions Fe^{2+} se seront diffusés car ceux-ci agissent comme centres de formation des radicaux. Les produits de la dégradation oxydative de la cellulose peuvent subir des réactions de condensation avec des composés qui contiennent de l'azote, ce qui produit des taches de couleur brune.

Stockflecken. Eine neue Erklärung für ein altes Problem

Es wurde eine Untersuchung durchgeführt mit dem Ziel, die Natur von Stockflecken aufzuklären. Dabei wurde ein Zusammenhang zwischen Stockflecken und Papierherstellung, der Dauer, in der das Papier dem Licht ausgesetzt war, dem Staubgehalt der Luft und insgesamt den Lagerbedingungen festgestellt. Beobachtung unter UV zeigte starke Fluoreszenz von Stockflecken im Anfangsstadium, die mit der Entwicklung der charakteristischen Färbung zurückgeht. ESR-Spektroskopie zeigte das Vorhandensein von Peroxid-Radikalen im Bereich von Stockflecken auf: im Anfangsstadium doppelt so viel wie im umgebenden Papier. In einigen wurde ein wenig mehr Eisen und Kupfer gefunden als in ihrer Umgebung. Als Erklärung wird folgendes angenommen: Fe(III)-Verbindungen finden sich in Staub und als Verunreinigungen. Peroxid-Radikale, die bei der Oxidation der Cellulose durch Luftsauerstoff entstehen, können sie im sauren Medium zu Fe(II)-Verbindungen reduzieren. Diese sind weitaus besser löslich, können also aus dem Staub und der Verunreinigung in die umgebenden Fasern eindringen. Der Oxidationsprozeß wird im Bereich der eingedrungenen Fe^{2+}-Ionen verstärkt, da diese als Zentren für die Bildung von Radikalen wirken. Die Produkte des oxidativen Abbaus von Cellulose können Kondensationsreaktionen mit stickstoffhaltigen Verbindungen eingehen, wobei dann die braun gefärbten Verbindungen entstehen, welche die Stockflecken ausmachen.

Fig. 1: An engraving of 1827. Foxing spots with deeply coloured center.

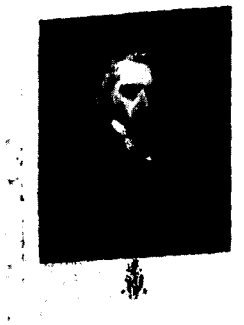

Fig. 2: An engraving in a book published in 1800. Foxing spots with deeply coloured center. Some of the foxing spots are located along print line: The ledge formed during printing prevented further penetration of dust particles and at the same time promoted the dusting of the margins. The typographical thickness of the leaf is 0,21–0,20 mm. The typographical paint is prepared on the base of iron-gall paste (reverse side).

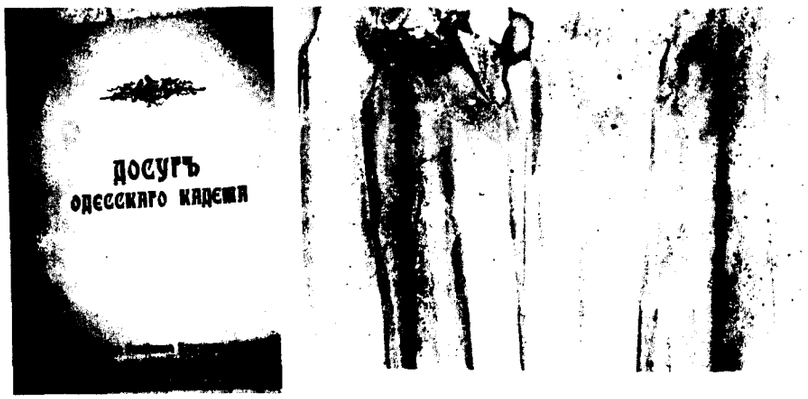

Fig. 3: A book published in 1955 with a pale green cover. This book was kept in a stack of books. The most part of the cover was protected from light and dust deposits by the other book. Foxing spots appeared on the parts of the cover that were not protected from light and dust.

Fig. 4: The lining paper of a drawing made in 1910. The drawing was attached to boards which were not evenly close to each other. Foxing spots have been formed where light and dust could penetrate throw the spaces.

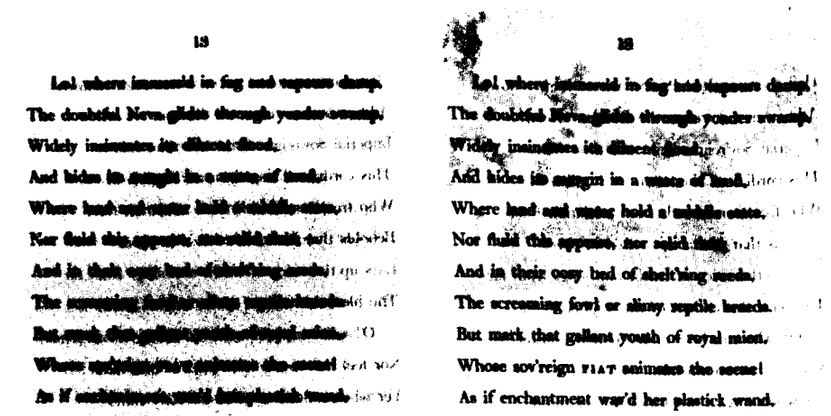

Fig. 5: A leaf in a book published in 1800, foxing spots in early stage. They have weak pale-yellow colour and are practically invisible (left), but are clearly distinguishable for their fluorescence in UV-light. (right).

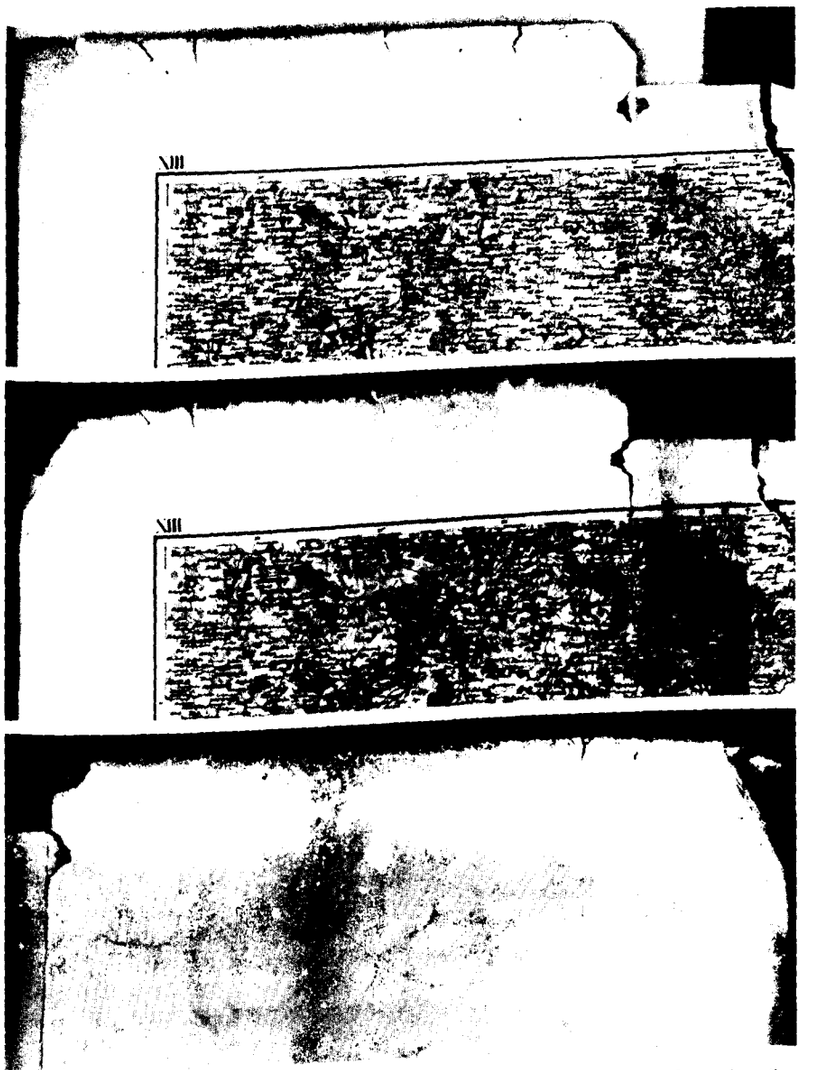

Fig. 6: A map printed 1846. Top: Invisible (early stage) foxing spots have been formed on the upper margin only, because this part of the sheet went over the edge of the stack in which the map was stored.
Middle: Fluorescence of invisible foxing spots in UV-light.
Bottom: Reverse side. Light and dust have promoted accelerating local oxidative ageing in the upper margin. This process had begun on the reverse and gone through the leaf (thickness: 0,21 mm).

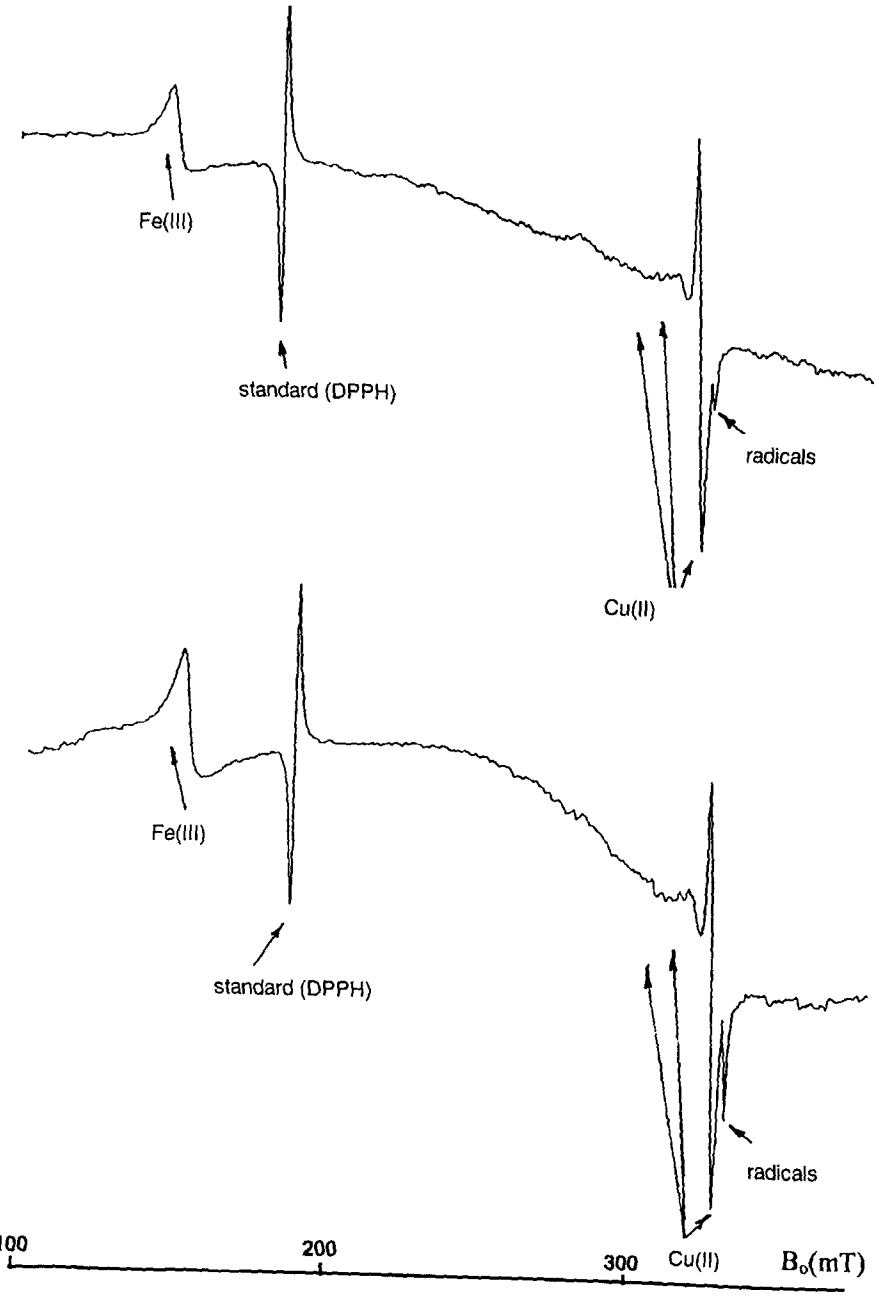

Fig. 7: The ESR spectra of the paper shown in Fig. 5 with (above) and without foxing (below) are clearly distinguishable.

THE

SOVEREIGN.

O THOU, great Monarch of a pow'rful reign,
That more than doubles Europe's whole domain!
Whom larger empires own their sov'reign lord,
Than bow'd before the Macedonian sword,
Or gaz'd with trembling at the awful height
Of Rome's proud eagle in her utmost flight!

Fig. 8: A leaf in a book published in 1800, foxing spots in early stage. They have weak pale-yellow colour and are practically invisible (left), but are clearly distinguishable for their fluorescence in UV-light. (right).

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Ethanol as Fungal Sanitizer in Paper Conservation

by MATTIAS NITTÉRUS

INTRODUCTION

The use of ethanol in paper conservation is widespread and multipurpose. It is used as a solvent/carrier for various substances, e.g. in poultices; mixed with cellulose ethers, as solvent in removal of stains, adhesives, pressure-sensitive tape, as wetting agent prior to aqueous wash[1]. Ethanol has also, during the last ten to fifteen years, become an important chemical sanitizer among paper conservators, in controlling and dealing with fungal attack. Relevant studies on this specific application and its actual efficiency are however very scarce and even contradictory. Some authors claim ethanol an efficient and safe sanitizer[2], possessing fungicidal properties[3], by others ethanol is referred to as inefficient, because lacking sporicidal properties[4, 5], and it is even suggested that ethanol might be an activator to spore germination[6, 7]. These contradictions make it clear that the method needs further investigation. As it is regularly used, and often, in larger infestations and disasters, in quite a routinely manner, the importance of thorough studies and performance testing is unquestionable.

FUNGAL BIODETERIORATION

There are several effects of fungal activity on paper. Primarily, the major part of the cellulolytic fungi need glucose and nitrogenous compounds to synthesize their own amino acids. Glucose is obtained by an enzymatic process, in which the cellulose polymers are broken up into smaller glucose molecules by the aid of cellulases, an intricate exoenzyme complex produced by the fungi[8]. As enzy-

* The following text is an extract of the author's Graduating Thesis and Diplomawork, BA-level, 1997, Göteborg University.

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matic breakdown continues, acidic metabolites are excreted by the organism causing oxidative processes. The oxidation of the cellulose molecule causes a fluffy and porous structure of weakened mechanical strength, discoloration[9] and increased sensitivity to light[10]. Not all papers are equally susceptible to fungal attack. Paper with a high percentage of pure cellulose fibres is more resistant than low-quality, heavily milled products[11]. The phenomenon known as "foxing" and which has been subject to innumerable investigations, is according to the most recent findings, believed to be the deed of micro fungi[12, 13].

Not all of the paper attacking fungi are cellulolytic: since paper in the production-phase, and/or by handling and use acquire various amounts of sizings, coatings, dirt and debris, the nutritional requisites of other fungi are often rapidly fulfilled[14]. It is even reported that certain conservation methods and materials introduce and facilitate fungal development in paper, e.g. resizing with gelatine and methyl cellulose[6].

Discussing fungal growth on paper also the filamentous growth of the hyphae and the formation of fruiting bodies within the paper matrix[10, 15] must be considered, and how this "embedding" correlates with the findings of others[7, 14, 16] indicating that biocide resistance increases when the fungal structure is protected by various substances, e.g. crystalline calcium and magnesium salts, often used as buffering agents[17].

Ethanol

Chemical and physical properties

Ethanol, C_2H_5OH; synonyms: ethyl alcohol, alcohol, spirit of wine, is in its pure state a clear colourless liquid with familiar odor. Ethanol is an aliphatic alcohol, commercially produced mainly by fermentation of sugar and starch by yeasts, bacteria and certain fungi. Industrial processes using catalytical hydration of ethene also yields ethanol. It is a good polar solvent, readily soluble in water and has countless applications as solvent for organic chemicals, as starting compound for the manufacture of dyes, cosmetics and explosives. Ethanol is a familiar constituent of many beverages and is considered to be the least toxic of the straight-chain alcohols (methanol, ethanol, propanol, butanol etc.), evaporates quickly at room temperature, not leaving any residues. Some of its specific properties[18]:

- Molecular weight: 46.07 g/mole
- Specific gravity: 0.7936 g/cm^3
- Boiling point: + 78.32 °C

- Flash point: +11°C
- Explosion limits in air mixture: 3.3–14 % by vol.

Working mechanisms of ethanol on fungi

Ethanol is a well known and widely adopted surface disinfectant, and a general consensus on its efficiency towards vegetative growth of fungi and bacteria is prevailing. Although the specific nature or site of action is not fully known, the most adopted theory is that it affects the semi-permeability of the plasma membrane, disturbing osmotic balance, causing leakage of cytosol constituents, e.g. amino-acids, ribose, K^+, PO_3^{4-}.

Due to the polar properties of ethanol, its short carbon chain and low hydrophobicity, it partitions poorly into the lipid part of the membrane, compared to the longer-chain alcohols which are more hydrophobic in nature, favouring their concentration in the membrane. Since considerably lower concentrations of longer-chain aliphatic alcohols are needed to induce inhibition and cellular death, it is believed that the hydrophobicity of these alcohols increases the permeability of the membrane, and thus enables leakage/passage of cytosol constituents[19].

Unbalanced cytoplasmic permeability and cytosol leakage ultimately leading to disintegration of the cell, is reported to be efficient in ethanol concentrations varying between 50–80%, with a maximum at 70%[20, 21]. Ethanol concentrations exceeding 80% have proven non-efficient since the rapid denaturation of lipid structures forms a protective coagulate around the cell, preventing further penetration[4, 22]. Concentrations below 30% does not exhibit any direct killing or cytolytic properties, but as prolonged treatment of cells with alcohols of lower concentrations maintain ion leakage, and since the coupling of proton currents and ion fluxes is believed to be one important energy source in the transportation system of nutrients into the cell, this leakage will interfere with nutrient accumulation and finally lead to an inhibition of cell growth.

Since the presence and availability of water is of such fundamental importance both in fungal growth processes as in efficient sanitizing techniques, it is not surprising that the fungal reproductive forms, the spores, impose sanitizing problems. The spores can, in contrast to the rather vulnerable and water containing nature of the hyphae, be considered almost a fortress-type of structure with a tough and practically impervious outer shield of polysaccharides; chitin, cellulose and other glucans[21, 23]. Mature, swollen spores from freely sporulating colonies are more easily killed than dry and dormant ones, implying that any rational sanitizing technique aiming at sporicidal action should if possible be applied to mature ones[17, 24]. It has even been stated that several common conservation

treatments even might activate dormant spores[7]. In fact it has been proposed that aliphatic alcohols, methanol, ethanol, propanol etc, possess ability to activate enzymes within dormant spores, e.g. cellulases[23].

Application methods

The way in which ethanol is used as sanitizer seems mainly to be as a 70% solution in water applied as spray-treatment, with the aid of atomizers, plant-sprayers etc. Some workers choose to dampen the object locally with the solution, using cotton swabs or brushes[2, 3]. Prior to ethanol treatment, standard practice is to dry damp material in open shelves, fanning out books etc, followed by mechanical cleaning of the object surface using vacuum cleaners, brushes, erasors, needles, scalpels etc.

Since a 70% solution evaporates rather quickly at ordinary room temperature (+20–22°C), and the treatment often is performed in fume-hoods, the air circulation speeding up the evaporation rate, one might suspect the added ethanol amounts to be quite large. Furthermore, from personal experience with ethanol sanitization, it is not uncommon in papers having extensive fungal infestations, that the surface of the paper seems almost hydrophobic, i.e. the added solution is not absorbed into the paper but tend to congregate on the surface. Thus, such papers need additional treatment until an even distribution of the solution is achieved.

THE EXPERIMENT

Experimental design

Anybody planning and performing a research project in the field of conservation will have learned by experience that such a project runs the risk of becoming too widespread and too much oriented on pure science rather than on practical use. Therefore, in order to keep this study within reasonable limits, and yet not losing relevance to paper conservation practice, the following three questions are addressed:

- Will ethanol affect viability of spores from a selection of paper attacking/ cellulolytic fungal species ?
- Will the condition of the spores prior to ethanol treatment influence their vulnerability?

- Will the application method of ethanol influence the recovery of treated spores?

By studying methods used by other conservators investigating similar problems[16, 25-27] and with methods used in industrial applications[28-30], a simple and rapid, yet informative testing and evaluation technique was designed in collaboration with the Botanical Institute of the Göteborg University, with the intention of providing some answers to the addressed questions. Since the application of ethanol as sanitizer, according to informal communications with professional paper conservators, often follows an adopted methodology, the test was designed to simulate such in-use methods, although with the following important deviations:

- The concentration of the prepared and utilized spore suspension was clearly defined.
- Only the effects of a 70% concentration of ethanol:water will be evaluated.
- As this study does not focus on the relationship between available nutrients in naturally contaminated paper and fungal colonization, a clearly defined medium (Malt-agar 2%) overlaid with pure, unsized, uniform and easily accessible paper with good wet-strength properties was chosen. (Whatman #1)
- Although several questions concerning the application method of ethanol would have been interesting to study, only two techniques were investigated;
  - spray application
  - immersion.
- The two techniques were performed in two separate series to investigate the behaviour and post-treatment recovery from:
  - A: paper contaminated with a mixed suspension of spores of known concentration and viability.
  - B: papers contaminated similar to A, but allowed to develop sporulating colonies prior to treatment, air-dried, ethanol treated, and re-incubated.

Naturally contaminated paper supposedly contains a varying amount and mixture of fungal tissue; spores, hyphae, also bacteria and sometimes actinomycetes. This study, however, investigates a set of four clearly defined cellulolytic, staining and mesophilic fungi, which have been selected as some of the most frequently sampled/used fungi by several authors[14, 31-36]:

- Aspergillus flavus. UPSC* 1768
- Aspergillus niger. USPC 1769

* Stock number at *Mykoteket*, Botanical Museum in Uppsala

- Chaetomium globosum. USPC 1726
- Trichoderma viride. UPSC 2011

The evaluating technique used in this study does not give any precise measure of sporicidal action, related to time/exposure expressed as death rates (K-values), decimal reduction times (D-values) or in comparison to phenol-coefficiency tests etc.[4, 21, 37], but merely indicates maintained or massive loss of viability of the treated spores as compared to untreated reference samples. Furthermore, since a mixed inoculum is used it is not possible to give any precise number of survivors from each separate species without additional research, and since incubation time has been uniform in all samples (14 days) and only controlled at this stage, possible suppression, succession, generation-shift or other such strategies, cannot be neglected. This mixed inoculum was chosen in order to resemble on-site fungal populations as close as possible and to evaluate what effects ethanol treatment might have on them.

Since species in a mixed inoculum behave quite differently from those in pure culture (suppression mechanisms etc.), the reference samples in this test do not and could not show ideal growth of all four species in each separate plate. The references are to be interpreted as infested and untreated samples resembling on-site contamination, and their colonizing organisms compared to the treated samples in series A and B. In this investigation which its author considers to be nothing else but an initial one on the topic, it was considered sufficient with two reference samples to each test series, since the number of samples in each series was fairly restricted. The sporicidal evaluation has been performed using only two parameters; growth or no growth, following ethanol treatment and incubation.

Materials and methods

The fungal strains used in this test were obtained from the culture collections (UPSC) maintained at Mykoteket; Botanical Museum in Uppsala. From these mature agar-grown cultures, a mixed spore suspension was prepared, according to Method 508.2[30], however with the following deviations:

- A wetting agent (sodium dioctyl sulfosuccinate) was omitted
- The spore suspension was only centrifuged/washed once since wetting agent had been omitted.
- The results from the test series were recorded as: Growth = +, no growth = 0.

The concentration of the undiluted suspensions was determined and calculated using a Bürcker-chamber, and the appropriate dilutions were made adding sterile

mineral salts solution, which serves to provide all the basic inorganic minerals needed for growth of the fungal species used. A mixed suspension was then prepared by combining equal volumes of the four separate suspensions. The concentration of the mixed suspension was 1.000.000 spores/ml, with a margin of error of 20%.

The vitality of the organisms used was tested and confirmed prior to preparation of the composite suspension by inoculation of a small volume (0,1–0,2 ml) on nutrient agar and incubating 7 days at +20°C. In order not to lose viability, the mixed suspension was used immediately in inoculation of the paper samples.

The papers used were Whatman #1 filter paper-discs, 7 cm in diameter. According to the manufacturer the paper pulp has not been acid or alkaline washed, no fillers have been used and the ash and metal ion content is low. Complete sterilization of paper was checked by taking random samples from the sterilized paper stock incubating on nutrient agar plates for 7 days at +20°C.

The ethanol solution was prepared by diluting 95% ethyl alcohol with purified sterile water, yielding a 70% v/v solution. The inoculations and spray treatments with ethanol were performed using an all-glass *Witeg* atomizer with rubber bulb, producing a very fine aerosol. The immersion treatment was made in a sterile glass container, all handling of the papers using sterilized tweezers. The temperature of the ethanol solution was +20°C in all treatments.

All incubations and recoveries were made on 2% malt extract (DIFCO) in 1,5% agar (DIFCO) and purified sterile water.

All materials and methods were applied using aseptic technique, working in a *laminar flow* biological safety cabinet.

Test series

Two series of tests were performed:

- Series A: 14 sterile Whatman papers were spray inoculated with the mixed suspension. After allowing the water to evaporate, 2 reference samples were directly transferred to malt agar (A 13–14), 6 were sprayed with ethanol until uniform dampening was achieved (A 1–6), and the remaining 6 samples were immersed in ethanol for 5 minutes , allowed to drain off surplus ethanol (A 7–12), and all 12 samples were allowed to dry separately for two hours to ascertain no retention of ethanol[38]. The treated samples were put on maltagar and together with references incubated at 20° C 95–98% RH for 14 days.
- In series B, 14 sterile Whatman papers were spray inoculated with the mixed suspension similar to series A. All 14 samples were directly transferred to malt agar, covered and incubated at 20°C 95–98% RH for 14 days.

After incubation of series A, growth was assessed with the two untreated samples as reference (A 13–14), and the type/types of colonizing organisms determined with the aid of the initial separate vitality plates. The results are given in Table 1.

Table 1: Test series A: colonizing species after treatment and 14 days incubation

	sample	A. flavus	A. niger	Ch. globosum	T. viride
Spray	1	0	+*	0	+
	2	0	+*	0	+
	3	0	+*	0	+
	4	0	+*	0	+
	5	0	+*	0	+
	6	0	+*	0	+
Immersion**	7	0	0	+	0
	8	0	+	+	0
	9	0	0	+	0
	10	0	0	+	0
	11	0	+	+	0
	12	0	0	+	0
	A13	0	0	0	+
	A14	0	0	0	+

0 no growth + growths

* The sporulating colonies of *A. niger* are concentrated to the center of the paperdiscs, covering an area of 2–4 cm in diameter, showing no inhibitory effect on adjacent *T. viride*, only a clearly visible discoloration (yellow/brown) of the paper substrate around the outer margins of the *A. niger* colonies.

** On all samples 7–12 the agar medium was coloured dark brown and had lost its original colour (clear amber). The minute *A. niger* colonies on samples 8 and 11 caused an inhibition zone of 3–5 mm in diameter on adjacent *C. globosum* colonies.

After incubation of series B, growth was assessed and taxonomic evaluation performed (Table 2), and these unnumbered samples were then lifted from the agar medium, air dried under controlled conditions for 48 hours (ca. 20°C, 40 % RH). 6 samples were then ethanol sprayed until uniform dampening was achieved (B 1–6), 6 samples were immersed in ethanol for 5 minutes and allowed to drain off the excess (B 7–12). The 12 samples were left to evaporate separately, for 2 hours, and then, together with 2 untreated reference samples (B 13–14), transferred to fresh malt agar, covered and incubated at 20°C 95–98% RH for 14 days. After this re-incubation, growth and type/types of colonizing

organisms were assessed and evaluated similar to series A. The results of series B are given in Table 2.

Table 2: Test series B: colonizing species after treatment and 14 days incubation

	sample	A. flavus	A. niger	Ch. globosum	T. viride
untreated*	–	0	0	0	+
Spray	1	0	+**	0	+
	2	0	+**	0	+
	3	0	+**	0	+
	4	0	+**	0	+
	5	0	+**	0	+
	6	0	+**	0	+
Immersion**	7	0	0	+	+
	8	0	0	+	+
	9	0	0	+	0
	10	0	0	+	0
	11	0	0	+	0
	12	0	0	+	+
References	B13	0	+	0	+
	B14	0	+	0	+

0 no growth + growths

* 14 untreated samples, identical in appearance and colonizing species

** Minute colonies

All observations evaluating fungal growth were performed by ocular inspection comparing the test samples to the untreated references. All determinations of colonizing species were made using an ordinary binocular microscope (magnification 20–40), comparing test samples to the initial viability plates. In evaluating the sporicidal properties of ethanol, only the absence or presence of clearly visible colonies are recorded.

RESULTS AND DISCUSSION

Fig. 1 and 2 show incubated treated samples compared to incubated and untreated. In no case was active growth absent after treatment with 70% ethanol, by either of the treatment methods in either of series A or B.

Table 1 shows the results of the A-series. Compared to the untreated reference-samples (A13–14; cf. Fig. 1b), which were evenly covered with Trichoderma

viride, the treated samples presented a shift in colonizing species. On the spray treated samples (A1–6) both Aspergillus niger and T. viride grew, the Aspergilli occupying the center of the substrate in all cases (Fig. 1a). On the immersion treated samples, however, T.viride was absent in all cases (A7–12) and the papers were instead evenly colonized by Chaetomium globosum, and A. niger only appeared as minute colonies on two samples. These A. niger-colonies caused an inhibition zone on adjacent C. globosum growth (A 8, 11).

Fig. 1: Several samples after 14 days incubation (A-series). left: spray treatment (A3); middle: untreated (A13) ; right: immersion 5 min (A10).

Fig. 2: Several samples after 14 days incubation, 2 days drying, ethanol treatment and 14 days re-incubation (B-series). left: spray treatment (B6); middle: untreated (B13); right: immersion 5 min (B11).

Table 2 shows the results of the B-series. Following incubation prior to treatment, all 14 samples were considered identical in colonization and appearance to the untreated reference samples A13–14 (cf. Fig. 1b) in that T.viride colonized all samples uniformly and no other species could be detected. After 48 hours of drying, ethanol treatment and 14 days re-incubation, a shift in species similar to phenomenon in series A was clearly visible. On the spray treated samples B 1–6 (Fig. 2a), both A. niger and T.viride grew, although the Aspergilli sporulating by minute, singly shattered conidiophores and T.viride as sparsely distributed

sporulating colonies. The immersion treated samples, B 7–12, showed presence of T. viride in 3 out of 6 samples, in contrast to the immersion treated samples A 7–12. A.niger did not grow at all on these samples (compare with A 8, A 11). Similar to samples A 7–12 , an abundant growth of C.globosum developed on immersion treated samples B 7–12. Aspergillus flavus did not sporulate in any of the samples although proven vital in the initial viability tests. This is an interesting result considering the study by Nyuksha[39] claiming A. flavus to be a species of considerable persistence, high biological activity and rapid growth, suppressing the growth of several other fungi in co-habitation. The strategies for growth and suppression interacting with a possible temporary growth inhibition caused by the ethanol are plausible explanations to the obtained results.

As is seen in Tables 1 and 2, there tends to develop some suppression mechanism mainly by T. viride and A. niger vs. C.globosum, – the latter colonizing habitats where T. viride and A. niger were absent, (A 7–12, B 9–11) or only present in minute amounts (A 8,11, (B 7,8,12). C. globosum retained viability even after immersion treatment, sporulating profusely in both series A and B, but failed to germinate on either of the untreated reference samples. Most probable, this is due to a concurrence situation of the co-habitants preventing colonization of C. globosum in their presence. Delaying the growth of A. niger and T. viride by rapid injury of vegetative parts with ethanol treatment makes conditions favorable for the germination of C. globosum.

The amount of germination potent spores treated by either of the methods, tends to be larger in the spray treated samples, presenting growth of both T. viride and A. niger. Comparing the viability of spores prior to treatment, A 13, 14, and B-series, no differences are detectable. Immersion treatment seemingly delays recovery of T. viride and A. niger in favour of C. globosum.

In comparing the study by Florian[7], stating ethanol as being a spore activator, to the results obtained in this study, it may be an explanation to why A. niger can establish on samples upon spray treatment (A and B 1–6), but not on untreated reference samples (A 13,14 and B-series prior to treatment). On the other hand, A. niger established on B 13, 14, which as references were left untreated, only air dried similar to the other samples in that group. After spray treatment, both samples A and B 1–6 showed similarities in colonization, although in A 1–6, the A. niger colonies were more developed (Table 1, Fig. 1a). There may be several explanations to these results; the 48 h drying period in test B might be beneficial to spore resistance, possibly inducing stasis (B 7, 8, 12–14), but explain the presence of A. niger on immersion treated samples in series A (A 8, 11).

The incubations and identification of colonizing species were made after 14 days. This time was recommended as sufficient by experienced researchers since prolonged incubation times very seldom presents any dramatic succession shifts

in these type of tests. No definite statements can however be made concerning these specific mechanisms since the number of influential variables are so diverse. In this particular set of organisms and under these given conditions, A. flavus might need more time to recover and develop, thus giving a possible explanation to its absence. Nutritional needs, pH, temperature etc., given in this test most certainly influence growth rates, suppressing mechanisms and reproduction strategies. Resistance to damage may also vary among strains of a particular species, even if they are cultured and stressed under identical conditions[40].

It must be emphasized that the obtained results in this study are somewhat sparse to draw generally applicable conclusions from. It goes without saying that results obtained from in-vitro testing cannot be directly applied to actual in-use/on-site conditions[28]. Further investigations, including larger series, strictly controlled variables etc., are needed in order to perform any statistical evaluations, and even in such studies, possible correlations in statistical data does not necessarily prove any connections or explanations. Since this study fails to acknowledge ethanol a complete inertness or inactive properties, it suggests paper conservators to put serious considerations into its continued use until the working mechanisms are fully investigated and the consequences for treated material are known.

Conclusions

Turning to the initially addressed questions and considering the obtained results, the following can be concluded:

- Ethanol applied as a 70% aqueous solution did not prove sporicidal, according to the evaluation parameters and conditions used in this test.
- The test indicates that ethanol immersion is more efficient than spray treatment in delaying the colonization of some species, however favouring growth of others in these tests.
- The test does not indicate whether the status of the spores (swollen or dried) prior to treatment affects their vulnerability to ethanol, although theoretically swollen, mature spores would be easier to injure[5]
- Indications on spore activating properties of ethanol, as claimed by Florian[7], could not be either verified or dismissed according to the evaluation method adopted in this test.

Due to these findings, the continued use of ethanol as fungal sanitizer in paper conservation is seriously questionable until further research has been performed, especially considering whether ethanol treatment lowers activation levels/arrests

stasis of spores. A situation which may prove fatal is otherwise close at hand if humidity levels would experience a sudden rise, or fluctuate: a situation not rarely occuring. The relation between pre-drying, ethanol sanitizing and survival of germination potent propagules is another important scope that needs further investigation.

The unrestricted use of toxic biocides has been far too common and is now hopefully rejected in conservation practice. However, the tendency of overbelief in "treatments" in the minds of many conservators, and the concept of ethanol sanitizing highlights this troublesome fact. The ideal "fungicide treatment" for conservation practice does not exist, and if it would, it could never solve the problem of fungal conditions; on the contrary: could enhance it. The overwhelming importance of preventive measures in order to control fungal biodeterioration in paper collections cannot be over-emphasized.

Summaries

Ethanol as fungal sanitizer in paper conservation

After discussing the basic data on fungal growth and the qualities of ethanol the results from a methodological study of the sporicidal efficiency of ethanol are evaluated. Spores from four different fungal species have been studied, applied as a mixed suspension inoculum. The sporicidal effects of ethanol applied as a 70% solution by spray and immersion to spore contaminated papers are compared to the effects of ethanol on mature and swollen spores from sporulating colonies on paper and to untreated reference samples. The results suggest that ethanol as applied is not sporicidal.

L'éthanol comme moyen fongicide dans la conservation du papier

Après une discussion de base sur la structure des champignons causant la moisissure et sur les conditions d'une infection fongique ainsi que sur les propriétés de l'éthanol nous présentons les résultats d'une analyse de l'effet sporicide de l'éthanol. Des spores de quatre différents types de champignons ont fait l'objet de l'étude réalisée sous forme de suspension inoculum mélangée. On a comparé les effets sporicides de l'éthanol appliqué en solution de 70% sous forme de pulvérisation ou d'immersion à des papiers contaminés par les spores aux effets de l'éthanol sur des spores mûres, séchées par le vent et créant des colonies de spores. On a abouti au résultat que l'éthanol appliqué sous cette forme n'est pas sporicide.

Äthanol als Mittel zur Schimmelbekämpfung

Nach einer Diskussion der Struktur von Schimmelpilzen und ihren Wachstumsbedingungen sowie der Eigenschaften des Äthanol werden die Ergebnisse einer Studie über die sporenabtötende

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1. Miles, C.: *Wood coatings for display and storage cases.* Studies in Conservation 31 (1986): 114–24.
2. Hon. D. N.-S.: *Yellowing of modern papers.* In: Williams, J. C., ed. Preservation of paper and textiles of historic and artistic value II. Advances in Chemistry Series, 193. Washington, DC: American Chemical Society, 1981: 119–42.

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Wirkung von Äthanol referiert. Sporen von vier unterschiedlichen Schimmelpilztypen waren Gegenstand der Untersuchung, appliziert als Misch-Inokulum. Der sporenabtötende Effekt von 70% Äthanol auf sporenpräpariertes Papier, aufgebracht als Spray oder in Immersion, wird mit dem Effekt von Äthanol auf reife und luftgetrocknete Sporen sporenbildendes Kolonien verglichen. Es ergab sich, daß Äthanol in der untersuchten Anwendungsform Schimmelsporen nicht abtötet.

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