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Investigation of the Fungicidal Activity of Sodium Tetraborate and on its Resistance to the Biological Attacks of a Polyvinyl Alcohol

by FAUSTA GALLO & LORENA BOTTI

Introduction

In time, paper materials undergo the process of deterioration due to physical, chemical and biological agents. Various processes are favoured or determined by special environmental conditions, by some physical and chemical characteristics of the paper itself, and by restorations made using inadequate methods. Concerning this last cause for deterioration, it seems obvious that it may be largely eliminated through a careful selection of the materials (adhesives, sizes, etc.) used for restoration. For this reason, experts in the conservation field have been carrying out investigations for many years, directed at singling out, from the wide range of such materials, those answering to a set of requisites; for example, their resistance to chemical and biological agents. The present research falls within the framework of these investigations aimed at evaluating the resistance to microbial attacks of a commercial product, Poval 205 which, according to preliminary tests performed at the Centro di Fotoriproduzione Legatoria e Restauro degli Archivi di Stato, seems to be applicable as a size.[1]

Material and Methods

Poval 205

Poval 205, manufactured by "Kurashiki Rayon", is a polyvinyl alcohol which occurs as a granulous white powder, giving a colourless solution in water. Among the various types of this commercial product, the 205 was selected because of certain characteristics such as high solubility in water, strong adhesion to cellulose and low viscosity, thus obtaining a satisfactory surface sizing. The viscosity of Poval 205 4% water solution is 4,7–5,4 cps at 20°C; the hydrolysis degree of this solution is 87,0–89,0 and its pH is in the range of 5 to 7.

1. Bicchieri, Bortolani, Veca "Investigation on the reinforcement of paper by means of Poval and of a Poval and borax solution". A report brought before the Direction of the Centro di Fotoriproduzione Legatoria e Restauro degli Archivi di Stato.

Restaurator 6: 1–20 © 1984 Munksgaard, Copenhagen

To obtain an alkaline pH and a better surface sizing, the manufacturers recommend adding an amount of sodium tetraborate ($Na_2B_4O_7 \cdot 10\ H_2O$) to the aqueous solution of Poval 205. This is also known to possess a microbicidal activity at given concentrations.[2]

The present research work, directed at evaluating the resistance of Poval 205 to the microbial agents, was organized as follows:

1) Examination of the fungicidal activity of borax at concentrations ranging from 0.15% to 2.4%;

2) examination of the resistance to the microbial attack, of 1% and 2% Poval, with or without addition of borax, applied on glass slides;

3) tests for evaluating the hygroscopicity of paper treated or not treated with Poval 205, with or without borax addition; and

4) examination of the resistance to microbial attacks offered by Poval 205 with or without the addition of borax applied on paper.

1. Examination of the fungicidal activity of borax

To investigate the fungicidal activity of borax, the dilution technique was adopted (3) (4), which consists of the inoculation of 0.1 cm^3 of water suspension of fungal spores in 10 cm^3 of Sabouraud's broth to which the following borax concentrations, 0.15%, 0.3%, 0.6%, 1.2%, 1.6%, 2.0%, 2.4%, were added. The culture media were then incubated for 14 days at 30°C. To estimate whether the tested borax concentrations did actually exert a fungistatic or fungicidal activity at the completion of the incubation period of the culture media, where no apparent development was observed, 1 cm^3 was removed, with which an inoculum was made on Sabouraud's agar in petri dishes. After a 14-day incubation, controls were performed.

Inocula were made with fungal spores taken from 14-day cultures of the following fungi:

Aspergillus niger Van Tieghem
Aspergillus terreus Thom
Chaetomium globosum Kunze
Alternaria tenuis (Fr) Keissler
Scopulariopsis brevicaulis (Sacc.) Bainier
Penicillium funiculosum Thom
Penicillium notatum Westling
Stachybotris atra Corda
Stemphylium botryosum Wallroth

2.This sodium salt of boric acid is commonly indicated by the name of borax, and will be thus mentioned by this terminology in the text for brevity.

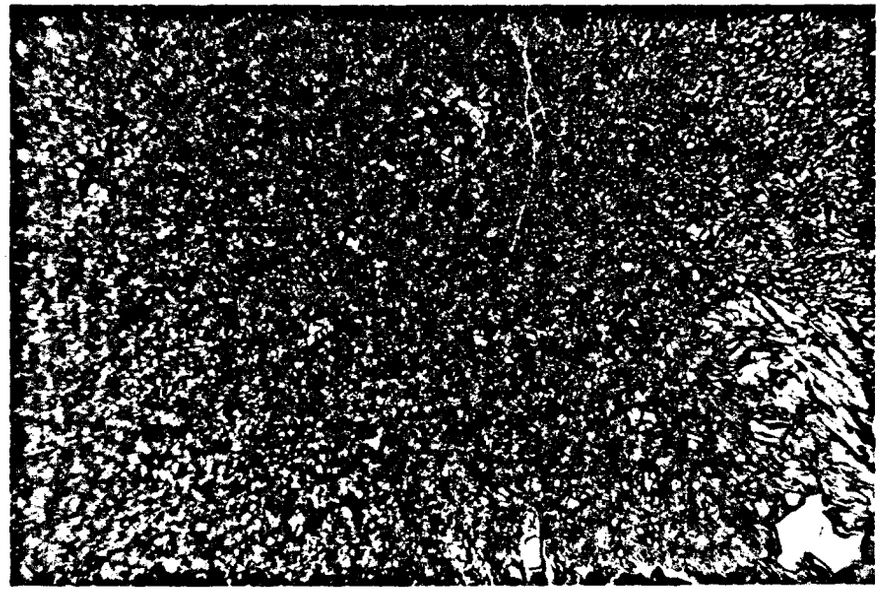

Fig. 1. Glass slide treated with Poval 1% (photo at microscope).
Fig. 1. Plaquette de verre traitée au Poval à 1% (préparation microscopique photographiée).
Abb. 1. Glasscheibe – behandelt mit 1%igem Poval (Mikroskop-Foto).

Fig. 2. Glass slide treated with Poval 1% + borax 2.0% (photo at microscope).
Fig. 2. Plaquette de verre traitée au Poval à 1% + borax 2,0% (préparation microscopique photographiée).
Abb. 2. Glasscheibe – behandelt mit 1%igem Poval und 2%igem Borax (Mikroskop-Foto).

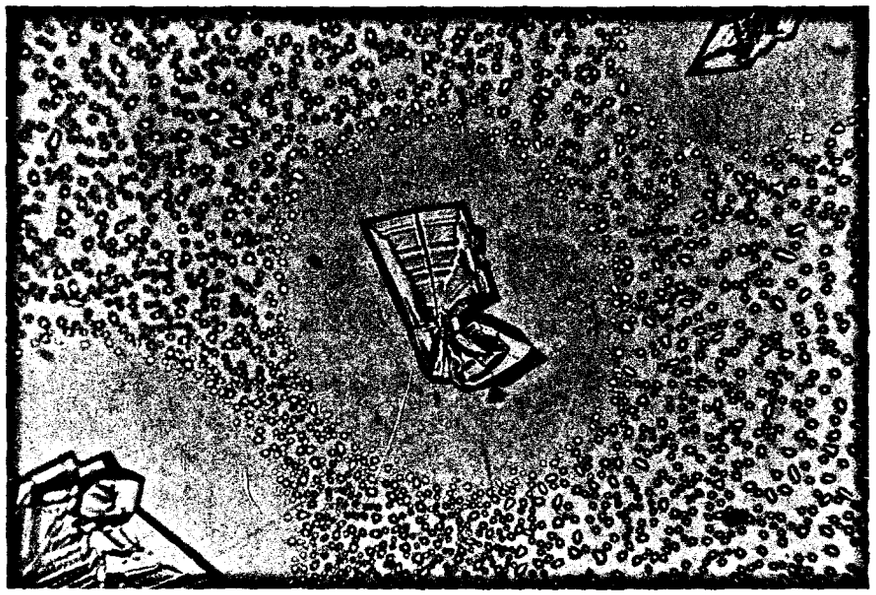

Fig. 3. Glass slide treated with Poval 2% + borax 0.6% (photo at microscope).
Fig. 3. Plaquette de verre traitée au Poval à 2% + borax 0,6% (préparation microscopique photographiée).
Abb. 3. Glasscheibe – behandelt mit 2%igem Poval und 0,6%igem Borax (Mikroskop-Foto).

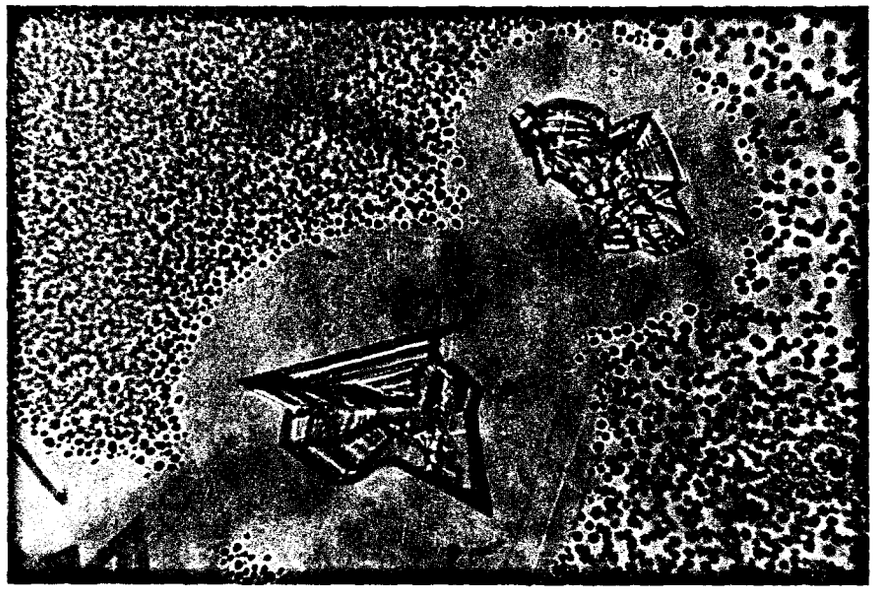

Fig. 4. Glass slide treated with Poval 2% + borax 1.2% (photo at microscope).
Fig. 4. Plaquette de verre traitée au Poval à 2% + borax 1.2% (préparation microscopique photographiée).
Abb. 4. Glasscheibe – behandelt mit 2%igem Poval und 1,2%igem Borax (Mikroskop-Foto).

Table 1.

Poval 205 concentration	Borax concentration
1%	–
1%	0.6%
1%	1.2%
1%	1.6%
1%	2.0%
1%	2.4%
2%	–
2%	0.6%
2%	1.2%

2. Examination of the resistance of Poval, with or without borax addition, applied on glass slides to microbial attacks

To evaluate the resistance opposed by Poval 205, with or without the addition of borax, to microbial attacks, the following technique was adopted:

Slides were immersed in the solutions indicated in Table 1 (Fig. 1,2,3,4). They were let dry for 24 h and then placed in dessiccators at 30°C and at the following R.H., which were obtained either with distilled water or with the saturated saline solutions indicated hereunder

R.H. 100% distilled water
R.H. 85% $Li_2SO_4 \cdot H_2O$
R.H. 63% $NaNO_2$

After incubation periods of 1,2 and 3 months, the slides were extracted from the dessiccators, laid on petri dishes on Sabouraud's agar, and incubated for 14 days at 30°C. Controls were made after 7 and 14 days.

3. Tests for evaluating the hygroscopicity of paper non-treated and treated with Poval 205 with or without borax added

For these tests, Whatman no. 1 was used. 20 cm × 20 cm sheets were immersed for 10 min into the size solutions indicated in Table 1.

To investigate the hygroscopicity variations occurring in the paper as a result of the sizing treatment, with or without borax, the following method was adopted:

Table 2.

R.H.	20°C	30°C
100%	H_2O	H_2O
92%	$BaCl_2$	KNO_3
85%	Li_2SO_4	Li_2SO_4
75%	NaCl	NaCl
63%	NH_4NO_3	$NaNO_2$

4 cm^3 of the mineral salt saturated solutions, as indicated in Table 2, were placed in test-tubes closed by means of a screw plug, and were incubated at 20°C and at 30°C for 4 days. On completion of this period, the paper samples were put in the test-tubes and incubated for 5 days at the same temperature[3]. The water absorption was then calculated to the ASTM D644–55 standard "Standard Method of Test for Moisture Content of Paper and Paperboard by Oven Drying".

4. Examination of the resitance to microbial attacks of Poval 205, with or without borax addition, applied on paper

To evaluate the resistance to the microbial attack of paper treated with sizes (treatment method as described in the foregoing paragraph) the Block technique[1] and that recommended by ASTM D2020 standard "Mildew (Fungus) Resistance of Paper and Paperboard", were adopted.

a. Block technique

Small (5 cm × 1 cm) paper rectangles were suspended in screw-plug test-tubes containing 4 cm^3 of the saturated solutions listed in Table 2, which permit R.H. percentages comprised in the range of 100% and 63%.

The sample incubated at 20°C and at 30°C were subjected to controls after 1,2,3,4,5,10, and 20 weeks.

To estimate the extent of the microbial attack, we used the arbitrary scale from 1 to 5 adopted by Block to numerically express the results:

3. To obtain, in the test-tubes, the desired thermohygrometric values, and to let the sample enter in balance with the environment, the times of 4 and 5 days were respectively chosen on the basis of the experiments conducted by F. Gallo, C. Marconi and M. Montanari[2].

0 = Absence of growth
T = Traces
1 = Very weak growth
2 = Weak growth
3 = Extensive growth
4 = Strong growth
5 = Very strong growth

b. ASTM D2020 Standard

These experiments were performed using the technique recommended by the above mentioned Standard, which consists in laying the samples to be examined on 14 days fungal culture media, and in estimating the extent of the fungal development on paper after a 7 and 14 day incubation.

In the course of the investigation, we would also have liked to evaluate the resistance to microbial attack of Poval 205 solutions, adopting the viscosimetric techniques recommended by ASTM D 1286–57 Standard (Riappr. 1965–72).

It was unfortunately impossible to adopt this method because the sizing solutions, with or without borax addition, which we considered, had a very low viscosity and, at any rate, no variations of it could be appreciated using the Brookfield viscosimeter in our possession.

RESULTS

A. Results concerning the tests on the fungicidal activity of borax

The findings shown in Table 3 reveal that borax, at concentration in the range of 0.15% and 0.6% exercised a fungistatic activity only on *Scopulariopsis brevicaulis* and on *Penicillium funiculosum.*

At concentrations comprised between 1.2% and 2.4% the above mentioned sodium salt of boric acid has acted as a fungistatic on such species as *Aspergillus terreus, Aspergillus niger, Penicillium notatum, Stemphylium botryosum, Stachybotrys atra, Chaetomium globosum* and *Scopulariopsis brevicaulis;* and at concentrations of 2.0% and 2.4% it performed a fungicidal activity on *Chaetomium elatum, Alternaria tenuis* and *Penicillium funiculosum.*

Table 3.

FUNGI	Broth cultures at various borax percentage. Bouillons à pourcentages variables de borax. Fleischbrühekulturen bei unterschiedlichem prozentualen Gehalt von Borax.												Subcultures on Sabouraud's agar. Sous-cultures sur agar de Sabouraud. Subkulturen auf Sabouraud-Agar.											
	0			0.15%			0.3%			0.6%			0			0.15%			0.3%			0.6%		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Aspergillus terreus	+	+	+	+	+	+	+	+	+	+	+	+												
Aspergillus niger	+	+	+	+	+	+	+	+	+	+	+	+												
Penicillium notatum	+	+	+	+	+	+	+	+	+	+	+	+												
Penicillium funiculosum	+	+	+	–	+	–	–	+	–	–	+	–				+		+	+		+	+		+
Scopulariopsis brevicaulis	+	+	+	+	+	+	+	+	+	–	–	–										+	+	+
Stachybotrys atra	+	+	+	+	+	+	+	+	+	+	+	+												
Alternaria tenuis	+	+	+	+	+	+	+	+	+	+	+	+												
Stemphylium botryosum	+	+	+	+	+	+	+	+	+	+	+	+												
Chaetomium elatum	+	+	+	+	+	+	+	+	+	+	+	+												
Chaetomium globosum	+	+	+	+	+	+	+	+	+	+	+	+												
	1.2%			1.6%			2.0%			2.4%			1.2%			1.6%			2.0%			2.4%		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Aspergillus terreus	–	–	+	–	+	–	–	–	–	–	–	–	+	+		+		+	+	+	+	+	+	+
Aspergillus niger	–	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+	+	+	+	+	+
Penicillium notatum	–	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+	+	+	+	+	+
Penicillium funiculosom	–	–	–	–	–	–	–	–	–	–	–	–	–	+	–	–	–	–	–	–	–	–	–	–
Scopulariopsis brevicaulis	–	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+	+	+	+	+	+
Stachybotrys atra	+	+	+	+	–	+	–	–	–	–	–	–					+		+	–	–	+	–	–
Alternaria tenuis	–	+	+	+	–	+	–	–	–	–	–	–	–				+		–	–	–	–	–	–
Stemphylum botryosum	–	–	–	–	+	–	–	–	–	–	–	–	–	–	–	+		–	+	–	+	–	+	–
Chaetomium elatum	–	–	–	–	–	–	–	–	–	–	–	–	+	–	–	–	–	–	–	–	–	–	–	–
Chaetomium globosum	–	–	–	–	–	–	–	–	–	–	–	–	+	+	–	–	+	+	–	+	+	–	+	+

B. Results concerning the resistance to microbial attacks of Poval 205 with or without the addition of borax applied on glass slides

From the data summarized in Table 4, it emerges that at 30°C and at 100% and 85% of R.H., an abundant microbial development occurred, after 30, 60 and 90 days of incubation, on all the samples treated with Poval 205 at 1%, 2%, 10% and 15% concentration and not containing borax (Fig. 5 and 6). At 63% R.H., fungal attacks occurred almost exclusively on the slides treated with the highest Poval concentrations (10%, 15%).

The results obtained further revealed that, at R.H. 100% and 85% and after the same incubation periods indicated above, the microbial attack occurred on a high number of samples on which borax-containing Poval had been applied

Table 4. Poval and borax applied on glass slides and incubated for 1,2,3 months at various relative humidity percentages.
Table 4. Poval et borax appliqués sur des plaques de verre et incubés durant 1, 2, 3 mois à diverses humidités.
Tabelle 4. Auftragung von Poval und Borax auf Glasplatten mit Inkubationszeiten von einem, zwei und drei Monaten bei unterschiedlichem prozentualen Gehalt an relativer Luftfeuchtigkeit.

	I series			II series			III series		
Samples %	100%	85%	63%	100%	85%	63%	100%	85%	63%
P 1	++	++	–	++	++	–	++	++	–
P 1 + B 0.6%	o	–	–	++	oo	–	++	oo	–
P 1 + B 1.2%	oo	oo	–	++	++	–	++	oo	–
P 1 + B 1.6%	–	–	–	++	oo	–	–	++	++
P 1 + B 2.0%	++	–	–	++	++	–	++	–	–
P 1 + B 2.4%	–	–	–	++	+o	–	++	–	–
P 2	++	++	+	+o	++	–	++	o	–
P 2 + B 0.6%	++	++	–	++	++	–	++	–	–
P 2 + B 1.2%	++	o	–	++	+	–	+o	–	–
P 10	++	++	+	++	+o	–	++	–	++
P 15	++	++	++	++	+	–	++	++	++

I series = 1 month of incubation
II series = 2 months of incubation
III series = 3 months of incubation
– = absence of development
\+ = weak fungal development
++ = abundant fungal development
o = weak bacterial development
oo = abundant bacterial development

Fig. 5. Development on glass slide treated with Poval 1%, incubated for 1 month at 100% RH and laid on Sabouraud's agar.
Fig. 5. Croissance observée sur plaquette traitée à 1% de Poval après incubation pendant 1 mois à H.R. 100% et couché sur agar de Sabouraud.
Abb. 5. Entwicklung, die sich auf einem Objektträger zeigt, der mit 1%igem Poval behandelt worden ist. Inkubationszeit 1 Monat bei 100% relativer Feuchtigkeit auf Sabouraud-Agar.

Fig. 6. Development on glass slide treated with Poval 2%, incubated for 1 month at 100% RH and laid on Sabouraud's agar.
Fig. 6. Croissance observée sur plaquette traitée à 2% de Poval après incubation pendant 1 mois à H.R. 100% et couché sur agar de Sabouraud.
Abb. 6. Entwicklung, die sich auf einem Objektträger zeigt, der mit 2%igem Poval behandelt worden ist. Inkubationszeit 1 Monat bei 100% relativer Feuchtigkeit auf Sabouraud-Agar.

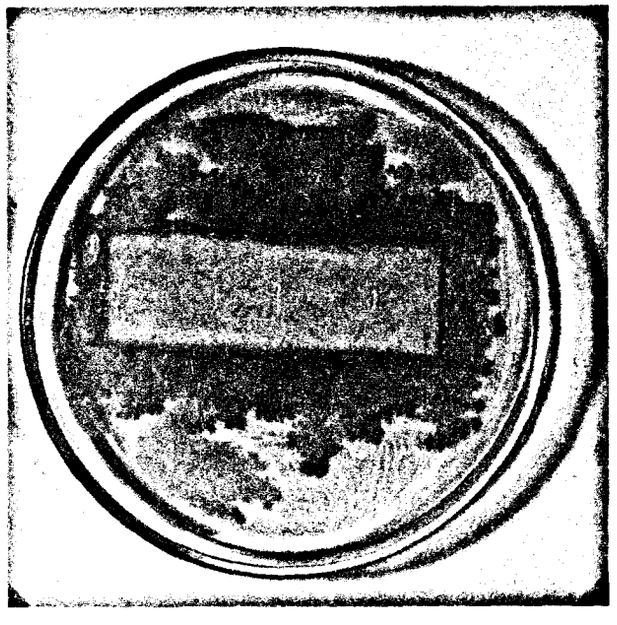

Fig. 7. Development on glass slide treated with Poval 1% + borax 0.6%, incubated for 1 month at 85% RH and laid on Sabouraud's agar.
Fig. 7. Croissance observée sur plaquette traitée à 1% de Poval + borax 0,6% après incubation pendant 1 mois à H.R. 85% et couché sur agar de Sabouraud.
Abb. 7. Entwicklung, die sich auf einem Objektträger zeigt, der mit 1%igem Poval und 0,6%igem Borax behandelt worden ist. Inkubationszeit 1 Monat bei 85% relativer Feuchtigkeit auf Sabouraud-Agar.

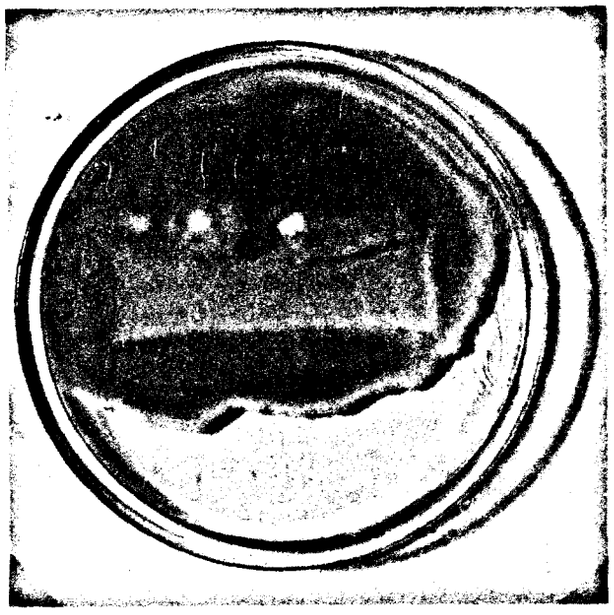

Fig. 8. Development on glass slide treated with Poval 1% + borax 2.0%, incubated for 1 month at 63% RH and laid on Sabouraud's agar.
Fig. 8. Croissance observée sur plaquette traitée à 1% de Poval + borax 2,0% après incubation pendant 1 mois à H.R. 63% et couché sur agar de Sabouraud.
Abb. 8. Entwicklung, die sich auf einem Objektträger zeigt, der mit 1%igem Poval und 2%igem Borax behandelt worden ist. Inkubationszeit 1 Monat bei 63% relativer Feuchtigkeit auf Sabouraud-Agar.

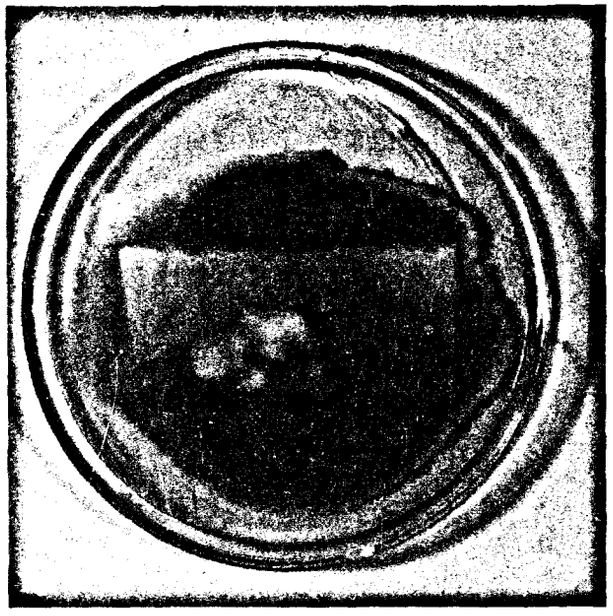

Fig. 9. Development on glass slide treated with Poval 2% + borax 0.6%, incubated for 1 month at 85% RH and laid on Sabouraud's agar.
Fig. 9. Croissance observée sur plaquette traitée à 2% de Poval + borax 0,6% après incubation pendant 1 mois à H.R. 85% et couché sur agar de Sabouraud.
Abb. 9. Entwicklung, die sich auf einem Objektträger zeigt, der mit 2%igem Poval und 0,6%igem Borax behandelt worden ist. Inkubationszeit 1 Monat bei 85% relativer Feuchtigkeit auf Sabourad-Agar.

(Fig. 7, 8 and 9). As can be seen, borax provided a protective action only in some cases.

At 63% R.H., borax prevented the development of microorganisms in nearly all cases. In fact, a fungal development occurred, after 3 months of incubation, only on a sample treated with 1% Poval contaning 1.6% borax.

C. Results concerning the tests on the hygroscopicity of paper not treated and treated with Poval 205 with or without addition of borax

A comparison made between the results obtained with Whatman not subjected to any treatment and that treated with 1% and 2% Poval, reveals that the size at these concentrations does not appreciably change the hygroscopicity of paper (Table 5). Moreover, from the data shown in Table 5, it shows that the paper sized with borax-containing Poval is more hygroscopic than that sized only with 1% and 2% Poval, and this hygroscopicity increases relatively to the increase of the borax concentration.

The examination of the data relating to the non-treated Whatman and of those relating to the Whatman treated only with borax shows that the latter is more hygroscopic than the former.

Table 5. Percentage of water lost by treated and not treated papers with Poval and Poval + borax.
Table 5. Pertes d'eau en % des papiers traités ou non traités avec du poval et du poval + borax.
Tabelle 5. Prozentualer Anteil des Wasserverlustes in Papieren, die mit Poval bzw. Poval-Borax behandelt/nicht behandelt sind.

Samples %	(1) 100% RH		(2) 91–92% RH		(3) 85% RH		(4) 75% RH		(5) 63% RH	
	20°C	30°C	20°C	30°C	20°C	30°C	20°C	30°C	20°C	30°C
P 1	14.05	17.04	12.20	12.82	10.79	10.6	9.34	8.20	8.01	6.98
P 1+B 1.2	15.96	17.65	13.36	14.65	11.86	13.13	10.24	10.14	8.85	8.06
P 1+B 1.6	17.36	18.21	13.96	15.40	12.42	13.38	10.64	10.37	9.17	8.48
P 1+B 2.4	16.90	20.66	14.47	15.71	12.66	13.08	10.93	10.59	9.47	8.63
P 2	14.14	18.56	11.70	13.53	10.29	11.39	8.71	9.05	7.36	7.08
P 2+B 0.6	14.88	18.50	12.61	12.84	11.31	11.32	9.82	9.37	8.34	7.60
P 2+B 1.2	15.31	19.19	12.94	14.73	11.43	11.77	10.17	9.92	8.56	8.30
B 1.2	15.40	18.60	13.38	14.24	11.94	12.27	10.27	9.54	8.64	7.91
B 2.4	15.99	19.31	13.51	14.43	12.10	12.88	10.53	9.94	9.13	8.14
Whatman No. 1.	15.60	15.16	12.48	12.21	10.72	10.71	8.92	8.52	7.50	6.90

D. Results relating to tests on the relationship between hygroscopicity of paper treated with Poval 205, and the development of microorganisms (Tests performed using the Block method)

The tests carried out with this method showed that the paper treated with 2% Poval 205, containing no fungicide, is more susceptible to microbial attacks than paper not treated with the size (Table 7).

The results obtained further revealed that on the paper treated with 1% Poval and containing 1.2%, 1.6% borax, and on that treated with 2% Poval and 0.6% and 1.2% borax, no microbial growth occurred even after 20 weeks of incubation at 20°C and 30°C and at R.H. in the range of 100% and 63% (Tables 6 and 7). A very weak growth of fungi took place only at 92% R.H. and at 20°C and at 100% R.H. on samples sized with 1% Poval containing 2.4% borax (Table 6).

It is interesting to note that on the unsized paper and on the paper sized with 1% Poval and with 1% and 2% Poval containing borax, no microbial attacks even occurred at 85%–75% and 63% R.H., whereas on the paper treated with 2% Poval, a moderate growth of microorganisms took place at 30°C and 85% RH. (Table 8).

Two other factors to be considered in the evaluation of the data obtained are the intensity of growth and the period of time in which such a growth takes

Table 6.

Concentration of Poval %	Concentration of borax %	Time in weeks	Temperature 30°C % of R.H. 100	92	85	75	63	Temperature 20°C % of R.H. 100	92	85	75	63
		1	0	0	0	0	0	0	0	0	0	0
		2	3	0	0	0	0	0	0	0	0	0
		3	3	0	0	0	0	1	0	0	0	0
1	–	4	3	0	0	0	0	2	0	0	0	0
		5	3	0	0	0	0	2	0	0	0	0
		10	3	0	0	0	0	2	0	0	0	0
		20	3	0	0	0	0	3	0	0	0	0
		1	0	0	0	0	0	0	0	0	0	0
		2	0	0	0	0	0	0	0	0	0	0
		3	0	0	0	0	0	0	0	0	0	0
1	1.2	4	0	0	0	0	0	0	0	0	0	0
		5	0	0	0	0	0	0	0	0	0	0
		10	0	0	0	0	0	0	0	0	0	0
		20	0	0	0	0	0	0	0	0	0	0
		1	0	0	0	0	0	0	0	0	0	0
		2	0	0	0	0	0	0	0	0	0	0
		3	0	0	0	0	0	0	0	0	0	0
1	1.6	4	0	0	0	0	0	0	0	0	0	0
		5	0	0	0	0	0	0	0	0	0	0
		10	0	0	0	0	0	0	0	0	0	0
		20	0	0	0	0	0	0	0	0	0	0
		1	0	0	0	0	0	0	0	0	0	0
		2	0	0	0	0	0	T	0	0	0	0
		3	0	0	0	0	0	1	0	0	0	0
1	2.4	4	0	0	0	0	0	1	0	0	0	0
		5	0	T	0	0	0	1	0	0	0	0
		10	0	1	0	0	0	1	0	0	0	0
		20	0	1	0	0	0	1	0	0	0	0

place. Table 9 shows that the most intensive microbial attacks occurred on the unsized samples and on the samples sized with 1% and 2% Poval 205. Infection on the latter took place after comparatively short incubation periods (Table 10).

Table 7.

Concentration of Poval %	Concentration of borax %	Time in weeks	Temperature 30°C % of R.H. 100	92	85	75	63	Temperature 20°C % of R.H. 100	92	85	75	63
		1	0	0	0	0	0	0	0	0	0	0
		2	2	0	0	0	0	1	0	0	0	0
		3	2	0	1	0	0	1	0	0	0	0
2		4	2	0	1	0	0	2	0	0	0	0
		5	2	0	1	0	0	2	0	0	0	0
		10	2	0	1	0	0	2	0	0	0	0
		20	2	0	1	0	0	2	1	0	0	0
		1	0	0	0	0	0	0	0	0	0	0
		2	0	0	0	0	0	0	0	0	0	0
		3	0	0	0	0	0	0	0	0	0	0
2	0.6	4	0	0	0	0	0	0	0	0	0	0
		5	0	0	0	0	0	0	0	0	0	0
		10	0	0	0	0	0	0	0	0	0	0
		20	0	0	0	0	0	0	0	0	0	0
		1	0	0	0	0	0	0	0	0	0	0
		2	0	0	0	0	0	0	0	0	0	0
		3	0	0	0	0	0	0	0	0	0	0
2	1.2	4	0	0	0	0	0	0	0	0	0	0
		5	0	0	0	0	0	0	0	0	0	0
		10	0	0	0	0	0	0	0	0	0	0
		20	0	0	0	0	0	0	0	0	0	0
		1	0	0	0	0	0	0	0	0	0	0
		2	0	0	0	0	0	0	0	0	0	0
		3	0	0	0	0	0	0	0	0	0	0
Whatman No. 1. Not treated		4	0	0	0	0	0	T	0	0	0	0
		5	0	0	0	0	0	1	0	0	0	0
		10	0	0	0	0	0	1	0	0	0	0
		20	0	0	0	0	0	2	0	0	0	0

Table 8. Percentages of relative humidity at which a microbial development did not occur after 10 and 20 weeks of incubation.
Table 8. Humidités relatives en % sans apparition de développement microbien après 10 et 20 semaines d'incubation.
Tabelle 8. Prozentualer Gehalt relativer Luftfeuchtigkeit, bei der sich nach 10 und 20 Wochen Inkubationszeit kein Mikroleben entwickelt.

Concentration of Poval %	Concentration of borax %	30°C		20°C	
		10 weeks	20 weeks	10 weeks	20 weeks
1	–	92%	92%	92%	92%
1	1.2	100%	100%	100%	100%
1	1.6	100%	100%	100%	100%
1	2.4	85%	85%	92%	92%
2	–	75%	75%	92%	85%
2	0.6	100%	100%	100%	100%
2	1.2	100%	100%	100%	100%
Whatman No. 1. Not treated		100%	100%	92%	92%

Table 9. Development intensity after 10 and 20 weeks at 100% relative humidity
Table 9. Ordre de grandeur du développement après 10 et 20 semaines a 100% d'humidité relative.
Tabelle 9. Entwicklungsintensität nach 10 und 20 Wochen bei 100% relativer Luftfeuchtigkeit.

Concentration of Poval %	Concentration of borax %	10 weeks 30°C	10 weeks 20°C	20 weeks 30°C	20 weeks 20°C
1	–	3	3	3	3
1	1.2	0	0	0	0
1	1.6	0	0	0	0
1	2.4	0	1	0	1
2	–	2	2	2	2
2	0.6	0	0	0	0
2	1.2	0	0	0	0
Whatman No. 1. Not treated		0	1	0	2

Table 10. Weeks in which a first microbial development occurred at 100% and at 20°C and 30°C incubation temperature.
Table 10. Semaines où un début de développement microbien est intervenu à une H.R. de 100% et à des températures d'incubation de 20 et 30°C.
Tabelle 10. Anzahl Wochen, nach denen sich bei 100% relativer Luftfeuchtigkeit und bei 20°C und 30°C Inkubationstemperatur eine erste mikrobiologische Entwicklung zeigt.

Concentration of Poval %	Concentration of borax %	30°C	20°C
1	–	2	3
1	1.2	0	0
1	1.6	0	0
1	2.4	5	2
2	–	2	2
2	0.6	0	0
2	1.2	0	0
Whatman No. 1. Not treated		0	4

E. Results relating to tests on the susceptibility to microorganisms of paper treated with Poval (Tests carried out according to the method recommended by ASTM D2020 Standard)

None of the examined samples appeared to be resistant to *Aspergillus niger*, *Aspergillus terreus* and *Chaetomium globosum* (Table 11).

From a more detailed evaluation of the data relating to the single strains, it emerges that the fungal development was lower on some samples of paper than on others, and that no such development ever occurred in some cases.

In estimating these findings which are, in some aspects, seemingly in conflict with those relating to the tests referred to in paragraph A, one should bear in mind that the inoculum of the paper samples was made with an amount of fungal spore suspension ten times higher than that used for the experiments on the fungal activity of borax. The ratio between the spore concentration and borax concentrations was thus different in the two tests, which accounts for the apparent differences recorded.

CONSIDERATIONS AND CONCLUSIONS

The results obtained in the course of the present research prompt us to put forth the following:

Table 11. Susceptibility of Whatman paper treated with poval and poval + borax.
Table 11. Susceptibilité de papier Whatman traité au poval et au poval + borax.
Tabelle 11. Anfälligkeit von Whatman-Papier, das mit Poval bzw. mit Poval-Borax behandelt worden ist Konzentration von Poval und Poval-Borax.

Concentration of Poval and Poval+borax %	Fungal species								
	Aspergillus terreus			Aspergillus niger			Chaetomium globosum		
	I	II	III	I	II	III	I	II	III
P 1	+++	+++	+++	++++	++++	++++	+++	+++	+++
P 1 + B 1.2	+++	+++	+++	+++	++++	++++	++	+++	+++
P 1 + B 1.6	+++	+++	+++	–	+++	+++	+++	+++	+++
P 1 + B 2.4	+++	+++	+++	+	++	+++	++++	++++	++++
P 2	++	+++	+++	+	+	–	+++	++++	+++
P 2 + B 0.6	+++	+++	+++	–	++	–	++++	++++	++++
P 2 + B 1.2	+++	+++	+++	+++	++	+++	++++	++++	++++
B 1.2	+++	+++	+++	+++	++	+++	++++	++++	++++
B 2.4	+++	+++	+++	++	++	–	++++	++++	++++
Whatman No. 1.	+++	+++	+++	+++	++++	++++	++++	++++	++++

I = I series
II = II series
III = III series
– = absence of development
\+ = presence of limited development
++ = presence of diffuse development with weak sporification
+++ = presence of diffuse development with abundant sporification
++++ = presence of diffuse development with formation of thick miceliar stratum and a very abundant sporification

I. Borax, when added to Poval 205 to obtain some given requisites, exerts on the whole, at the higher concentrations we used, a fungistatic and not fungicidal action. The paper materials subjected to this type of sizing, if not kept in optimal climatic conditions may, in time, undergo microbial attacks.

These considerations are mostly confirmed by the results found on glass slides (see paragraph B) from which, at 63% R.H., no growth of microorganisms occurred after a 3 month incubation at 30°C, in the presence of lower borax concentrations and without borax.

II. As shown by the test results mentioned in paragraph C, borax increases the hygroscopicity of paper. Therefore, whilst on the one hand this sodium salt of boric acid exercises a somewhat protective action, it could, on the other

hand, bring about conditions more favourable to the development of certain microbial species that do not fall within its action spectrum[4].

III. The results of tests performed by the Block method were chiefly directed at estimating the ratios between the water content of paper and the growth of microbial agents. These results are corroborated by data appearing in the literature, according to which the onset of infection occurs when the water content of paper is higher than 8–10%, as well as by the results of a previous research carried out by the biology laboratory of ICPL, which showed that this hygrometric level can be exceeded even by several units without any microbial attacks ever occurring.

These tests further revealed that the paper treated with Poval containing no borax is more sensitive to microbial attacks than that treated with Poval plus borax.

The above mentioned considerations allow the conclusion that paper treated with borax-containing Poval, although presenting a remarkable resistance to microbial agents, may still undergo degradation processes if kept in environments with high thermohygrometric values.

It would be of value to further investigate the spectrum and persistence of borax, in order to more comprehensively evaluate the protective action this compound is likely to exercise on paper.

SUMMARIES

Investigation of the Fungicidal Activity of Sodium Tetraborate and on its Resistance to the Biological Attacks of a Polyvinyl Alcohol.

In this study a research on the fungicidal activity of sodium tetraborate was developed. Moreover, a positive action is evident when this sodium salt of boric acid is added to the polyvinylic alcohol that is used as a size in the restoration of paper materials.

Étude de l'activité fongique du tetraborate de sodium et de la resistance d'un alcool polyvinylique aux dégradations d'ordre biologique.

Ces travaux de recherche portent sur l'activité fongique du tétraborate de sodium. De plus, l'action de ce produit a été mise en évidence lors de l'emploi du sel de sodium de l'acide borique comme adjuvant de l'alcool polyvinylique utilisé lors de la restauration de matériels à base de papier.

4. To better evaluate the influence these hygroscopic variations may exercise on the onset of possible infections, it would be advisable that the phenomenon we observed should be examined by chemists, with a view to quantitatively assessing whether such variations are due to actual changes in paper hygroscopy, or to the loss of water molecules by borax. In fact, the literature data show that this sodium salt of boric acid loses 3.4% molecules of water at 80°C.

Untersuchung über die pilztötende Tätigkeit von Natriumtetraborat und über die Widerstandsfähigkeit von Polyvinylalkohol gegenüber biologischer Zerstörung.

In dieser Arbeit wurde eine Untersuchung über die pilztötende Wirksamkeit von Natriumtetraborat durchgeführt. Darüber hinaus wurde dessen Wirksamkeit bewiesen, wenn Natriumsalz der Borsäure als Zusatzstoff in Polyvinylakohol verwendet wird, der bei der Restaurierung von Papiermaterialien Anwendung findet.

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Die Aussagekraft einer künstlichen Alterung von Papier für Prognosen über seine zukünftige Benutzbarkeit*

von HELMUT BANSA *und* HANS H. HOFER

1. Situation

In der Presse[1] und in populärwissenschaftlichen[2] sowie in archivalischen und bibliothekarischen Zeitschriften[3] finden sich seit rund fünfundzwanzig Jahren immer wieder Situationsschilderungen aus Archiv und Bibliothek über die Folgen der mangelhaften Dauerhaftigkeit des modernen, industriell hergestellten Papiers. Es werden Prognosen gestellt, daß hohe Prozentsätze der gesamten Buchproduktion unseres und des vergangenen Jahrhunderts im nächsten nicht mehr benutzbar sein werden. Gegen sie wurde von verschiedenen Seiten darauf hingewiesen[4,5], daß die Wirklichkeit in den Magazinen von Bibliothek und Archiv ihnen nicht ganz entspricht. Das Papier mancher – nicht aller – Bücher und Archivalien ist zwar schlecht genug, aber zum Glück ist die Gesamtheit des Sammelgutes keineswegs in so desolatem Zustand wie sie es nach den Prognosen von früher sein müßte.

Die Diskrepanz zwischen Prognose und Wirklichkeit hat vor allem zwei Gründe. Zum einen orientierte sich der Begriff der prognostizierten Benutzbarkeit in Bibliothek und Archiv an den Festigkeitsanforderungen, die ganz andere Anwender an das Papier stellen, z.B. die Verpackungs- und die Druckindustrie. Der Rückgang entsprechender Festigkeitswerte wurde als Verlust der Benutzbarkeit in Bibliothek und Archiv interpretiert. Zum anderen setzte man die Veränderungen, die eine künstliche Alterung, d.h. das Lagern bei erhöhter Temperatur in kurzer Zeit an Papier hervorruft, gleich mit den Veränderungen, die durch das Lagern bei Zimmertemperatur über eine längere Zeit eintreten. Die einschlägigen Meß- und Prüfkriterien haben auch Eingang in die Forschung zur Restaurierungskunde gefunden und haben dort, wie es scheint, zu teilweise irrigen oder zu anzweifelbaren Aussagen über die langfristige Wirksamkeit von Konservierungs- und Restaurierungsmaßnahmen geführt.

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* Bericht über einen Versuch, der im Institut für Buch- und Handschriftenrestaurierung im Rahmen eines von der Stiftung Volkswagenwerk geförderten Forschungsprojektes über die Alterungsbeständigkeit von Papier durchgeführt wurde.

Restaurator 6: 21–60 © 1984 Munksgaard, Copenhagen

Zur Arbeit an einem größeren Forschungsprojekt der Restaurierungskunde, das mit Hilfe der Stiftung Volkswagenwerk in Zusammenarbeit mit anderen Forschungseinrichtungen im Institut für Buch- und Handschriftenrestaurierung der Bayerischen Staatsbibliothek durchgeführt wird, war es notwendig diese Meß- und Prüfkriterien näher zu untersuchen mit dem Ziel, ihren Bezug zur Wirklichkeit in Archiv und Bibliothek zu definieren. Zum realitätsbezogenen meßtechnischen Erfassen des Begriffes »Benutzbarkeit« von gealtertem Papier in Archiv und Bibliothek wurde eine Studie veröffentlicht[6]. Zum Evaluieren der Aussagekraft der künstlichen Alterung war zunächst eine reichhaltige Literatur durchzusehen.

2. Bisherige Forschung

In der Forschung wird schon lange daran gezweifelt, ob die Gleichsetzung der Veränderungen, die das Lagern bei erhöhter Temperatur in kurzer Zeit an Papier hervorruft, mit den Veränderungen, die beim langfristigen Lagern bei Zimmertemperatur eintreten, zulässig ist[7,8]. Eine interessante Veröffentlichung[9] behauptet zwar die Parallelität von künstlicher und natürlicher Alterung, liefert in ihren Meßwert-Tabellen aber gute Argumente dagegen. Sie berichtet über einen 1973 durchgeführten Vergleich der Meßwerte von 36 Jahre alten Papieren, Laborprüfblätter von 1937, mit den Meßwerten, die die gleichen Papiere nach einer unmittelbar nach ihrer Herstellung durchgeführten künstlichen Alterung aufwiesen. Das Verhältnis zwischen den Meßwerten für Alpha-Cellulose kann, um die stärkste Diskrepanz aufzuzeigen, 17.5 oder 1.75 oder jeden Wert dazwischen betragen. Die künstliche Alterung im Jahre 1937 hätte, wenn man eine Parallelität zwischen künstlicher Alterung und natürlicher als Voraussetzung für jeden Schluß von dieser auf jene annimmt, das eine Papier so verändert, wie es 36 Jahre: 17.5 = 2 Jahre, das andere wie es 36 Jahre: 1.75 = 20 Jahren entspricht. Die Falzzahl nach der künstlichen Alterung von 1937 ist teils größer und teils kleiner als die nach der natürlichen Alterung seit 1937; aus ihr ließe sich unter der Voraussetzung einer Parallelität die damals stattgehabte künstliche Alterung als Äquivalent zu beträchtlich mehr und zu beträchtlich weniger als 36 Jahre natürlicher Alterung errechnen.

Der Zweifel an der Aussagekraft einer künstlichen Ofenalterung drängt sich auch deshalb auf, weil es nicht möglich ist, durch sie das Papier in einen Zustand zu versetzen, der in Bezug auf eine *Mehrzahl* von meßbaren Eigenschaften dem Zustand von natürlich gealterten Papieren gleicht. Die bisherige Forschung untersuchte die Bedingungen der Ofenalterung, Höhe von Temperatur und Feuchtigkeit mit dem Ziel, die aussagekräftigsten, um nicht zu

sagen die »richtigen« zu finden; sie suchte nach besseren Methoden der Auswertung[10,11] und sie beschäftigte sich mit ganz anderen Möglichkeiten der Belastung, um in beobachtbaren Zeiträumen zu Prognosen über das langfristige Verhalten von Papier zu kommen[12,13,14]. Für die Arbeit an dem Forschungsprojekt des Instituts für Buchrestaurierung schienen die vorliegenden Forschungsergebnisse trotz ihrer Fülle nicht auszureichen. Die bisheringen einschlägigen Untersuchungen zeichen sich dadurch aus, daß obwohl es an gegenteiligen Empfehlungen nicht fehlt[7,15], fast immer bei relativ hohen Temperaturen gealtert wurde. Sodann wurde stets mit Modellpapieren gearbeitet, nicht mit Papieren der wirklichen Produktion für den Buchdruck, und schon gar nicht mit bereits gebrauchten Papieren. Von dem Verhalten eines bereits längere oder kürzere Zeit natürlich gealterten Papiers beim nachfolgenden künstlichen Altern waren interessante Aufschlüsse zu erwarten. Ein weiterer Grund dafür, warum man sich im Institut für Buchrestaurierung noch einmal mit den Bedingungen der künstlichen Alterung beschäftigte, soll nicht verschwiegen werden: man wollte Argumente finden für die Entscheidung, bei der künftigen Arbeit die eine der zahlreichen in der Literatur empfohlenen Methoden zu übernehmen und alle anderen zu verwerfen. Auf eine nähere Untersuchung der trockenen Ofenalterung wurde dabei verzichtet, da die Bedeutung der Feuchtigkeit für die Alterung nicht nur evident ist, sondern auch von niemandem bestritten wird.

3. Versuch

3.1 Papiere

Der Untersuchung wurde eine Auswahl von Papieren verschiedenen Alters und verschiedener Zusammensetzung in möglichst großer Variationsbreite zugrunde gelegt. Soweit wie möglich wählte man die gleichen Papiere, die auch schon für die Untersuchung über den Begriff der Benutzbarkeit[6] herangezogen worden waren. Vier Papiere waren fabrikneu, 14 waren gebraucht; sie stammen aus fünf Jahrhunderten. Einige Kennzahlen zur Beschreibung dieser Papiere finden sich in Tab. 1. Die Herkunft der Papiere 1 bis 19 ist in dem früheren Bericht[6] enthalten; bei den anderen handelt es sich um folgende:

Nr. 20: Hadernpapier des 19. Jahrhunderts: W. Heinsius, Allgemeines Deutsches Bücher-Lexikon, Band 3,1: Leipzig: Brockhaus 1848.

Nr. 21: Hadernpapier des 16. Jahrhunderts: Constitutionens . . . in provinciali synodo Salisb. edita. Dillingen: Sebald Mayer 1574.

Nr. 22: gut erhaltenes Hadernpapier des 19. Jahrhunderts: Blackwood's Edinburgh Magazine vol. 69 No. 425. New York: Scott 1851.

Die Arbeit mit alten Papieren, die nur in begrenzter Menge zu Verfügung stehen, hat den Nachteil, daß der Vorrat zu Ende gehen kann, bevor alle versuchsrelevanten Messungen durchgeführt sind. Man muß ihn grundsätzlich in Kauf nehmen und kann versuchen ihm dadurch zu begegnen, daß man weitere Papiere aussucht, die den vorher verwendeten in möglichst vielen der unveränderlichen Qualitätsmerkmale nahekommen.

3.2. Künstliche Alterung

Die ausgewählten Papiere wurden einer künstlichen Ofenalterung ausgesetzt. Es sollte wie gesagt bei relativ niederen Temperaturen gealtert werden. Man begann willkürlich bei 50°C und setzte ebenso willkürlich eine Steigerungsrate von 15°C fest. Bei der Festlegung der Feuchtigkeit für die Alterung wurde von der Überlegung ausgegangen, daß es wohl am ehesten zu vergleichbaren Ergebnissen führe, wenn bei den verschiedenen Temperaturen der Alterung stets die gleiche Wassermenge im Papier vorhanden sei[13]. Als Norm wurde diejenige Wassermenge gewählt, die Papier bei 23°C 65% rF aufnimmt. Sie beträgt ca. 6,5% absolut Wasser im Papier. Die Ergebnisse eines Vorversuchs zur Ermittlung dieser Wassermengen finden sich in Abb. 1–4. Die für die Beobachtungsbereiche angenommene lineare Regression beinhaltet sicher einen merklichen Fehler, dürfte aber für die hier verfolgten Zwecke auf Grund der großen Streuung ausreichend sein. Mit ihr ergeben sich folgende Klimawerte für die Aufnahme der 6,5% Wasser:

50°C und 55–65% rF
65°C und 52–67% rF
80°C und 58–75% rF
95°C und ca. 84% rF (extrapoliert).

Daher wurde für 50°, 65° und 80° ein einheitlicher Luftfeuchtigkeitswert innerhalb der obigen drei Bereiche zu 65% rF festgelegt, für 95° die Luftfeuchtigkeit auf 85% fixiert. Um den Aufwand nicht ins Unüberschaubare wachsen zu lassen, begnügte man sich mit zwei Zeiträumen, die aber lang genug sein mußten, um auch bei den niederen Temperaturen noch meßbare Veränderungen an den Versuchspapieren hervorzurufen. Es wurden 305 und 750 Stunden festgesetzt. Man fand so zu acht verschiedenen Alterungsbedingungen:

50°C 65% rF 305 h
50°C 65% rF 750 h
65°C 65% rF 305 h
65°C 65% rF 750 h
80°C 65% rF 305 h
80°C 65% rF 750 h
95°C 85% rF 305 h
95°C 85% rF 750 h

Gemessen wurden, vor und jeweils nach den Alterungen, folgende Kennzahlen:

Bruchlast nach Falzung MD
Bruchlast nach Falzung CD
pH
Kappa-Zahl
Carboxylgruppengehalt
Alkalilöslichkeit

4. AUSWERTUNG

4.1. Bruchlast nach Falzung

Die Bruchlast nach definierter Falzung wird entsprechend der früheren Arbeit[6] als Kriterium für die Benutzbarkeit in Bibliothek und Archiv gewertet. Betrachtet man die Absolutwerte dieser Messung, so ist Papier Nr. 14 mit 1.38 N MD bzw. 2.44 N CD das schlechteste der 18 Muster. Es ist als »gefährdet« einzustufen[6]. Die fabrikneuen Papiere Nr. 1–4 sind sämtlich »fest« oder »sehr fest«. In Tabelle 2 sind diese Bruchlastwerte mit sich daraus zu einer Reihe ergebenden Rangziffern (RZ) zusammengestellt. Da die Rangeinstufung für MD und CD mit mehr als 99.9% statistischer Sicherheit korreliert, wurde für die weitere Betrachtung der Mittelwert (Tab. 2 Sp. 5) als Basis herangezogen. In Tab. 7 sind die prozentualen Veränderungen der Bruchlastwerte zusammengestellt, die die verschiedenen künstlichen Alterungen an ausgewählten Papieren hervorgerufen haben; Abb. 5 zeigt zusätzlich für die Papiere Nr. 3 und 16 diese Werte in graphischer Darstellung. Außer der überraschenden Tatsache, daß unter »milden« Alterungsbedingungen (z.B. 50°C 65% rF und 65°C 65% rF) auch eine deutliche Verbesserung der Bruchlast nach Falzung

Tabelle 1a: Papierzusammensetzung.
Table 1a: Composition du papier.
Table 1a: Paper composition.

Papier Nr. *Paper no.*	Fasern (% geschätzt) *Fibres (est. %)*					pH[1]				
	Masse (g/m²) Weight	Zellstoff *Chemical pulp*	Hanf, Flachs, Jute *Hemp, flax, jute*	Baumwolle *Cotton*	Holzschliff *Mechanical pulp*	Oberfläche *Surface*	Kaltextrakt *Cold extract*	Heißextrakt *Hot extract*	Pufferkapazität[2] *Buffer capacity*[2]	Kappazahl[3] *Kappa number*[3]
1	60	100	0	0	0	7,4	7,8	9,4	35,8 Sr	<5
2	80	100	0	0	0	5,5	5,1	5,3	0,5 A	<5
3	80	20	0	0	80	5,7	5,7	5,2	0,25 A	103
4	80	80	0	20	0	4,7	5,7	5,7	0,65 A	<5
5	60	0	100	0	0	4,7	4,8	4,8	1,2 A	8,1
6	60	0	100	0	0	8,1	8,0	8,7	10,45Sr	<5
7	100	40	0	0	60	4,3	4,4	4,5	1,6 A	93,1
8	70	20	0	0	80	4,4	4,5	4,5	1,6 A	100.5
9	75	20	0	0	80	5,0	4,8	4,7	1,7 A	105,4
11	85	30	10	0	60	4,3	5,8	5,3	0,9 A	65,9
14	80	90	0	10	0	4,2	5,1	5,1	2,3 A	9,8
15	55	40	0	0	60	3,5	5,0	4,5	2,1 A	89,7
16	85	80	20	0	0	3,5	4,6	5,0	1,3 A	21,3
18	60	0	100	0	0	7,2	6,2	6,7	0,4 A	<5
19	150	80	20	0	0	4,5	5,3	5,1	1,6 A	<5
20	60	0	100	0	0	5,7	6,0	6,8	0,3 A	<5
21	80	0	100	0	0	6,5	6,9	6,9	0,9 Sr	<5
22	60	0	80	20	0	4,8	5,3	5,1	0,1 A	<5
Spalte *Column*	1	2	3	4	5	6	7	8	9	10

1. Nach Zellcheming Merkblatt V/17/62 bzw. DIN 53124.
2. Der Kaltextrakt aus 1 g Papier mit 50 ml 0,1 n·HCl wird mit 0,1 n NaOH titriert. Angegeben werden die ml unter (A) oder über (Sr) 50.
3. Nach DIN 54357; füllstoffbereinigt.

1. Conformément aux spécifications Zellcheming V/17/62. respectivement DIN 53124.
2. L'extrait à froid d'l g de papier traité avec 50 ml de HCl 0,1 n est titre au NaOH 0,1 n. Noter les volumes en ml inférieurs à (A) ou supérieurs à (Sr) 50.
3. Conformément à DIN 54357; adopté en fonction de la charge.

1. According to Zellcheming specifications V/17/62, resp. DIN 53124.
2. The cold extract from 1 g paper with 50 ml 0,1 n HCl is titrated with 0,1 n NaOH. Ml below (A) or above (Sr) 50 are recorded.
3. According to DIN 54357; filler-adjusted.

Tabelle 1b: Papierzusammensetzung.
Table 1b: Composition du papier.
Table 1b: Paper composition.

Papier Nr. *Paper no.*	Carboxylgruppen[1] *Carboxyl groups*[1]	Alkalilöslichkeit[2] *Alkali solubility*[2]	In Prozent *In percentages*						
			Asche *Ash*	Magnesium	Calcium	Aluminium	Eisen *Iron*	Sulfat *Sulfate*	Kieselsäure *Silicic acid*
1	0,49	15,5	16,1	0,2	10,3	0	0,04	0	1,0
2	0,33	30,3	15,8	0,1	0,3	3,3	0,05	0,3	7,5
3	0,51	7,3	30,9	0,3	0,2	6,5	0,15	0	14,0
4	0,18	10,0	0	0	0	0	0	0	0
5	0,40	–	0,9	0	0,4	0	0	0,1	0,1
6	0,54	–	5,7	0	3,3	0	0,06	0,4	0,7
7	0,63	22,8	31,2	0,2	4,2	2,7	0	9,7	6,5
8	0,60	22,3	11,9	0,1	0,4	2,0	0.006	0	6,6
9	0,55	18,7	12,0	0	0,4	2,7	0,1	0	6,5
11	0,50	17,2	30,4	0	0,2	6,2	0	0	18,0
14	0,29	46,7	10,9	0	0,6	2,2	0,06	0	5,5
15	0,53	19,8	9,6	0	0,4	2,2	0,1	0,3	5,5
16	0,79	42,0	23,8	0	0,3	4,5	0,12	0	14,5
18	0,30	8,4	0,8	0	0,5	0	0	0	0,006
19	0,35	26,5	27,5	0	0,4	5,4	0,13	0	16,0
20	0,15	16,7	1,4	0	0,4	0,16	0,02	0	0,4
21	0,23	14,5	1,65	0	0,64	0	0,15	0	0,2
22	0,08	15,2	0,5	0,07	0,3	0	0	0,1	0,05
Spalte *Column*	11	12	13	14	15	16	17	18	19

1. Nach Doering: Das Papier 10 (1956): 140–141; füllstoffbereinigt.
2. Nach DIN 54356; füllstoffbereinigt.

1. Conformément à Doering: Papier 10 (1956): 140–141; adapté en fonction de la charge.
2. Conformément à DIN 54356; adapté en fonction de la charge.

1. According to Doering: Papier 10 (1956): 140–141; filler-adjusted.
2. According to DIN 54356; filler-adjusted.

Tabelle 2a: Bruchlast nach Falzung (N) als Maß für die Benützbarkeit.
Table 2a: Résistance à la rupture après pliage (N) comme critère d'emploi.
Table 2a: Breaking strength after folding (N) as criterion for usability.

Papier Nr. Paper no.	MD	RZ	CD	RZ	MD+CD / 2	RZ n=18	RZ n=15	RZ n=15
1	66,5	2	43,2	1	54,9	1	1	1
2	67,6	1	32,0	2	49,8	2	2	2
3	28,2	7,5	10,8	11,5	19,5	8	7	6
4	37,3	3,5	25,7	3	31,5	3	3	3
5	5,4	17	3,7	17	4,6	17	–	15
6	33,2	5	16,2	6,5	24,7	5	–	4
7	19,3	9	9,3	13	14,3	12,5	10,5	10,5
8	15,1	13	11,1	11,5	13,1	12,5	10,5	10,5
9	17,1	12	16,3	6,5	16,7	10	8,5	8
11	28,1	7,5	15,8	6,5	22,0	7	6	5
14	1,4	18	2,4	18	1,9	18	15	–
15	6,4	16	7,1	16	6,8	16	14	14
16	11,8	14,5	8,2	14,5	10	14,5	12,5	12,5
18	36,6	3,5	14,6	9	25,6	5	4,5	–
19	30,0	6	20,8	4	25,4	5	4,5	–
20	18,0	10,5	13,6	10	15,8	10	8,5	8
21	11,8	14,5	8,5	14,5	10,2	14,5	12,5	12,5
22	18,3	10,5	15,6	6,5	17	10	–	8
Spalte *Column*	1	2	3	4	5	6	7	8

resultieren kann, ist aus dieser Graphik zu erkennen, daß die Ergebnisse für MD und CD weitgehend analog verlaufen. Daher ist in Abb. 6–9 um der Übersichtlichkeit willen immer nur die MD angegeben. Für die statistischen Überprüfungen dagegen werden durchgehend sowohl MD als auch CD herangezogen. Da diese in allen Fällen mit hoher statistischer Sicherheit übereinstimmen, wurde mit den Mittelwerten aus MD + CD weitergerechnet (s. Tab. 16).

4.1.1. Alterungsklima 50°C und 65% rF

Die unter diesen Alterungsbedingungen gefundenen Werte für die Bruchlast nach Falzung sind in Tab. 3 zusammengestellt, die prozentualen Veränderun-

Tabelle 2b: Bruchlast nach Falzung (N) als Maß für die Benützbarkeit.
Table 2b: Résistance à la rupture après pliage (N) comme critère d'emploi.
Table 2b: Breaking strength after folding (N) as criterion for usability.

Papier Nr. *Paper no.*	RZ n=14	RZ n=14	RZ n=13	RZ n=13	RZ n=9	RZ n=9	RZ n=8	RZ n=8	RZ n=7	RZ n=6
1	1	1	1	1	1	1	1	1	1	1
2	2	2	2	2	2	2	2	2	2	2
3	5	6	5	5	6	6	6	5	5	5
4	3	3	3	3	3	3	3	3	3	3
5	14	–	13	–	8	8	–	7	–	–
6	–	–	–	–	–	–	–	–	–	–
7	9,5	9,5	9,5	9,5	–	–	–	–	–	–
8	9,5	9,5	9,5	9,5	–	–	–	–	–	–
9	7	7,5	7	7	7	7	7	6	6	6
11	4	5	4	4	5	5	–	4	4	–
14	–	14	–	–	9	9	8	8	7	–
15	13	13	–	13	–	–	–	–	–	–
16	11,5	11,5	11,5	11,5	–	–	–	–	–	–
18	–	–	–	–	4	–	4,5	–	–	–
19	–	4	–	–	–	4	4,5	–	–	4
20	7	7,5	7	7	–	–	–	–	–	–
21	11,5	11,5	11,5	11,5	–	–	–	–	–	–
22	7	–	7	7	–	–	–	–	–	–
Spalte *Column*	9	10	11	12	13	14	15	16	17	18

gen in Tab. 7 und Abb. 6. Aus den Werten ist zu entnehmen, daß unter diesen Bedingungen einerseits ein Anstieg der Bruchlast nach Falzung bis auf 264% des Ausgangswertes (Papier Nr. 14 MD nach 305 h Alterung) sowie andererseits ein Absinken auf 57% (Papier Nr. 18 MD nach 750 h) auftritt. Eine Überprüfung der Festigkeitswerte vor und nach der küntslichen Alterung zeigt (Tab. 16 Zeile 10 + 11), daß der Rangkorrelationskoeffizient nach Spearman[16] hierfür 0.8786 bzw. 0.9080 beträgt und daß damit statistische Übereinstimmung besteht. Das bedeutet, daß in der Reihenfolge der Benutzbarkeit durch die Alterung bei 50°C 65% rF keine signifikante Änderung eingetreten ist, trotz der z.T. relativ starken Änderung einzelner Werte.

4.1.2 Alterungsklima 65°C 65% rF

Unter diesen Bedingungen der Ofenalterung treten die Effekte in Bezug auf die

Tabelle 3a: Alterung bei 50°C und 65% rF 305 h, Bruchlast nach Falzung (N).
Table 3a: Vieillissement à 50°C et à 65% H.R. pendant 305 heures. Résistance à la rupture après pliage (N).
Table 3a: Ageing at 50°C and 65% RH 305 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	$\frac{MD+CD}{2}$	RZ n=15	RZ n=14
1	66,9	1	29,2	1	48,1	1	1
2	56,7	2	26,5	2	41,6	2	2
3	28,5	4,5	11,2	10	19,9	6	6
4	32,2	3	20,2	3	26,2	3	3
5	–	–	–	–	–	–	–
6	–	–	–	–	–	–	–
7	16,9	10	9,7	13,5	13,3	10,5	9,5
8	14,7	12	10,9	12	12,8	12,5	11,5
9	15,0	12	12,1	10	13,6	10,5	9,5
11	28,7	4,5	16,4	6	22,5	4	4
14	3,7	15	2,0	15	2,8	15	14
15	14,2	12	9,0	13,5	11,6	14	13
16	19,6	8,5	11,1	10	15,3	9	8
18	22,1	6,5	16	6	19,1	7	–
19	22,8	6,5	18,3	4	20,5	5	5
20	12,8	14	12,8	8	12,8	12,5	11,5
21	19,3	8,5	15,9	6	17,6	8	7
22	–	–	–	–	–	–	–
Spalte *Column*	1	2	3	4	5	6	7

Festigkeit ähnlich auf wie bei 50°C 65% rF (Tab. 4). Es wird ein größter Anstieg auf 210% der Ausgangsfestigkeit (Papier Nr. 16 nach 305 h) und ein Abfall auf 46% (Papier Nr. 18 nach 750 h) registriert. Die Reihenfolge der Benutzbarkeit stimmt auch hier mit der Rangeinstufung der Ausgangswerte statistisch gesichert überein (Tab. 16 Zeile 12 + 13). Der Zusammenhang für die Mittelwerte ist in Abb. 7 gegeben.

4.1.3. Alterungsklima 80°C 65% rF

Die bei 50°C und 65% rF beobachtete Steigerung der Meßwerte für die Bruchlast nach Falzung tritt hier nur noch vereinzelt auf (Tab. 5, Abb. 8; Papier Nr. 5 und 21). In den meisten Fällen ist eine deutliche und auch eine regelmäßige

Tabelle 3b: Alterung bei 50°C und 65% rF 750 h, Bruchlast nach Falzung (N).
Table 3b: Vieillissement à 50°C et à 65% H.R. pendant 750 heures. Résistance à la rupture aprés pliage (N).
Table 3b: Ageing at 50°C and 65% RH 750 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	$\frac{MD+CD}{2}$	RZ n=15	RZ n=14
1	70,6	1	30	1	50,1	1	1
2	59,8	2	26,2	2	43,1	2	2
3	31,3	4,5	10,9	11,5	21,2	6	6
4	34,4	3	20,7	4	27,6	3	3
5	–	–	–	–	–	–	–
6	–	–	–	–	–	–	–
7	20,1	8,5	10,1	13	15,1	10,5	9,5
8	15,8	12	10,8	11,5	13,3	12	11
9	17,7	10,5	14	9,5	15,8	10,5	9,5
11	31,4	4,5	15,9	5,5	23,6	5	5
14	3,6	15	2,8	14	3,2	15	14
15	12,5	13,5	6,3	15	9,4	14	13
16	23,9	7	14,1	9,5	19	7	7
18	21	8,5	15,3	5,5	18,1	8	–
19	28,3	6	25,6	3	26,9	4	4
20	18	10,5	16,5	7,5	17,2	9	8
21	13,2	13,5	12,1	7,5	12,6	13	12
22	–	–	–	–	–	–	–
Spalte *Column*	9	10	11	12	13	14	15

Abnahme des Meßwertes sowohl nach 305 h als auch nach 750 h zu beobachten. Abb. 8 mit ihren fallende Kurven gleicht den graphischen Darstellungen, die man aus Untersuchungen zur künstlichen Alterung von Papier gewohnt ist. Überraschenderweise bleibt aber auch hier die Rangeinstufung gleich der Einstufung der Ausgangsmuster (Tab. 16 Zeile 14 + 15). Die Reihenfolge der Benutzbarkeit der untersuchten Papiere wird auch durch die Alterung bei 80°C nicht signifikant verändert.

4.1.4. Alterungsklima 95°C 85% rF

Die Ergebnisse sind aus Tab. 6 und Abb. 9 ersichtlich. Häufig wird beobachtet, daß die Papiere bereits nach 305 h mechanisch keine Festigkeit mehr besitzen.

Tabelle 4a: Alterung bei 65°C und 65% rF 305 h, Bruchlast nach Falzung (N).
Table 4a: Vieillissement à 65°C et à 65% H.R. pendant 305 heures. Résistance à la rupture après pliage (N).
Table 4a: Ageing at 65°C and 65% RH 305 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	$\frac{MD+CD}{2}$	RZ n=15
1	65,6	1	28,6	1	47,1	1
2	58,3	2	26,3	2,5	42,3	2
3	28,1	4	11,0	9	19,6	6
4	30,8	3	20,6	4	25,7	4
5	–	–	–	–	–	–
6	–	–	–	–	–	–
7	18,8	8,5	8,6	12	13,7	10
8	11,0	13	8,3	12	9,6	13,5
9	14,3	11	9,3	10	11,8	11
11	24,5	6,5	13,5	7,5	19,0	6
14	2,7	15	2,1	15	2,4	15
15	10,9	13	7,1	14	9,0	13,5
16	24,8	6,5	15,0	5,5	19,9	6
18	18,7	8,5	15,2	5,5	17,0	8
19	26,3	5	26,9	2,5	26,6	3
20	17,1	10	13,3	7,5	15,2	9
21	11,8	13	8,5	12	10,1	12
22	–	–	–	–	–	–
Spalte *Column*	1	2	3	4	5	6

Nach 750 h war kein Papier der aus Materialmangel verkürzten Musterreihe mehr meßbar, auch die fabrikneuen Papiere Nr. 1–4 und das Hadernpapier Nr. 18 nicht.

4.2 pH

Von den Ausgangsmustern wurden die pH-Werte mit Hilfe der in der Papierindustrie üblichen Methoden (Oberflächen-pH, pH des Kaltextrakts, pH des Heißextrakts) bestimmt. Die in Tab. 9 zusammengestellten Werte ergeben in der Rangeinstufung eine gute Korrelation mit der Benutzbarkeit; der Zusammenhang ist zu mehr als 99% gesichert (Tab. 16 Zeile 50). Da das Oberflächen-pH am einfachsten und am schnellsten zu bestimmen ist, wurde für die weiteren Untersuchungen nur mehr dieser Wert herangezogen. In Abb. 10 ist

Tabelle 4b: Alterung bei 65°C und 65% rF 750 h, Bruchlast nach Falzung (N).
Table 4b: Vieillissement à 65°C et à 65% H.R. pendant 750 heures. Résistance à la rupture après pliage (N).
Table 4b: Ageing at 65°C and 65% RH 750 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	$\frac{MD+CD}{2}$	RZ n = 15
1	66,4	1	33,3	1	49,9	1
2	56,3	2	26,7	2	41,5	2
3	27,3	4,5	9,8	12	18,6	7
4	32,1	3	20,0	4	26,0	3
5	–	–	–	–	–	–
6	–	–	–	–	–	–
7	18,7	9,5	12,7	9	15,7	9,5
8	11,8	13	8,1	13	9,9	13
9	16,5	12	10,1	10,5	13,3	12
11	23,0	7	14,5	6	18,7	7
14	2,3	15	2,8	15	2,5	15
15	8,9	14	6,5	14	7,7	14
16	21,4	8	13,8	8	17,6	7
18	17,0	11	15,0	6	16,0	9,5
19	26,4	4,5	21,2	3	23,8	4
20	25,4	6	15,3	6	20,3	5
21	18,3	9,5	11,1	10,5	14,7	11
22	–	–	–	–	–	–
Spalte *Column*	9	10	11	12	13	14

der Zusammenhang zwischen Bruchlast nach Falzung und Oberflächen-pH dargestellt. Die eingezeichneten Regressionsgeraden zeigen mit und ohne Berücksichtigung der fabrikneuen Papiere eine positive Steigung. Daraus kann man, unter Verallgemeinerung der an den untersuchten Mustern gefundenen Werte, den Schluß ziehen, daß die Benutzbarkeit von Papier umso größer ist, je höher sein pH-Wert liegt. Dies wäre eine statistisch gesicherte Formulierung für den allgemein als gegeben betrachteten Zusammenhang von Papierqualität und pH für den hier vorliegenden pH-Bereich von 3,5–8,1.

Nach der künstlichen Alterung zeigen die pH-Werte jedoch unterschiedliches Verhalten. Niedrige Ausgangswerte scheinen mit der Alterung zu steigen, hohe scheinen eher abzusinken. Der pH-Bereich 3,5 bis 8,1 wird durch die künstliche Alterung bei 80°C 65% rF auf den Bereich 4,0 bis 6,8 eingeengt. Betrachtet man die einzelnen Alterungsstufen, so ergibt sich nach Tab. 19 kein

Tabelle 5a: Alterung bei 80°C und 65% rF 305 h, Bruchlast nach Falzung (N).
Table 5a: Vieillissement à 80°C et à 65% H.R pendant 305 heures. Résistance à la rupture après pliage (N).
Table 5a: Ageing at 80°C and 65% RH 305 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	MD+CD / 2	RZ n=15	RZ n=14	RZ n=13	RZ n=13
1	62,2	1	37,7	1	50,0	1	1	1	1
2	54,3	2	27,4	2	40,8	2	2	2	2
3	24,1	4,5	9,6	8,5	16,9	5,5	4,5	4,5	4,5
4	29,6	3	19,5	3	24,6	3	3	3	3
5	7,3	13	4,7	13	6,0	13,5	12,5	12,5	–
6	23,7	4,5	17,9	4	20,8	4	–	–	–
7	16,6	7,5	7,5	10,5	12,0	9	8	8	8
8	12,9	10,5	7,0	10,5	9,9	11	10	10	10
9	14,3	9	8,9	8,5	11,6	9	8	8	8
11	21,3	6	14,0	6	17,6	5,5	4,5	4,5	4,5
14	–	–	–	–	–	–	–	–	–
15	4,2	15	4,0	15	4,1	15	14	–	13
16	9,0	12	5,3	13	7,1	12	11	11	11
18	–	–	–	–	–	–	–	–	–
19	–	–	–	–	–	–	–	–	–
20	6,9	14	5,0	13	5,9	13,5	12,5	12,5	12
21	13,3	10,5	11,3	7	12,3	9	8	8	8
22	16,5	7,5	15,5	5	16,0	7	6	6	6
Spalte *Column*	1	2	3	4	5	6	7	8	9

einheitliches Bild. Korrelation zwischen pH-Wert und Benutzbarkeit besteht nur bei den Alterungen 50°C 65% rF 305 h und 80°C 65% rF 750 h.

4.3. Cellulosechemische Kennzahlen

Trotz vieler Bedenken, cellulosechemische Kennzahlen wie Alkalilöslichkeit, Carboxylgruppengehalt und Kappazahl in Papieren zu bestimmen, wurde dieser Versuch unternommen. Die vor und nach den Alterungen gefundenen Werte sowie ihre Rangeinstufung finden sich in Tab. 10–15. Auch die chemischen Kennzahlen vor und nach Alterung zeigen eine gute Korrelation mit den Werten der Ausgangsmuster mit Ausnahme der Alterung bei 95°C (Tab. 17); hier bleibt nur beim Oberflächen-pH-Wert und der Kappa-Zahl die Übereinstimmung erhalten. Daraus kann man schließen, daß sich die chemischen

Tabelle 5b: Alterung bei 80°C und 65% rF 750 h, Bruchlast nach Falzung (N).
Table 5b: Vieillissement à 80°C et à 65% H.R. pendant 750 heures. Résistance à la rupture après pliage (N).
Table 5b: Ageing at 80°C and 65% RH 750 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	MD+CD / 2	RZ n=14	RZ n=13	RZ n=13
1	65,7	1	28,9	1	47,3	1	1	1
2	39,5	2	24,3	2	31,9	2	2	2
3	18,4	4	7,2	8	12,8	6	6	6
4	20,6	3	15,9	3	18,3	3	3	3
5	6,8	11	4,3	11,5	5,6	11	11	–
6	–	–	–	–	–	–	–	–
7	5,0	12	3,9	11,5	4,5	12	12	11
8	12,0	8	8,0	8	10,0	8	8	8
9	8,9	9,5	6,6	10	7,8	9,5	9,5	9,5
11	15,8	6	9,5	6	12,6	6	6	6
14	–	–	–	–	–	–	–	–
15	2,0	14	1,4	14	1,7	14	–	13
16	3,2	13	2,7	13	2,9	13	13	12
18	–	–	–	–	–	–	–	–
19	–	–	–	–	–	–	–	–
20	17,3	5	13,8	4,5	15,6	4	4	4
21	8,7	9,5	7,8	8	8,2	9,5	9,5	9,5
22	14,0	7	12,9	4,5	13,5	6	6	6
Spalte *Column*	10	11	12	13	14	15	16	17

Kennzahlen bis zu der Ofenalterung bei 80°C bei allen Papieren annähernd gleichartig verändern.

Vergleicht man dagegen die Veränderung der chemischen Kennzahlen vor und nach der Ofenalterung mit der Benutzbarkeit der Ausgangsmuster (Tab. 18), so findet man eine teilweise Übereinstimmung bei den Oberflächen-pH-Werten und den Kappa-Zahlen.

Zwischen Alkalilöslichkeit und Benutzbarkeit wurde nur nach künstlicher Alterung der Papiere bei 80°C 65% rF eine Korrelation gefunden. Bei den Carboxylgruppen gab es nur nach der Alterung bei 95°C 85% rF 305 h eine Korrelation zur Benutzbarkeit. Die Kappazahlen zeigen genau das Umgekehrte: Keine Korrelation zur Benutzbarkeit nach der Alterung bei 95°C, gesicherte Korrelation bei allen anderen hier untersuchten Bedingungen.

Tabelle 6a: Alterung bei 95°C und 85% rF 305 h, Bruchlast nach Falzung (N).
Table 6a: Vieillissement à 95°C et à 85% H.R. pendant 305 heures. Résistance à la rupture après pliage (N).
Table. 6a: Ageing at 95°C and 85% RH 305 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	MD+CD / 2	RZ n=9	RZ n=7	RZ n=7
1	0	7,5	2,8	6	1,4	6	6	5
2	12,1	1	7,9	1	10,0	1	1	1
3	6,9	2,5	3,5	4,5	5,2	3	3	3
4	7,1	2,5	5,3	2,5	6,2	2	2	2
5	0	7,5	0	8	0	8	–	–
6	–	–	8,7	–	–	–	–	–
7	–	–	–	–	–	–	–	–
8	–	–	–	–	–	–	–	–
9	5,2	4	3,1	4,5	4,2	4,5	4,5	4
11	0	7,5	0	8	0	8	–	6,5
14	0	7,5	0	8	0	8	7	6,5
15	–	–	–	–	–	–	–	–
16	–	–	–	–	–	–	–	–
18	4,0	5	4,5	2,5	4,2	4,5	4,5	–
19	–	–	0	–	–	–	–	–
20	–	–	–	–	–	–	–	–
21	–	–	8,6	–	–	–	–	–
22	–	–	–	–	–	–	–	–
Spalte *Column*	1	2	3	4	5	6	7	8

5. Einzelheiten

Im Vorstehenden war mehrfach von überraschenden und widersprüchlichen Ergebnissen zu berichten. Das Gleiche zeigt sich auch bei einer Betrachtung von Einzelheiten.

5.1. Festigkeitsverlust

Es ist nur mit der 305stündigen Alterung bei 95°C und 85% rF gelungen, eines der fabrikneuen Papiere Nr. 1 bis 4 in einen Benutzbarkeitszustand zu versetzen, der dem der schlechten Papiere Nr. 14 und 15 gleicht. Bei dieser künstlichen Alterung zeigen aber alle Papiere – mit Ausnahme von Nr. 21 CD – einen Festigkeitsverlust um ca. 70–100%, auch Papier Nr. 18, d.h. eines, das

Tabelle 6b: Alterung bei 95°C und 85% rF 750 h, Bruchlast nach Falzung (N).
Table 6b: Vieillissement à 95°C et à 85% H.R. pendant 750 heures. Résistance à la rupture après pliage (N).
Table 6b: Ageing at 95°C and 85% RH 750 h, breaking strength after folding (N).

Papier Nr. *Paper no.*	MD	RZ	CD	RZ	MD+CD / 2	RZ n=9	RZ n=8	RZ n=7	RZ n=6
1	0	5	0	5,5	0	5,5	5	4,5	4
2	0	5	0	5,5	0	5,5	5	4,5	4
3	0	5	0	5,5	0	5,5	5	4,5	4
4	0	5	0	5,5	0	5,5	5	4,5	4
5	0	5	0	5,5	0	5,5	5	–	–
6	–	–	–	–	–	–	–	–	–
7	–	–	–	–	–	–	–	–	–
8	–	–	–	–	–	–	–	–	–
9	0	5	0,9	1	0,5	1	1	1	1
11	0	5	0	5,5	0	5,5	5	4,5	–
14	0	5	0	5,5	0	5,5	5	4,5	–
15	–	–	–	–	–	–	–	–	–
16	–	–	–	–	–	–	–	–	–
18	0	5	0	5,5	0	5,5	–	–	4
19	–	–	0	–	–	–	–	–	–
20	–	–	–	–	–	–	–	–	–
21	–	–	0	–	–	–	–	–	–
22	–	–	–	–	–	–	–	–	–
Spalte *Column*	9	10	11	12	13	14	15	16	17

seine gute Alterungsbeständigkeit zum einen durch das unversehrte Überstehen von 127 Jahren Lagerung bei Raumtemperatur bewiesen hat und zum anderen von seiner Zusammensetzung her, im Vergleich zu weitaus älteren ähnlich zusammengesetzten Papieren, auch weiterhin erwarten läßt. Die längere Alterungsdauer bei 95°C macht dieses Papier ebenso wie alle anderen einschließlich Nr. 21 völlig unbenutzbar. Sie versetzt alles Papier in einen Zustand, der als Ergebnis natürlicher Alterung noch niemals beobachtet wurde. Die Muster lagen in einem so schwachen, fast verkohlten Zustand vor, wie er allenfalls in Form von Brandschäden bekannt ist (Abb. 11).

5.2. Holzschliffgehalt

Der prozentuale Festigkeitsverlust, den das 305stündige Altern bei 95° eintre-

Tabelle 7: Veränderung der Bruchlast nach Falzung (Mittelwert) in Prozent des Ausgangswertes.
Table 7: Modification de la résistance à la rupture après pliage (valeur moyenne) exprimée en pourcentage de la valeur initiale.
Table 7: Change of breaking strength after folding (average value) in percentage of the original value.

Papier Nr. *Paper no.*	MD+CD / 2	%	50°C 65% rF		65°C 65% rF		80°C 65% rF		95°C 85% rF	
			305 h	750 h	305 h	750 h	305 h	750 h	305 h	750h
1	54,9	100	87,7	91,3	85,9	90,8	91,0	86,2	2,6	0
2	49,8	100	83,6	86,5	85,9	83,3	82,0	64,0	20,1	0
3	19,5	100	101,8	108,6	100,4	95,3	86,6	65,6	26,8	0
4	31,5	100	82,3	86,6	80,7	81,7	77,3	57,5	19,6	0
5	4,5	100	–	–	–	–	132,5	200,1	0	0
6	24,7	100	–	–	–	–	48,6	–	–	–
7	14,3	100	92,9	106,0	95,7	109,9	84,0	31,5	–	–
8	13,1	100	97,8	101,7	73,5	75,5	75,5	76,3	–	–
9	16,6	100	81,9	95,5	71,4	80,4	70,1	47,1	25,4	2,6
11	22,0	100	102,5	107,5	86,5	85,0	80,0	57,3	0	0
14	1,9	100	147,1	167,5	125,1	130,9	–	–	0	0
15	6,8	100	172,0	139,2	132,5	113,9	60,7	25,2	–	–
16	10,0	100	153,1	189,9	198,6	175,8	70,9	29,0	–	–
18	25,6	100	74,4	70,8	66,2	62,5	–	–	16,6	0
19	25,4	100	80,7	105,9	104,6	93,6	–	–	–	–
20	15,8	100	81,0	109,0	96,4	128,5	37,3	98,7	–	–
21	10,1	100	174,2	124,8	100,1	145,3	121,5	81,0	–	–
22	17,0	100	–	–	–	–	94,3	79,6	–	–
Spalte *Column*	1	2	3	4	5	6	7	8	9	10

Bemerkung: Vereinzelte Zuwachsraten bei den alten Papieren Nr. 5, 20 und 21 sind mit Zurückhaltung zu interpretieren: verschiedene Blätter aus dem gleichen Buch (als gleiche Produktion angenommen) sind oft so ungleich, daß die verschiedenen Meßwerte sich eher hieraus als aus Veränderungen erklären lassen, die die künstliche Alterung hervorgerufen hätte.
Note: Les accroissements individuels des valeurs obtenues avec des papiers anciens n^{os} 5, 20 et 21 devraient faire l'objet d'une interprétation prudente: les diverses pages d'un même livre (en supposant une uniformité de production) sont souvent tellement variables que les différentes valeurs mesurées peuvent être plus vraisemblablement dues à ce phénomène qu'à des changements produits par un vieillissement artificiel.
Note: Individual increment values for the old papers Nos. 5, 20 and 21 should be interpreted conservatively: different pages from the same book (and assuming uniform production) are often so unequal that the different values measured can more likely be ascribed to this than to changes generated by artificial ageing.

Tabelle 8: pH an der Oberfläche.
Table 8: pH en surface.
Table 8: Surface pH.

Papier Nr. *Paper no.*	Meßwert *Measured value*	RZ n=18	RZ n=15	RZ n=15	RZ n=14	RZ n=7
1	7,4	2	1	2	1	1
2	5,5	7	6	6	5	3
3	5,7	5,5	4,5	4,5	3,5	2
4	4,7	10,5	8	9,5	8,5	5
5	4,7	10,5	–	9,5	8,5	–
6	8,1	1	–	1	–	–
7	4,3	14,5	11,5	12,5	11,5	–
8	4,4	13	10	11	10	–
9	5,0	8	7	7	6	4
11	4,3	14,5	11,5	12,5	11,5	6
14	4,2	16	13	–	–	7
15	3,5	17,5	14,5	14,5	13,5	–
16	3,5	17,5	14,5	14,5	13,5	–
18	7,2	3	2	–	–	–
19	4,5	12	9	–	–	–
20	5,7	5,5	4,5	4,5	3,5	–
21	6,5	4	3	3	2	–
22	4,8	9	–	8	7	–
Spalte *Column*	1	2	3	4	5	6

ten läßt, ist, wieder mit Ausnahme von Papier Nr. 21, am geringsten bei den 80% Holzschliff enthaltenden und ein saures pH aufweisenden Papieren Nr. 3 und 9. Dies ist ein Widerspruch zu der allenthalben in Archiv und Bibliothek zu treffenden Beobachtung, daß holzhaltiges Papier beim natürlichen Altern stärker an Festigkeit verliert als holzfreies.

5.3. Festigkeitszuwachs

Alle Papiere verloren ihre Festigkeit bei 95°C, der stärksten Belastung, der die Papiere ausgesetzt wurden. Bei den schwachen Belastungen 50°C und 65°C gewannen sie teilweise. Eine Verbesserung findet sich häufiger und stärker an den bereits natürlich gealterten Papieren. Es kommen alle Varianten vor: andauerndes Steigen bei der kürzeren und bei der längeren Alterungsdauer; zu-

Tabelle 9: pH an der Oberfläche nach den Alterungen.
Table 9: pH en surface après les traitements de vieillissement.
Table 9: Surface pH after the ageing processes.

Papier Nr. *Paper no.*	50°C und 65% rF 305 h Meßwert *Measured value*	RZ	50°C und 65% rF 750 h Meßwert *Measured value*	RZ	80°C und 65% rF 305 h Meßwert *Measured value*	RZ	80°C und 65% rF 750 h Meßwert *Measured value*	RZ	95°C und 85% rF 305 h Meßwert *Measured value*	RZ	95°C und 85% rF 750 h Meßwert *Measured value*	RZ
1	8,5	1	8,7	1	7,1	2	6,8	1	7,3	1	7,1	1
2	5,1	6,5	5,3	8,5	4,5	8,5	4,8	6	5,2	4	5,6	2
3	5,5	4	5,5	6,5	4,3	11,5	5,0	5	5,4	2	5,5	3
4	4,8	11,5	5,1	11,5	5,4	3	4,6	7	4,8	5	4,8	6
5	–	–	–	–	4,3	11,5	4,3	9	–	–	–	–
6	–	–	–	–	7,9	1	–	–	–	–	–	–
7	4,6	13,5	4,9	14	4,0	14,5	4,1	11	–	–	–	–
8	4,8	11,5	5,1	11,5	4,5	8,5	4,0	13,5	–	–	–	–
9	5,0	9	5,3	8,5	4,1	13	4,1	11	5,3	3	5,4	4
11	5,0	9	5,6	4	4,5	8,5	4,5	8	4,4	6	4,6	7
14	4,6	13,5	5,2	10	–	–	–	–	4,1	7	5,0	5
15	4,5	15	5,0	13	4,0	14,5	4,0	13,5	–	–	–	–
16	5,0	9	4,7	15	4,5	8,5	4,1	11	–	–	–	–
18	5,6	3	5,6	4	–	–	–	–	–	–	–	–
19	5,3	5	5,6	4	–	–	–	–	–	–	–	–
20	5,1	6,5	5,5	6,5	5,1	5	5,3	3	–	–	–	–
21	6,0	2	6,1	2	5,3	4	6,6	2	–	–	–	–
22	–	–	–	–	5,0	6	5,2	4	–	–	–	–
Spalte *Column*	1	2	3	4	5	6	7	8	9	10	11	12

Tabelle 10: Carboxylgruppengehalt.
Table 10: Teneur en groupes carboxyliques.
Table 10: Carboxyl group content.

Papier Nr. *Paper no.*	Meßwert *Measured value*	RZ n=18	RZ n=15	RZ n=14	RZ n=13	RZ n=9
1	0,49	10	8	7	7	6
2	0,33	7	6	5	5	4
3	0,51	12	10	9	9	8
4	0,18	3	2	2	3	1
5	0,40	9	–	–	6	5
6	0,54	14	–	–	–	–
7	0,63	17	14	13	12	–
8	0,60	16	13	12	11	–
9	0,55	15	12	11	10	9
11	0,50	11	9	8	8	7
14	0,29	5	4	4	–	2
15	0,53	13	11	10	–	–
16	0,79	18	15	14	13	–
18	0,30	6	5	–	–	3
19	0,35	8	7	6	–	–
20	0,15	2	1	1	2	–
21	0,23	4	3	3	4	–
22	0,08	1	–	–	1	–
Spalte *Column*	1	2	3	4	5	6

nächst Steigen, dann Sinken und umgekehrt; kontinuierliches Sinken. Wäre es bei neuen Papieren allenfalls noch vorstellbar, daß die chemischen Vorgänge in ihnen, die ihr natürliches Altern ausmachen, zunächst, während der unbekannten Anzahl von Jahren, die mit 305 oder 750 h künstlicher Alterung bei 50°C oder bei 65°C gleichzusetzen wären, in derartiger Reihenfolge und gegenseitiger Beeinflussung oder Überlagerung ablaufen, daß sich die Benutzbarkeitsqualität verbessert, bevor sie nach diesem Zeitraum den aus aller Erfahrung als unvermeidlich zu postulierenden Weg der Verschlechterung geht, so ist dies bei bereits gealterten Papieren unwahrscheinlich. Es ist kaum vorstellbar, daß z.B. die Papiere Nr. 15, 16 und 21, bei denen man ohne Bedenken einen seit ihrer Herstellung vor 43, 75 bzw. 407 Jahren stattgehabten Festigkeitsverlust postulieren kann, der sie in Klasse IV »benutzbar[6]« gebracht hat, von nun an, allein durch weiteres Lagern im Magazin über die unbekannte

Tabelle 11: Carboxylgruppengehalt nach den Alterungen.
Table 11: Teneur en groupes carboxyliques après les traitements de vieillissement.
Table 11: Carboxyl group content after the ageing processes.

	50°C und 65% rF				65°C und 65% rF				80°C und 65% rF				95°C und 85% rF			
	305 h		750 h		305 h		750 h		305 h		750 h		305 h		750 h	
Papier Nr. *Paper no.*	Meß-wert *Measured value*	RZ	Meß-wert *Measured value*	RZ	Meß-wert *Measured value*	RZ	Meß-wert *Measured value*	RZ	Meß-wert *Measured value*	RZ	Meß-wert *Measured value*	RZ	Meß-wert *Measured value*	RZ	Meß-wert *Measured value*	RZ
1	0,32	8	0,17	8	0,31	8	0,22	9	0,19	7	0,17	7	0,54	6,5	0,49	6
2	0,17	4	0,10	3	0,16	5	0,15	6,5	0,12	4,5	0,11	3	0,18	3	0,55	7
3	0,44	11	0,20	9	0,41	11	0,30	10	0,34	12,5	0,34	13	0,42	4	0,31	2,5
4	0,10	1	0	1	0,06	1	0,05	3	0,03	1	0	1	0,07	1	0	1
5	–	–	–	–	–	–	–	–	0,15	6	0,14	5	0,55	8	0,47	5
6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7	0,60	14	0,46	14	0,36	10	0,38	13	0,34	12,5	0,33	12	–	–	–	–
8	0,50	13	0,45	13	0,51	15	0,41	14	0,22	9	0,26	9	–	–	–	–
9	0,48	12	0,31	11	0,43	12	0,35	12	0,26	11	0,30	11	0,45	5	0,35	4
11	0,22	6	0,22	10	0,48	13	0,34	11	0,25	10	0,28	10	0,54	6,5	0,90	8
14	0,26	7	0,16	6,5	0,26	7	0,15	6,5	–	–	–	–	0,75	9	1,58	9
15	0,42	10	0,41	12	0,49	14	0,44	15	–	–	–	–	–	–	–	–
16	0,40	9	0,11	4	0,32	9	0,19	8	0,21	8	0,25	8	–	–	–	–
18	–	–	–	–	0,11	3	0,02	1	–	–	–	–	0,14	2	0,31	2,5
19	0,21	5	0,16	6,5	0,21	6	0,03	2	–	–	–	–	0,16	–	0,37	–
20	0,11	2	0,09	2	0,11	3	0,10	4	0,11	3	0,14	5	–	–	–	–
21	0,12	3	0,13	5	0,11	3	0,13	5	0,12	4,5	0,14	5	–	–	–	–
22	–	–	–	–	–	–	–	–	0,07	2	0,07	2	–	–	–	–
Spalte *Column*	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

Tabelle 12: Kappazahlen.
Table 12: Nombres Kappa.
Table 12: Kappa numbers.

Papier Nr. *Paper no.*	Meßwert *Measured value*	RZ n=18	RZ n=15	RZ n=14	RZ n=9	RZ n=8
1	<5	5	4	3,5	2,5	2
2	<5	5	4	3,5	2,5	2
3	103	17	14	13	8	7
4	<5	5	4	3,5	2,5	2
5	8,1	10	–	7	5	4
6	<5	5	–	–	–	–
7	93,1	15	12	11	–	–
8	100,5	16	13	12	–	–
9	105,4	18	15	14	9	8
11	65,9	13	10	9	7	6
14	9,8	11	8	–	6	5
15	89,7	14	11	10	–	–
16	21,3	12	9	8	–	–
18	<5	5	4	–	2,5	–
19	<5	5	4	–	–	–
20	<5	5	4	3,5	–	–
21	<5	5	4	3,5	–	–
22	<5	5	–	3,5	–	–
Spalte *Column*	1	2	3	4	5	6

Zahl von Jahren, die den 305 oder 750 Stunden der künstlichen Alterung bei den hier gewählten Bedingungen entsprechen würden, diese Festigkeit soweit zurückgewinnen, daß sie wieder »uneingeschränkt benutzbar« oder »fest« werden.

6. Ergebnisse

6.1. Aussagekraft der künstlichen Alterung

Die Technik der künstlichen Alterung beruht auf der Annahme einer Parallelität. Es wird angenommen, daß die chemischen Vorgänge, die in ihrer Summe, ihrer gegenseitigen Beeinflussung und Überlagerung das »Altern« ausmachen, bei höherer Temperatur und bei längerer Dauer der Temperaturbelastung gleichmäßig verstärkt und damit zeitlich gerafft ablaufen und daß diese

Tabelle 13: Kappazahlen nach den Alterungen.
Table 13: Nombres Kappa après les traitements de vieillissements.
Table 13: Kappa numbers after the ageing processes.

Papier Nr. *Paper no.*	50°C und 65% rF 305 h Meßwert *Measured value*	50°C und 65% rF 305 h RZ	50°C und 65% rF 750 h Meßwert *Measured value*	50°C und 65% rF 750 h RZ	80°C und 65% rF 305 h Meßwert *Measured value*	80°C und 65% rF 305 h RZ	80°C und 65% rF 750 h Meßwert *Measured value*	80°C und 65% rF 750 h RZ	65°C und 65% rF 305 h Meßwert *Measured value*	65°C und 65% rF 305 h RZ	65°C und 65% rF 750 h Meßwert *Measured value*	65°C und 65% rF 750 h RZ	95°C und 85% rF 305 h Meßwert *Measured value*	95°C und 85% rF 305 h RZ	95°C und 85% rF 750 h Meßwert *Measured value*	95°C und 85% rF 750 h RZ
1	<5	3,5	<5	3,5	<5	2,5	<5	2,5	<5	3,5	<5	3,5	19,5	4	33,6	4
2	<5	3,5	<5	3,5	<5	2,5	<5	2,5	<5	3,5	<5	3,5	<5	2	8,1	2
3	97	12	99	13	103	12	103	12,5	105	13	107	13,5	110	8	117	8
4	<5	3,5	<5	3,5	<5	2,5	<5	2,5	<5	4	<5	3,5	<5	2	<5	1
5	–	–	–	–	8,1	6,5	8,6	6,5	–	–	–	–	25,8	5,5	25,4	3
6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7	92,0	11	91,8	11	92,1	10	92,6	10	91,8	11	102,4	12	–	–	–	–
8	105,0	14	105,8	14	109,9	14	95,5	11	106,4	14	108,8	15	–	–	–	–
9	107,9	15	110,8	15	107,1	13	107,8	14	109,4	15	106,7	13,5	112,9	9	112,9	7
11	67,3	10	67,3	10	69,1	9	70,5	9	68,2	10	68,5	10	76,1	7	89,1	6
14	9,8	8	9,8	8	–	–	–	–	9,7	8	10,8	8	35,5	5,5	61,2	5
15	99,1	13	94,4	12	95,8	11	103,3	12,5	97,9	12	97,4	11	–	–	–	–
16	21,3	9	21,3	9	22,3	8	24,4	8	14,6	9	15,4	9	–	–	–	–
18	<5	3,5	<5	3,5	–	–	–	–	<5	4	<5	3,5	<5	2	12,0	–
19	<5	3,5	<5	3,5	–	–	–	–	<5	4	<5	3,5	12,1	–	20,3	–
20	<5	3,5	<5	3,5	8,4	6,5	9,0	6,5	<5	4	<5	3,5	–	–	–	–
21	6,7	7	5,5	7	6,5	5	7,8	5	<5	4	7,8	7	–	–	–	–
22	–	–	–	–	5	2,5	<5	2,5	–	–	–	–	–	–	–	–
Spalte *Column*	1	2	3	4	9	10	11	12	5	6	7	8	13	14	15	16

Tabelle 14: Alkalilöslichkeit.
Table 14: Solubilité aux alcalins.
Table 14: Alkali solubility.

Papier Nr. *Paper no.*	Meßwert *Measured value*	RZ n=15	RZ n=13	RZ n=7	RZ n=5
1	15,5	5	4,5	4	3
2	20,3	10	10	6	5
3	7,3	1	1	1	1
4	10,0	3	2	3	2
5	–	–	–	–	–
6	–	–	–	–	–
7	22,8	11,5	11,5	–	–
8	22,3	11,5	11,5	–	–
9	18,7	8	8	5	4
11	17,2	7	7	–	–
14	46,7	15	–	7	–
15	19,8	9	9	–	–
16	42,0	14	13	–	–
18	8,4	2	–	2	–
19	26,5	13	–	–	–
20	16,7	6	6	–	–
21	14,0	4	3	–	–
22	15,2	–	4,5	–	–
Spalte *Column*	1	2	3	4	5

Vorgänge sich in gleichmäßigen Veränderungen der an dem gealterten Material zu treffenden Messungen zeigen. Der Versuch, über den hier berichtet wird, hat gezeigt, daß es solche Gleichmäßigkeiten nicht gibt. Dies wird besonders deutlich, wenn man die Veränderungen betrachtet, die die parallelen Änderungen der Versuchsbedingungen hervorgerufen haben, nämlich die Temperatursteigerungen um 15°, von 50° auf 65°, von 65° auf 80°, von 80° auf 95° bei gleichem Zeitraum, oder die längere Versuchsdauer, 750 h statt 305 h, bei sonst gleichen Bedingungen. Die gefundenen Meßwerte vermitteln vielmehr den Eindruck, daß sich Reihenfolge und gegenseitige Beeinflussung der Vorgänge, die das Altern ausmachen, temperaturspezifisch unterscheiden. Sie sind bei 50°C durchaus anders als bei 65°, 80° und 95°. Es wäre ein Zufall, wenn sie bei einer Temperatur mit denen bei einer anderen gleich wären, so daß die verschiedene Stärke der Vorgänge als Kriterium für ihre zeitliche Raffung faßbar würde.

Tabelle 15: Akalilöslichkeit nach den Alterungen.
Table 15: Solubilité aux alcalins après les traitements de vieillissement.
Table 15: Alkali solubility after the ageing processes.

Papier Nr. *Paper no.*	50°C und 65% rF 305 h Meß-wert *Measured value*	RZ	50°C und 65% rF 750 h Meß-wert *Measured value*	RZ	80°C und 65% rF 305 h Meß-wert *Measured value*	RZ	80°C und 65% rF 750 h Meß-wert *Measured value*	RZ	95°C und 85% rF 305 h Meß-wert *Measured value*	RZ	95°C und 85% rF 750 h Meß-wert *Measured value*	RZ
1	18,2	6	17,4	6	21,7	5	19,0	7	18,2	5	20,0	5
2	19,8	10	19,1	8	20,3	4	20,9	8	19,3	7	19,6	4
3	10,1	1	9,5	1	12,3	2	10,5	1	11,1	1	11,4	1
4	11,4	2	11,9	2	12,6	1	12,0	2	12,9	2	12,4	2
5	–	–	–	–	–	–	–	–	–	–	–	–
6	–	–	–	–	–	–	–	–	–	–	–	–
7	26,5	12	24,6	11	36,9	12	23,6	11	22,0	9	32,0	12
8	19,6	9	22,9	9	35,0	11	21,6	9,5	23,4	11,5	28,7	11
9	18,6	7	18,6	7	24,0	6	18,6	6	20,0	8	23,0	8
11	23,2	11	25,6	12	30,7	10	25,3	12	23,2	11,5	24,0	9
14	48,8	15	55,1	15	–	–	55,1	15	59,7	15	–	–
15	19,1	8	23,6	10	29,8	9	21,9	9,5	22,9	10	26,6	10
16	39,5	14	42,5	14	49,7	13	36,7	14	42,6	14	43,7	13
18	15,5	4	15,2	3	–	–	16,4	3,5	16,5	3	–	–
19	30,1	13	30,0	13	–	–	27,8	13	33,8	13	17,8	3
20	16,7	5	16,8	5	19,0	3	16,6	3,5	17,2	4	20,8	6
21	14,1	3	15,6	4	27,3	8	17,2	5	18,2	5,5	21,2	7
22	–	–	–	–	25,0	7	–	–	–	–	–	–
Spalte *Column*	1	2	3	4	5	6	7	8	9	10	11	12

Tabelle 16: Korrelationen nach Spearman (ϱ) zwischen den einzelnen Rangeinstufungen (I verglichen mit II) mit Angabe des Stichprobenumfangs n, der Prüfgröße P und der sich daraus ergebenden statistischen Sicherheit s in %.
Table 16: Corrélations selon Spearman (ϱ) entre les classifications de taux individuesl (I comparé à II) avec indication de l'évaluation de l'échantillonnage fortuit n, de l'ordre de grandeur du test P et de l'écart statistique de sécurité résultant s exprimée en %.
Table 16: Correlations according to Spearman (ϱ) between classifications of individual rates (I compared to II), with indication of the extent of random sampling n, test size P, and the resulting statistical margin of safety s in %.

Zeile *Line*	I Tabelle *Table*	I Spalte *Column*	II Tabelle *Table*	II Spalte *Column*	n	ϱ	P	S
1	2	3	4	5	6	7	8	9
1	2	2	2	4	18	0,8865	16,56	>99,9
2	3a	2	3a	4	15	0,5357	2,71	>95,0
3	3b	10	3b	12	15	0,7321	5,69	>99,9
4	4a	2	4a	4	15	0,8821	14,34	>99,9
5	4b	10	4b	12	15	0,8411	10,36	>99,9
6	5a	2	5a	4	15	0,9179	21,01	>99,9
7	5b	10	5b	12	14	0,9440	30,01	>99,9
8	6a	2	6a	4	9	0,9208	16,02	>99,9
9	6b	10	6b	12	9	0,8500	8,10	>99,9
10	2	7	3a	6	15	0,8786	13,89	>99,9
11	2	7	3b	14	15	0,9080	18,66	>99,9
12	2	7	4a	6	15	0,8696	12,87	>99,9
13	2	7	4b	14	15	0,8384	10,17	>99,9
14	2	8	5a	6	15	0,9089	18,85	>99,9
15	2	9	5b	14	14	0,8484	10,48	>99,9
16	2	13	6a	6	9	0,5625	2,18	<95,0
17	2	13	6b	14	9	0,2000	0,55	<95,0
18	8	3	9	2	15	0,8518	11,19	>99,9
19	8	3	9	4	15	0,7571	6,40	>99,9
20	8	3	9	6	15	0,6473	4,02	>99,0
21	8	3	9	8	15	0,7250	5,51	>99,9
22	8	4	9	10	15	0,6339	3,82	>99,0
23	8	5	9	12	14	0,8440	10,16	>99,9
24	8	6	9	14	7	0,9643	2,00	>99,0
25	8	6	9	16	7	0,8571	8,00	>95,0
26	10	4	11	2	14	0,8901	14,85	>99,9
27	10	4	11	4	14	0,7198	5,17	>99,9
28	10	3	11	6	15	0,8179	8,91	>99,9
29	10	3	11	8	15	0,7616	6,54	>99,9
30	10	5	11	10	13	0,8514	10,49	>99,9
31	10	5	11	12	13	0,8077	7,71	>99,9
32	10	6	11	14	9	0,2208	0,61	<95,0
33	10	6	11	16	9	–0,4708	1,60	<95,0

Zeile *Line*	I Tabelle *Table*	I Spalte *Colum*	II Tabelle *Table*	II Spalte *Column*	n	ϱ	P	S
1	2	3	4	5	6	7	8	9
34	12	3	13	2	15	0,9634	48,33	>99,9
35	12	3	13	4	15	0,9741	68,71	>99,9
36	12	3	13	6	15	0,9929	251,48	>99,9
37	12	3	13	8	15	0,9696	58,47	>99,9
38	12	4	13	10	14	0,9484	32,65	>99,9
39	12	4	13	12	14	0,9473	31,95	>99,9
40	12	5	13	14	9	0,9708	44,68	>99,9
41	12	6	13	16	8	0,9048	8,00	>99,0
42	14	2	15	2	15	0,9420	30,13	>99,9
43	14	2	15	4	15	0,9259	23,39	>99,9
44	14	2	15	6	15	0,9071	18,47	>99,9
45	14	2	15	8	15	0,9196	21,50	>99,9
46	14	3	15	10	13	0,8187	8,23	>99,9
47	14	3	15	12	13	0,7473	5,61	>99,9
48	14	4	15	14	7	0,3571	36,00	<95,0
49	14	5	15	16	5	0,5000	10,00	<95,0
50	2	6	8	2	18	0,5759	3,45	>99,0
51	2	7	9	2	15	0,5031	2,43	>95,0
52	2	7	9	4	15	0,5018	2,42	>95,0
53	2	7	9	6	15	0,4071	1,76	<95,0
54	2	7	9	8	15	0,4768	2,22	>95,0
55	2	8	9	10	15	0,5473	2,82	>95,0
56	2	8	9	12	15	0,5099	2,39	>95,0
57	2	17	9	14	7	0,4643	30,00	<95,0
58	2	17	9	16	7	0,4643	30,00	<95,0
59	2	6	10	2	18	0,1785	0,74	<95,0
60	2	10	11	2	14	0,3330	1,30	<95,0
61	2	10	11	4	14	0,2857	1,08	<95,0
62	2	7	11	6	15	0,3554	1,47	<95,0
63	2	7	11	8	15	0,3973	1,70	<95,0
64	2	11	11	10	13	0,1346	0,45	<95,0
65	2	11	11	12	13	0,1456	0,49	<95,0
66	2	13	11	14	9	0,5875	2,37	=95,0
67	2	13	11	16	9	0,2042	0,56	<95,0
68	2	6	12	2	18	0,5387	3,04	>99,0
69	2	7	13	2	15	0,6000	3,38	>99,0
70	2	7	13	4	15	0,5750	3,10	>99,0
71	2	7	13	6	15	0,5018	2,42	>95,0
72	2	7	13	8	15	0,5679	3,02	>99,0
73	2	9	13	10	14	0,4099	1,71	<95,0
74	2	9	13	12	14	0,4132	1,73	<95,0
75	2	13	13	14	9	0,6292	2,76	>95,0
76	2	16	13	16	8	0,3810	52,00	<95,0
77	2	7	14	2	15	0,4580	2,09	<95,0
78	2	7	15	2	15	0,3375	1,37	<95,0
79	2	7	15	4	15	0,0339	0,12	<95,0
80	2	7	15	6	15	0,4116	1,79	<95,0
81	2	7	15	8	15	0,1013	0,37	<95,0
82	2	12	15	10	13	0,6456	3,67	>99,0
83	2	12	15	12	13	0,6566	3,83	>99,0
84	2	15	15	14	8	0,0893	76,50	<95,0
85	2	18	15	16	6	–0,6000	56,00	<95,0
86	3a	6	9	2	15	0,5982	3,36	>99,0
87	3a	7	11	2	14	0,3846	1,56	<95,0
88	3a	6	13	2	15	0,5536	2,88	>95,0
89	3a	6	15	2	15	0,2750	1,07	<95,0
90	3b	14	9	4	15	0,3473	1,42	<95,0
91	3b	15	11	4	14	0,4022	1,66	<95,0
92	3b	14	13	4	15	0,5518	2,86	>95,0
93	3b	14	15	4	15	0,2402	0,92	<95,0
94	4a	6	9	6	15	0,2777	1,08	<95,0
95	4a	6	11	6	15	0,3420	1,40	<95,0
96	4a	6	13	6	15	0,5330	2,68	>95,0
97	4a	6	15	6	15	0,1813	0,68	<95,0
98	4b	14	9	8	15	0,3929	1,68	<95,0
99	4b	14	11	8	15	0,1732	0,64	<95,0
100	4b	14	13	8	15	9,6625	4,26	>99,9
101	4b	14	15	8	15	0,3920	1,67	<95,0
102	5a	6	9	10	15	0,5116	2,50	>95,0
103	5a	8	11	10	13	0,0646	0,22	<95,0
104	5a	7	13	10	14	0,4824	2,18	=95,0
105	5a	9	15	10	13	0,5343	2,48	>95,0
106	5b	14	9	12	14	0,6923	4,61	>99,9
107	5b	15	11	12	13	0,4299	1,75	<95,0
108	5b	14	13	12	14	0,6187	3,47	>99,0
109	5b	16	15	12	13	0,7266	5,11	>99,9
110	6a	8	9	14	7	0,4107	33,00	<95,0
111	6a	6	11	14	9	0,8667	9,21	>99,9
112	6a	6	13	14	9	0,4167	1,33	<95,0
113	6a	7	15	14a	7	0,6161	21,50	<95,0
114	6b	17	9	16	7	0,3125	38,50	<95,0
115	6b	14	11	16	9	0,4292	1,39	<95,0
116	6b	15	13	16	8	0,0952	76,00	<95,0
117	6b	16	15	16	6	0,5429	16,00	<95,0

Tabelle 17: Zusammenstellung der Korrelationen zwischen den Kenngrößen vor und nach den Alterungen.
Table 17: Résumé des corrélations entre les valeurs caractéristiques avant et après les traitements de vieillissement.
Table 17: Summary of the correlations between characteristic values before and after the ageing processes.

	unge-altert *not aged*	Alterungen bei *Ageing at* 50°C 65% rF 305 h	50°C 65% rF 750 h	65°C 65% rF 305 h	65°C 65% rF 750 h	80°C 65% rF 305 h	80°C 65% rF 750 h	95°C 85% rF 305 h	95°C 85% rF 750 h
Bruchlast n. Falzung *Breaking strength n. folding*	***	***	***	***	***	***	***	–	–
pH Oberfläche *Surface pH*	***	***	***	**	***	**	***	**	*
Carboxylgruppen *Carboxyl groups*	***	***	***	***	***	***	***	–	–
Kappazahlen *Kappa numbers*	***	***	***	***	***	***	***	***	***
Alkalilöslichkeit *Alkali solubility*	***	***	***	***	***	***	***	–	–

Statistische Sicherheit der Korrelationen: *** 99.9%
Ecart statistique de sécurité des corrélations: ** 99%
Statistical margin of safety for the correlations: * 95%
– 95%

6.2. Wie soll man künstlich altern?

Der Zufall, daß Summe, Reihenfolge, gegenseitige Beeinflussung und Überlagerung der Vorgänge des Alterns bei einer höheren Temperatur mit denen bei Zimmertemperatur identisch sind und daß nur ihre Stärke verschieden ist, liegt mit Sicherheit nicht bei 50°, 65° oder 95° vor. Wenn es einen solchen Zufall gibt, liegt er am ehesten von den untersuchten Alterungsbedingungen bei 80°C und 65% rF vor. Hierzu sei auf Abb. 8 und auf Tab. 17–19 verwiesen, die eine

Tabelle 18: Zusammenstellung der Korrelationen zwischen Bruchlast nach Falzung der ungealterten Papiere und den anderen Kenngrößen vor und nach den Alterungen.
Table 18: Résumé des corrélations entre la résistance à la rupture après pliage de papiers sans vieillissement et les autres valeurs caractéristiques avant et après les traitements de vieillissement.
Table 18: Summary of the correlations between the breaking strength after folding of unaged paper and the other characteristic values before and after the ageing processes.

	unge-altert *not aged*	Alterungen bei *Ageing at* 50°C 65% rF 305 h	50°C 65% rF 750 h	65°C 65% rF 305 h	65°C 65% rF 750 h	80°C 65% rF 305 h	80°C 65% rF 750 h	95°C 85% rF 305 h	95°C 85% rF 750 h
pH Oberfläche *Surface pH*	**	*	*	–	*	*	*	–	–
Carboxylgruppen *Carboxyl groups*	–	–	–	–	–	–	–	*	–
Kappazahlen *Kappa numbers*	**	**	**	*	**	–	–	*	–
Alkalilöslichkeit *Alkali solubility*	–	–	–	–	–	**	**	–	–

Statistische Sicherheit der Korrelationen: *** 99.9%
Ecart statistique de sécurité des corrélations: ** 99%
Statistical margin of safety for the correlations: * 95%
– 95%

Übersicht über die gefundenen statistischen Zusammenhänge geben. Die künstliche Alterung bei 80°C und 65% rF führt jedenfalls zu praktikablen Meßwerten. Das ist ihr Nutzen. Bei der Bewertung ihrer Ergebnisse – wie auch der Ergebnisse anderer Alterungsmethoden, die anderenorts üblich sind und die ebenfalls zu praktikablen Ergebnissen führen – muß man sich ihres geschilderten Charakters jedoch bewußt sein. Vielleicht muß man soweit gehen, auch die trockene Ofenalterung, die hier nicht näher untersucht wurde, in diese Betrachtungsweise einzubeziehen. Ihre Bedingungen sind freilich allzu weit von den Bedingungen des natürlichen Alterns entfernt, und die Wahrscheinlichkeit des oben geschilderten Zufalls dürfte deshalb bei ihr besonders gering sein.

Tabelle 19: Zusammenstellung der Korrelationen zwischen Bruchlast nach Falzung und den anderen Kenngrößen in den verschiedenen Alterungszuständen.
Table 19: Résumé des corrélations entre la resistance à la rupture après pliage et les autres valeurs caractéristiques à divers niveau de vieillissement.
Table 19: Summary of the correlations between the breaking strength after folding and the other characteristic values at the different stages of ageing.

	ungealtert *not aged*	Alterungen bei *Ageing at* 50°C 65% rF 305 h	50°C 65% rF 750 h	65°C 65% rF 305 h	65°C 65% rF 750 h	80°C 65% rF 305 h	80°C 65% rF 750 h	95°C 85% rF 305 h	95°C 85% rF 750 h
pH Oberfläche *Surface pH*	**	**	–	–	–	*	***	–	–
Carboxylgruppen *Carboxyl groups*	–	–	–	–	–	–	–	*	–
Kappazahlen *Kappa numbers*	**	*	*	*	***	*	**	–	–
Alkalilöslichkeit *Alkali Solubility*	–	–	–	–	–	*	***	–	–

Statistische Sicherheit der Korrelationen: *** 99.9%
Ecart statistique de sécurité des corrélations: ** 99%
Statistical margin of safety for the correlations: * 95%
– 95%

Anhang:
Die Rangkorrelation nach Spearman ϱ (16) berechnet sich nach der Formel

$$\varrho = 1 - 6 \frac{\sum_{i=1}^{n} (u_i - v_i)^2}{n\,(n^2 - 1)}$$

u_i, v_i: Rangzifferen der Beurteilung
u - durch die eine Messung
v - durch die andere Messung
n: Zahl der Proben der Meßreihe

ϱ nähert sich bei Übereinstimmung der Beurteilung durch die beiden Meßreihen dem Wert + 1,000.

Erläuterung zu Abb. 1–4: Die durchgezogenen Linien sind die Regressionsgeraden, die gestrichelten Linien geben die Bereiche an.

Explication des fig. 1–4: Les droites en trait continu sont les lignes de régression et les droites en pointillé correspondent aux surfaces.

Explanation to figs. 1–4: The full-drawn lines are the regression lines, and the dotted lines indicate the areas.

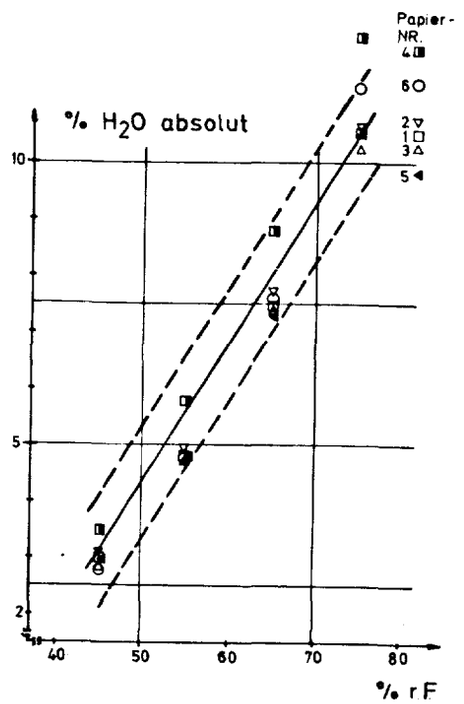


Abb. 1: Wasseraufnahme ausgewählter Papiere bei 50°C.

Fig. 1: Absorption d'eau de papiers sélectionnés à 50°C.

Fig. 1: Absorption of water of selected papers at 50°C.

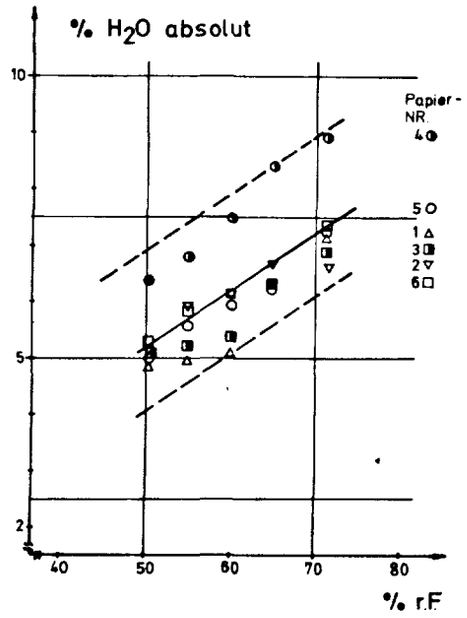


Abb. 2: Wasseraufnahme ausgewählter Papiere bei 65°C.

Fig. 2: Absorption d'eau de papiers sélectionnés à 65°C.

Fig. 2: Absorption of water of selected papers at 65°C.

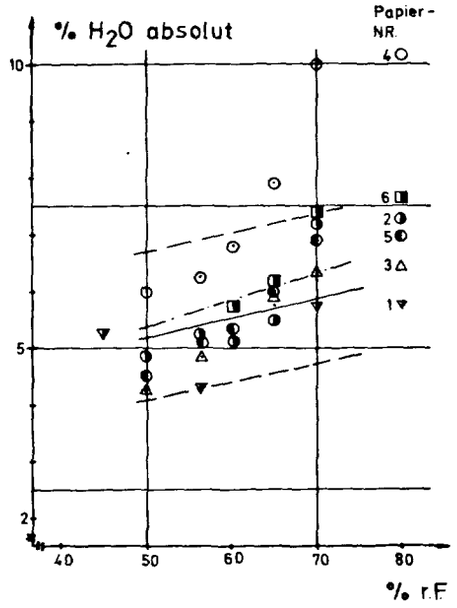


Abb. 3: Wasseraufnahme ausgewählter Papiere bei 80°C.

Die strich-punktierte Linie (.–.–) gibt die Regression für die bereits alten Papiere ohne die Muster 1–4 wieder.

Fig. 3: Absorption d'eau de papiers sélectionnés à 80°C.

La droite en trait mixte correspond à la régression de papiers prévieillis sans échantillons 1 à 4.

Fig. 3: Absorption of water of selected papers at 80°C.

The dot-and-dash line shows the regression for the already aged papers, without patterns 1–4.

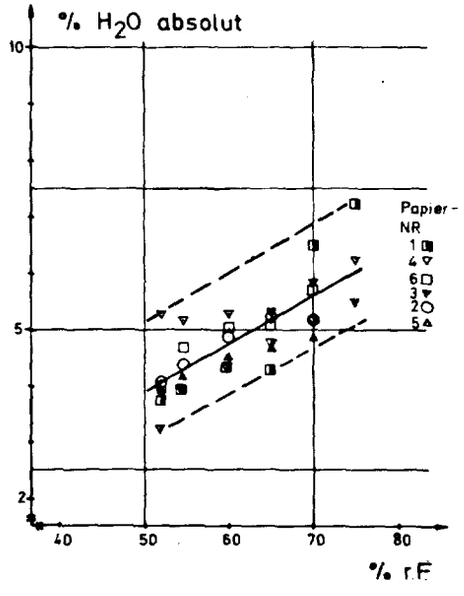


Abb. 4: Wasseraufnahme ausgewählter Papiere bei 95°C.

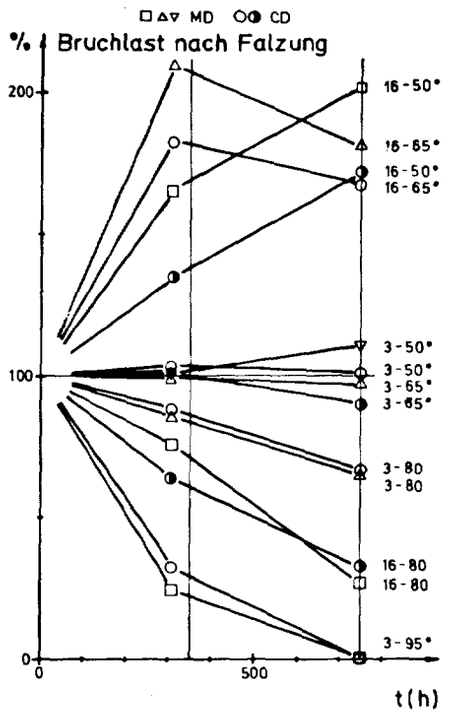
Fig. 4: Absorption d'eau de papiers sélectionnés à 95°C.

Fig. 4: Absorption of water of selected papers at 95°C.

Abb. 5: Prozentuale Veränderung der Festigkeit von Papier Nr. 3 und Nr. 16 durch die verschiedenen Alterungen.

Fig. 5: Changement relatif en % de la résistance des papiers n°s 3 et 16 durant les différents processus de vieillissement.

Fig. 5: Percentage change of strength of papers nos. 3 and 16 through the different ageing processes.



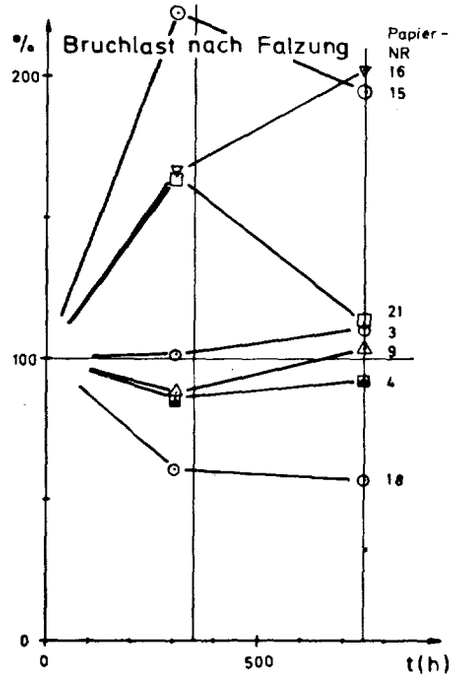


Abb. 6: Prozentuale Veränderung der Festigkeit MD ausgewählter Papiere durch die künstliche Alterung bei 50°C und 65% rF.

Fig. 6: Changement relatif en % de la résistance MD de papiers sélectionnés par vieillissement artificiel à 50°C et 65% HR.

Fig. 6: Percentage change of the MD strength of selected papers throughs artificial ageing at 50°C and 65% RH.

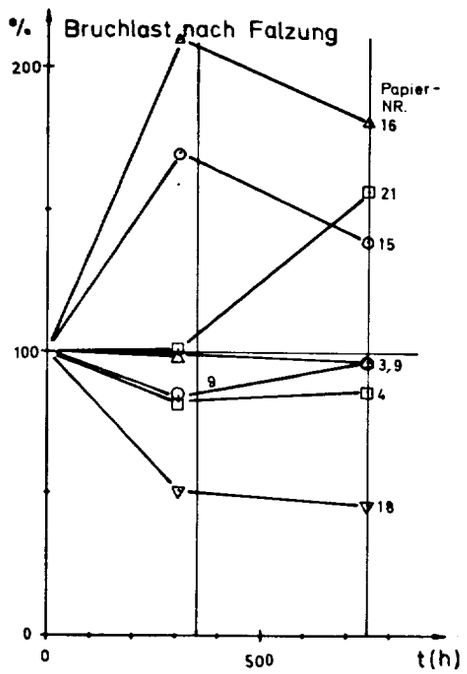


Abb. 7: Prozentuale Veränderung der Festigkeit MD ausgewählter Papiere durch die künstliche Alterung bei 65°C und 65% rF.

Fig. 7: Changement relatif en % de la résistance MD de papiers sélectionnés par vieillissement artificiel à 65°C et 65% HR.

Fig. 7: Percentage change of the MD strength of selected papers through artificial ageing at 65°C and 65% RH.

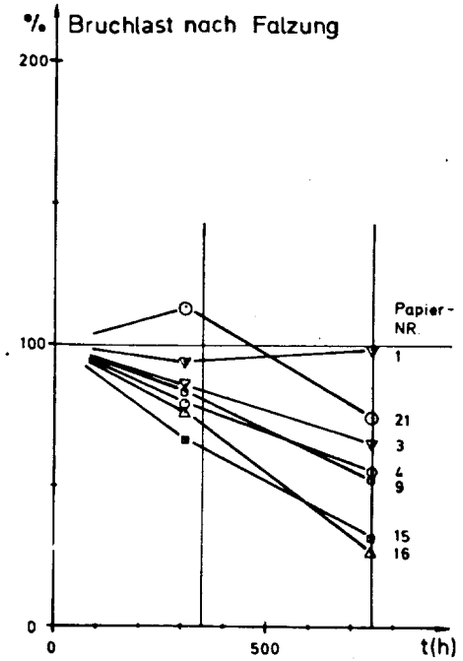


Abb. 8: Prozentuale Veränderung der Festigkeit MD ausgewählter Papiere durch die künstliche Alterung bei 80°C und 65% rF.

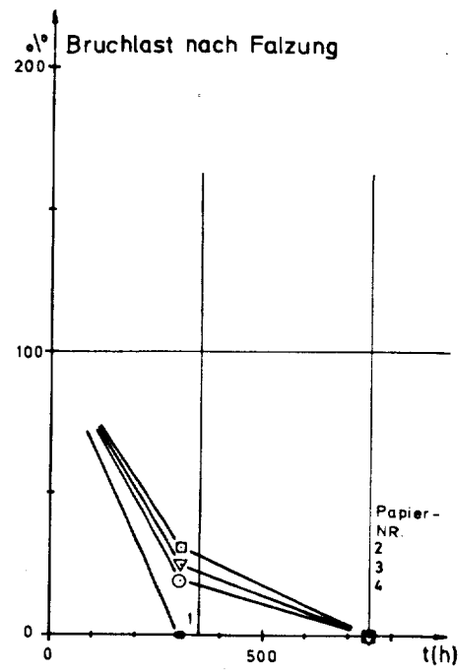
Fig. 8: Changement relatif en % de la résistance MD de papiers sélectionnés par vieillissement artificiel à 80°C et 65% HR.

Fig. 8: Percentage change of the MD strength of selected papers through artificial ageing at 80°C and 65% RH.

Abb. 9: Prozentuale Veränderung der Festigkeit MD ausgewählter Papiere durch die künstliche Alterung bei 95°C und 85% rF.

Fig. 9: Changement relatif en % de la résistance MD de papiers sélectionnés par vieillissement artificiel à 95°C et 85% HR.

Fig. 9: Percentage change of the MD strength of selected papers through artificial ageing at 95°C and 85% RH.



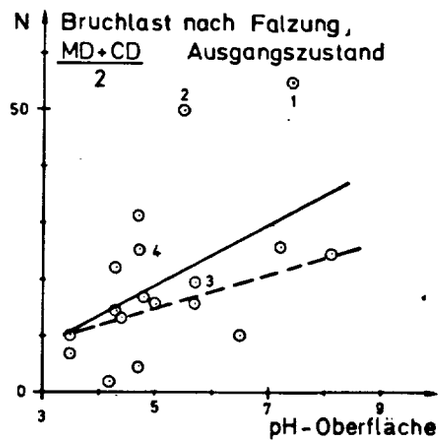
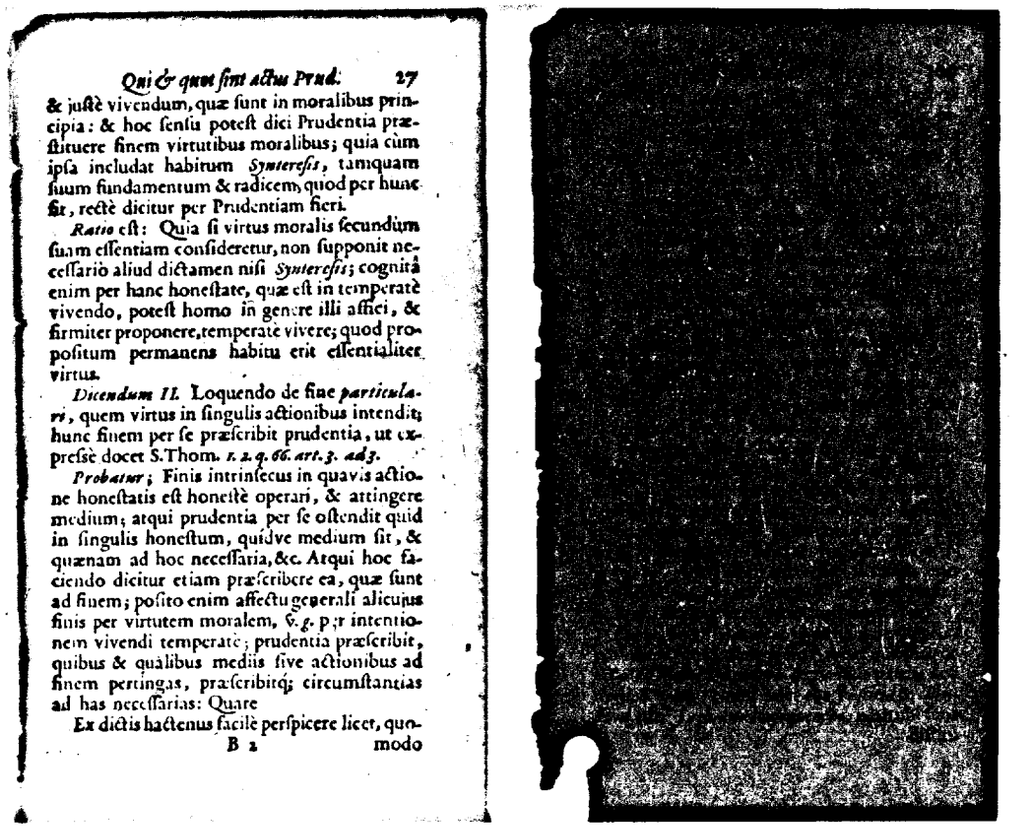


Abb. 10: Zusammenhang zwischen Bruchlast nach Falzung und Oberflächen-pH-Wert. Die gestrichelte Regressionsgerade gilt unter Ausschluß der fabrikneuen Papiere Nr. 1 bis 4.

Fig. 10: Corrélation existant entre la charge à la rupture après pliage et la valeur du pH en surface. La ligne de régression en tirets s'applique à tous les papiers à l'exception des papiers n^{os} 1 et 4 nouvellement produits et livrés par l'usine.

Fig. 10: Relation between breaking load after folding and surface pH value. The dashed regression line applies, except for papers Nos. 1 to 4 as supplied fresh from factory.



Qui & quot ſint actus Prud. 27

& juſtè vivendum, quæ ſunt in moralibus principia: & hoc ſenſu poteſt dici Prudentia præſtituere finem virtutibus moralibus; quia cùm ipſa includat habitum *Synteresis*, tanquam ſuum fundamentum & radicem, quod per hunc fit, rectè dicitur per Prudentiam fieri.

Ratio eſt: Quia ſi virtus moralis ſecundùm ſuam eſſentiam conſideretur, non ſupponit neceſſariò aliud dictamen niſi *Synteresis*; cognitâ enim per hanc honeſtate, quæ eſt in temperatè vivendo, poteſt homo in genere illi affici, & firmiter proponere, temperatè vivere; quod propoſitum permanens habitu erit eſſentialiter virtus.

Dicendum II. Loquendo de fine *particulari*, quem virtus in ſingulis actionibus intendit; hunc finem per ſe præſcribit prudentia, ut expreſsè docet S. Thom. *1. 2. q. 66. art. 3. ad 3.*

Probatur; Finis intrinſecus in quavis actione honeſtatis eſt honestè operari, & attingere medium; atqui prudentia per ſe oſtendit quid in ſingulis honeſtum, quidve medium ſit, & quænam ad hoc neceſſaria, &c. Atqui hoc faciendo dicitur etiam præſcribere ea, quæ ſunt ad finem; poſito enim affectu generali alicujus finis per virtutem moralem, v. g. p;r intentionem vivendi temperatè; prudentia præſcribit, quibus & qualibus mediis ſive actionibus ad finem pertingas, præſcribitq; circumſtantias ad has neceſſarias: Quare

Ex dictis hactenus facilè perſpicere licet, quo-

B 2 modo

Abb. 11: Ein Hadernpapier des frühen 16. Jahrhunderts vor und nach der Künstlichen Alterung bei 95°C, 85% rF, 750 h.

Fig. 11: Papier de chiffon du début du 16ème siècle, avant et après le vieillissement artificiel à 95°C, 85% HR pendant 750 heures.

Fig. 11: Rag paper from the beginning of the 16th century, before and after artificial ageing at 95°C, 85% RH, 750 h.

ZUSAMMENFASSUNG:

Die Aussagekraft einer künstlichen Alterung von Papier für Prognosen über seine zukünftige Benutzbarkeit.

Ein Versuch zur künstlichen Alterung, der abweichend vom Üblichen bei relativ niederen Temperaturen (50°C bis 95°C) und nicht an Laborprüfblättern, sondern an bereits natürlich gealterten Papieren der wirklichen Produktion aus vier Jahrhunderten durchgeführt wurde, ergab Werte, die zu der These berechtigen, daß zwischen den Ergebnissen einer künstlichen Alterung durch erhöhte Temperatur und den Ergebnissen des natürlichen Alterns bestenfalls eine zufällige Übereinstimmung bestehen kann. Die chemischen Vorgänge, welche das Altern von Papier ausmachen, scheinen in temperaturspezifisch verschiedener Weise abzulaufen, so daß es nicht möglich ist, von dem kurzzeitigen Ablauf bei der einen (erhöhten) Temperatur auf den langzeitigen Ablauf bei einer anderen (Zimmertemperatur) zu schließen. Wenn trotz dieser Unsicherheit auf künstliche Alterung nicht verzichtet werden kann, sollte man bei 80°C und 65% rF altern.

RÉSUMÉ:

Valeur du vieillissement artificiel du papier permettant un pronostic de son utilisation future.

Un essai de vieillissement artificiel à des températures relativement basses (50°C à 95°C) contrairement aux essais habituels et sur du papier ayant vieilli de façon naturelle provenantd'une production remontant à quatre siècles au lieu de feuilles d'essai en laboratoire a permis d'obtenir des valeurs justifiant la thèse de l'existance éventuelle dans le cas le plus favorable d'une relation fortuite entre les résultats d'un traitement de vieillissement artificiel à hautes températures et les résultats du processus de vieillissement naturel. Les processus chimiques contribuant au vieillissement du papier semblent adopter des dynamiques différentes spécifiques en fonction des températures rendant impossible l'établissement de conclusions résultant de l'exposition brève à une température (accrue) d'une part et de l'exposition prolongée à une température (accrue) d'autre part. Si le vieillissement artificiel ne peut pas être abandonné en dépit de cette incertitude, le vieillissement devrait être effectué à 80°C et à 65% HR.

SUMMARY

The value of artificial ageing of paper for prognoses of its future usability.

An experiment with artificial ageing which in contrast to the usual tests was carried out at relatively low temperatures (50°C to 95°C), and not on laboratory test sheets, but on naturally aged paper from the real production of four centuries, produced values justifying the thesis that there may at best be an accidental consistency between the results of an artificial ageing process by means of high temperatures and the results of the natural ageing process. The chemical processes, of which the ageing of paper consists, appear to take different temperature specific courses, so that it is not possible to draw any conclusions from the short-term expiration at one (increased) temperature on one hand, and the long-term expiration at one (increased) temperature on the other hand. If artificial ageing cannot be dispensed with despite this uncertainty, ageing should take place at 80°C and 65% RH.

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Microbiodeterioration of Library Materials
Part 2
Microbiodecomposition of Auxiliary Materials
Chapter 5–9

by ROMUALD KOWALIK

Contents

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5.1.1. Adhesives and Products Used for Strengthening Purposes

Adhesives of both natural and synthetic origin may be destroyed by biological agents, and therefore can also stimulate the growth of microorganisms on paper, leather, ink, etc.

As sizing materials for leather texts and leather bookbindings, gluten, casein, starch, natural and synthetic rubber, polyvinyl acetate, polyvinyl chloride, cellulose derivatives and polyurethane resins have been used. From the conservation point of view, the value of these adhesives is not always advisable and should therefore be used carefully. Adhesives employing synthetic polymers are

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more resistant or even impervious to microbial degradation. Protein-based adhesives such as gluten and casein are usually attacked by bacteria, whereas those containing starches, dextrins and sugars are generally more susceptible to attack by fungi and yeasts. The amount of water also determines the nature of attack since bacteria require approximately 100% R.H. while fungi may grow even when R.H. ranges below 70%. The microbial enzymes decompose the adhesives by reducing their viscosity and pH and by producing undesirable odours and stains.

The oldest and cheapest adhesives for cellulosics are the starches, which are generally more susceptible to attack by fungi and yeasts, very often observed on papyrus, sometimes sized with wheat and barley starch, and on china paper, where rice starch was used in its manufacture. Starch adhesives cause the increase of acidity in paper[2,3,9,14,21,25] and propagate the origin of coloured metabolic products stimulated by microorganisms. Etherified and estherified starch offers improved properties at a slightly higher cost.[2] At present, an adhesive in bookbinding and conservation is based on 80% rice starch and 20% polyvinyl alcohol. Protein glues, which are usually attacked by bacteria, were used in paper manufacture in the 14th century. The most important commercial sources of starch at the present time are corn and potato. Starch has a more compounded and controversial chemical structure than the closely related cellulose. Starch is a polymer of glucose and one type of molecule has a linear chain-structure amylose, while amylopectin, the other type, has a tree-like branched structure. The diameter of granules vary from 0.005 mm (corn starch) to 0.090 mm (potato starch).[22] Starch can be degraded by enzymes, acids, oxidizing agents and heat into adhesives having a wide range of aqueous viscosity. Oxidized starch is utilized for surface sizing of high grade paper. Starch adhesives are subject to a quick fermentation and change their physical properties. Microbial enzyme amylase destroy starch into simple sugars and decrease its ability as an adhesive, causing the spines of bookbinding to lose their strength and warp. Bacterial and fungal slimes, which develop on starch employed as paper size in the manufacture of paper, may block the machinery in paper mills.

In medieval times, sheets of hand-made paper were immersed in protein-animal glue and then suspended for drying. Animal glues are obtained by hydrolysis of collagenic materials such as hides and bones and connective tissues. At the present time they are rarely used, and only as a coating adhesive for specialty products. A more highly purified form of animal protein-gelatin from hides gives a slightly alkaline adhesive used in conservation, but gelatin from bones are slightly acidic and free acids may damage the paper owing to the susceptible dyes of its decorations. Therefore, neutralization is necessary. It

is worth mentioning that the spine folds of books, where animal glue is deeply entrenched and retains water, are especially conducive to a prolific growth of microorganisms. This was noted, for example, in Florence during the restoring of codices damaged by flood waters.[20]

Soluble nylon[8,18,26] and parchment glue are advised for the repair of manuscripts, particularly collagenic ones.

Considering the gums, gum arabic extracted from acacia pods is the best known adhesive used in the manufacture of persian inks[15] and in postage stamps.

Silicates have been used to laminate paper-to-paper in the manufacture of boards. At present, these have been replaced by starches and synthetics.[22]

Many adhesives, as well as strengthening materials for paper, are based on synthetic polymers. From the biological point of view, synthetic polymers give the best protection to various products because biological agents do not destroy highly polymerized organic compounds. Some additives, however, may inform the enzyme to attack different plastics. The attack increases on the surface area of the plastic material, thus rendering it more susceptible to chemical and mechanical degradation.[6,7] As a rule plastics are not easily accessible to enzyme systems of living organisms. The use of polymers, however, or the procedure of blocking, for instance, hydroxyl groups of cellulose by acethylation, ethylation, carboxymethylation[13,14,21] etc. do not provide complete security against microbiodeterioration and the application of microbiocide may still be necessary.

Most important in bookbinding and conservation work are synthetic vinyl adhesives and, above all, polyvinyl acetate.[22] An excellent adhesive used in the preservation of cellulosic materials is polyvinyl alcohol, produced by hydrolysis of nonbacterial resistant[6] polyvinyl acetate. However, polyvinyl alcohol is not heat resistant.[22]

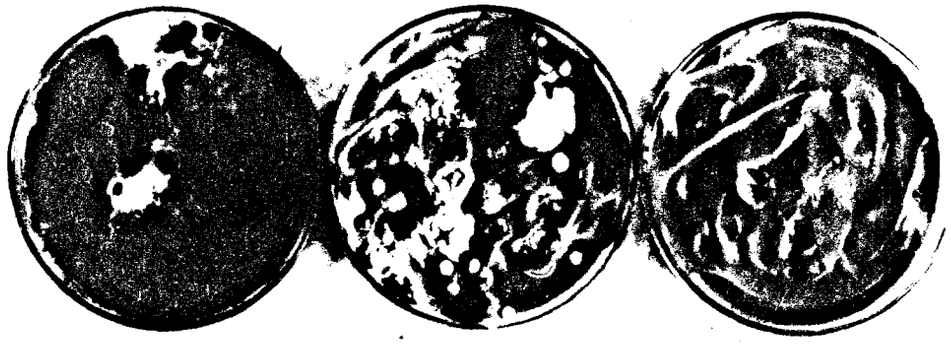
Many adhesives used in conservation and restoration of library materials are based on cellulose derivatives. Adhesives based on two esters: cellulose acetate and cellulose acetobutyrate are excellent for paper and leather.[22] The ethers of cellulose and especially hydroxyethylcellulose and carboxymethylcellulose are the best for strengthening paper.[11,19,28] The adhesives based on cellulose derivatives are microbioresistant. The microbioresistance changes from moderate for hydroxyethylcellulose, fair for carboxymethylcellulose, very good for cellulose acetate to excellent for methyl- and ethylcellulose.[16,22]

Of the different fungicides and bactericides mentioned in literature[4,5,10,13,17,23,24] for the protection of adhesives, sodium salt of 4-chloro-3-cresol and 2.2'-dihydroxy-5.5'-dichlorodiphenylmethane (common name dichlorophen) seems to be the most suitable in the conservation of library materials and works

of art. Salicylanilide as a fungicide for adhesives based on polyvinyl alcohol or methylcellulose has also been proposed.[27]

Experiments made in our laboratory[14,21] regarding microbioresistance of adhesives used in library materials conservation confirmed the general opinion that adhesives of natural origin, and especially the starches, are the least microbioresistant. These adhesives are readily metabolized by many genuses of fungi and some species of bacteria. Starch is quickly hydrolyzed by spore forming bacteria and their enzyme amylase reduces its viscosity. The experiments made on rice starch adhesive infected with bacteria have shown that the decrease of viscosity of this adhesive stored for 48 h in airtight flasks ranged about 90% and in air-containing flasks about 45%.

The selected microbiocides: 4-chloro-3-cresol and dichlorophen may kill fungi by the inclusion of 0.2% per weight, but they are only biostatic against bacteria; this has been observed several times in our laboratory (Fig. 1). These biocides used at the concentration of 1% per weight of adhesive were not effective against *Pseudomonas fluorescens*, Migula and *Bacillus subitilis*, Cohn and it



A B C

Fig. 1. The tests of fungicidal and bacterostatic activity of 4-chloro-3-cresol, as adhesive preservative. A: Control. B: Concentration of 0.2% of sodium salt of 4-chloro-3-cresol. C: Concentration of 0.5% of 4-chloro-3-cresol.

Fig. 1 Essais d'activité fongicide et bactériostatique du 4-chloro-3-crésol à titre d'agent de conservation des produits adhésifs. A: Contrôle. B: Concentration: 0,2% de sel de sodium du 4-chloro-3-crésol. C: Concentration: 0,5% de 4-chloro-3-crésol.

Abb. 1. Tests der fungiziden und bakteriologischen Tätigkeit von von 4-Chloro-3-Cresol als Konservierungsmittel für Klebstoff. A: Kontrolle. B: 0,2%ige Konzentration Natriumsalz von 4-Chloro-3-Cresol. C: 0,5%ige Konzentration von 4-Chloro-3-Cresol.

was found that dichlorophen was a slightly better preservative than 4-chloro-3-cresol.

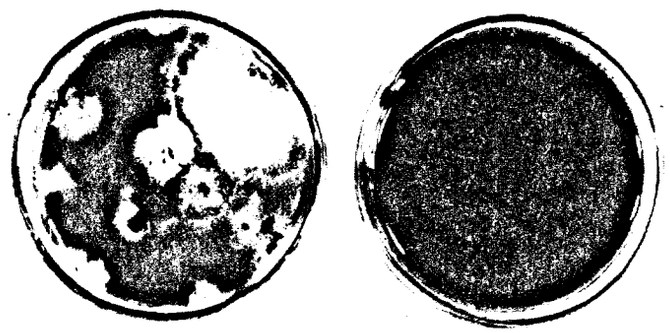
Animal glue composed of 40% bone glue, 11% kaolin and 5% ethyl polyglycol used for bookbinding was more bioresistant than starch adhesive. Bone glue composition could also be a source of carbon and nitrogen for some fungi and bacteria and was destroyed above all by *Aspergillus flavus*, Link, producing cancerogenic metabolite aflatoxin, by *Aspergillus terreus*, Thom, *Paecilomyces varioti*, Bainier and *Candida albicans*, (Robin) Berkhout. We also tested the microbioresistance of parchment glue, prepared according to the prescription given by Reed.[20] The use of this glue in conservation and restoration practice and particularly in the manuscript field seemed to us very advisable. This glue was used by mediaeval craftsmen as an adhesive and strengthener of old and weak parchments, and these manuscripts are still in excellent condition after more than a thousand years.[20] According to our experiments, parchment glue is strongly destroyed by microorganisms (Fig. 2) and 1% dichlorophen protects it sufficiently for two weeks only (Fig. 3 a,b). It is worth mentioning that *Aspergillus sp.*, probably candidus, isolated from parchment glue is especially resistant to dichlorophen.

Synthetic adhesives are much more microbioresistant than natural ones. However, they may be attacked by biological agents difficult to inhibit. Our experiments made on adhesives based on cellulose acetate, hydroxyethylcellulose, polyvinyl acetate and polyvinyl alcohol have shown that the most resistant

Fig. 2. Growth of fungi on parchment glue after 3 weeks of cultivation.

Fig. 2. Développement des moisissures sur de la colle à parchemin après 3 semaines de culture.

Abb. 2. Wachstum von Pilzen auf Pergamentkleber nach dreiwöchiger Züchtung.



A B

Fig. 3. Parchment glue sprayed with spores suspensions. A: Untreated. B: Treated with 1% of dichlorophen.

Fig. 3. Colle à parchemin avec pulvérisation d'une suspension de spores. A: Sans traitement. B: Traitée avec 1% de dichlorophène.

Abb. 3. Pergament, das mit Sporenaufschlämmungen besprüht worden ist. A: Unbehandelt. B: Behandelt mit 1%igem Dichlorophen.

is polyvinyl alcohol and the least resistant, hydroxyethylcellulose. The following fungi were isolated from the above mentioned synthetic adhesives: *Aspergillus terreus*, Thom, some species of the genus Penicillium, for example *Penicillium luteum*, Zukal and *Paecilomyces varioti*, Bainier and apart from these *Trichoderma viride*, (Persoon) Harz and *Cladosporium herbarum* (Persoon) Link were isolated from hydroxyethylcellulose. Synthetic adhesives were also damaged by bacteria, as *Bacillus subtilis*, Cohn, *Pseudomonas fluorescens*, Migula and *Nocardia sp.* The deterioration of synthetic adhesives by fungi is slow and after four weeks the decrease of the viscosity of ethylhydroxyethylcellulose amounted to about 7.5%, polyvinyl acetate to 6% and carboxymethylcellulose to about 3%. Decomposition of synthetic adhesives by bacteria is much more distinct. The decrease of the viscosity of polyvinyl acetate contaminated by *Bacillus subtilis*, *Pseudomonas fluorescens* and *Proteus vulgaris* amounted, after four weeks, to about 50%. From our experiments on synthetic adhesives with selected biocides: dichlorophen and 4-chloro-3-cresol, it may be concluded that polyvinyl acetate adhesive needs a higher concentration of microbiocides against bacteria than natural glues and sizes. The same property could be observed in our laboratory during the preservation of different synthetic adhesives destined for industrial purposes. It was established that 4-chloro-3-cresol and dichlorophen at the amount of 1% per weight of adhesive can assure the preservation of polyvinyl

acetate only against fungi. These biocides at the above mentioned concentration did not sufficiently protect synthetic adhesives against *Bacillus subtilis* and *Pseudomonas fluorescens*. It has been found that dichlorophen is a little more effective than 4-chloro-3-cresol.

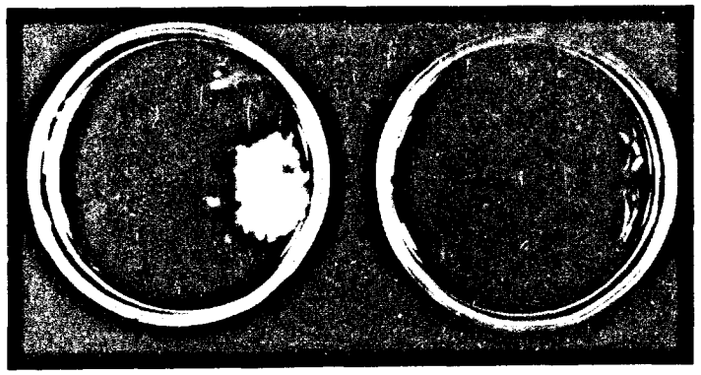
Modocoll E 300 produced by Mo and Domsjö, Stockholm, and based on ethylhydroxyethylcellulose, is not resistant to fungi and bacteria but 1% of dichlorophen effects protection for at least one month.

Glicocel TA 5% produced by Pronit, Poland, and based on carboxymethylcellulose is moderately attacked by microorganisms and may effect protection by 1% of dichlorophen for more than one month, but this biocide causes discolouration of the adhesive.

Klucel G 2% produced by the Hercules Incorporation, Wilmington, Delaware U.S.A., and based on hydroxypropylcellulose is also moderately contaminated by microorganisms and 1% of dichlorophen adds protection for more than one month (Fig. 4).[12]

Klucel J 5% produced by Hercules Incorporation, Wilmington, Delaware U.S.A., and based also on hydroxypropylcellulose is nearly microbioresistant (we have noticed only one colony on plate during a two-month period) and with 1% of dichlorophen is a good microbiotoxicant.

Nylon soluble (N-methoxymethylnylon=Calaton CB), produced by Picreator Enterprises Ltd., London, is completely resistant.



A B

Fig. 4. 2% Klucel G sprayed with spores suspensions. A: Untreated. B: Treated with 1% of dichlorophen.

Fig. 4. Klucel G à 2% avec pulvérisation de suspensions de spores. A: Sans traitement. B: Traité avec 1% de dichlorophène.

Abb. 4. 2% Klucel G, das mit Sporenaufschlämmungen besprüht worden ist. A: Unbehandelt. B: Behandelt mit 1% igen Dichlorophen.

Intensity of microbiodeterioration of synthetic adhesives depends on the chemicals of lower molecular weight such as lubricants, stabilizers, plasticizers, and antioxidants, which may act as a source of food for the microorganisms better than the molecular itself.

Considering these data and the risk of the difficulty in killing bacteria, particularly the spore-forming ones, the adhesives applied in conservation should be prepared immediately before use. If it is impossible to fulfill these conditions, attention must be paid to a short period of storage of the particular adhesive. Adhesives distinguished by their high microbioresistance are especially recommended for use in the conservation of library materials, archives and works of art. In our opinion the standardization of this property in the field of conservation is urgent. We have adapted, therefore, the industrial standards of microbioresistance of adhesives, namely: ASTM 1174–55 and ASTM 1286-57.[1] On the basis of our experiments we propose to enlarge the set of fungi of ASTM standards and include *Paecilomyces varioti* and *Aspergillus terreus*, which occurred on all synthetic adhesives examined by us. Moreover it seems advisable to evaluate the microbioresistance, not only on the measurement of viscosity, but also on the determination of the presence of living cells of fungi and bacteria in the examined sample. Additional microbiological analysis can provide some insight into the cause of changes of viscosity due to the growth of microorganisms. This is important, particularly in estimating the effects of the preservative.

5.1.2 Abstract

Adhesives and Products Used for Strengthening Purposes

Adhesives of vegetable, animal and synthetic origin may be destroyed by fungi and bacteria. Experiments made in our laboratory regarding microbioresistance of adhesives used in library materials confirmed the general opinion that adhesives of natural origin are readily metabolized by many genuses of fungi and some species of bacteria. The experiments made on rice starch adhesive infected with bacteria have shown that the viscosity of this adhesive, stored for 48 h in airtight flasks, ranged about 90%, and in air-containing flasks about 45%. The deterioration of synthetic adhesives by fungi is slow and, after four weeks, the decrease of the viscosity of hydroxyethylcellulose amounted to about 7.5%, polyvinyl acetate to 6% and carboxymethylcellulose to about 3%. Decomposition of synthetic adhesives by bacteria is much more distinct. For example, after four weeks the decrease of the viscosity of polyvinyl acetate contaminated by *Bacillus subtilis*, *Pseudomonas fluorescens* and *Proteus vulgaris* amounted to about 50%.

Two microbiocides:dichlorophen and 4-chloro-3-cresol were selected against bacteria and fungi. Dichlorophen was found to be a little more active. To be noted is that out of various adhesives examined in our laboratory only the adhesive based on hydroxypropylcellulose is nearly microbioresistant (one colony on plate during two months) and soluble nylon is completely resistant. Adhesives distinguished by their microbioresistance are especially recommended for use in conservation of library materials. Considering the results of our experiments, we propose to enlarge the

set of fungi of ASTM standards and include *Paecilomyces varioti* and *Aspergillus terreus*, which occurred (excluding soluble nylon) on all adhesives examined.

5.1.2 Résumé

Produits adhésifs et produits à effet de renforcement

Les produits adhésifs d'orignie végétale, animale et synthétique peuvent être détruits par des moisissures et des bactéries. Des assais menés dans notre laboratoire portant sur la résistance des adhésifs utilisés dans les matériels de librairie à l'action des microbes ont confirmé l'opinion généralement reconnue selon laquelle les produits adhésifs naturels sont aisément métabolisés par des types nombreux de moisissures et quelques espèces microbiennes. Les expériences effectuées sur des adhésifs à base d'amidon de riz contaminés par des cultures microbiennes ont montré que la valeur de la viscosité de ce produit adhésif entreposé pendant 48 heures dans des bouteilles hermétiques à l'air s'est établie à 90% environ de la valeur initiale et à 45% environ dans le cas de bouteilles contenant de l'air. La détérioration des produits adhésifs synthétiques par les moisissures est lente et, après quatre semaines, la diminution de la viscosité est de l'ordre de 7,5% pour l'hydroxyéthylcellulose, de 6% pour l'acétate de polyvinyle et de 3% pour la carboxyméthylcellulose. La décomposition des adhésifs de synthèse par les bactéries est beaucoup plus nette. Par exemple, aprés 4 semaines, la chute de viscosité de l'acétate de polyvinyl contaminé par Bacillus subtilis, Pseudomonas fluorescens et Proteus vulgaris est de l'ordre de 50%. Deux bactéricides: le dichlorophène et le 4-chloro-3-crésol ont été sélectionnés comme bactéricide et fongicide. L'activité du dichlorophène s'est avérée être légèrement supérieure. Noter toutefois que parmi les divers produits adhésifs passés en revue dans notre laboratoire, seul l'adhésif à base d'hydroxypropulcellulose résiste pratiquement à l'action des microorganismes (une colonie sur boîte pendant deux mois) et le nylon soluble offre une résistance absolue. Les produits adhésifs sélectionnés en raison de leur résistance à l'action microbienne sont spécialement recommandés pour la conservation des matériels de bibliothèque. Sur la base des résultats de nos essais, nous proposons d'étendre la gamme des moisissures utilisées dans les standards ASTM et d'inclure pascilomyces varioti et Aspergillus terreus présents dans tous les échantillons d'adhésifs passés en revue, à l'exception du nylon soluble.

5.1.2 Resümee

Klebstoffe und Produkte, die zu Verstärkungszwecken verwendet werden

Klebstoffe vegetabilischen, animalischen und synthetischen Ursprungs können durch Pilze und Bakterien zerstört werden. Experimente, die in unserem Laboratorium in bezug auf die mikrobiologische Beständigkeit von Klebstoffen, die in Bibliotheksmaterialien verwendet werden, durchgeführt worden sind, haben die Ansicht bestätigt, dass Klebstoffe natürlicher Herkunft leicht von vielen Pilz- und Bakterienarten verändert werden. Experimente, die mit Klebstoff der Reisstärke, die mit Bakterien infiziert wurden, durchgeführt worden sind, zeigten, dass die Viskosität der 48 Stunden in luftdicht verschlossenen Flaschen aufbewahrten Klebstoffe 90% betrug, während die der in Luft enthaltenden Flaschen bei 45% lag. Synthetische Klebstoffe dagegen werden nur langsam von Pilzen angegriffen. Nach 4 Wochen war die Viskosität von Hudroxyl-Äthylzellulose auf etwa 7,5%, von Polyvinyl-Azetat auf 6% und von Karboxy-Methylzellulose auf etwa 3% abgefallen. Die Zersetzung von synthetischen Klebstoffen durch Bakterien verläuft dagegen völlig anders. Die Viskosität von Polyvinyl-Azetat, das mit Bacillus subtilis, Pseudomonas fluorescens und Proteus vulgaris verseucht wurde, war nach 4 Wochen auf etwa 50% abgesunken.

Gegen den Befall durch Bakterien und Pilze wurden zwei Mikrobiozide gewählt, und zwar Dichlorophen und 4-Chlor-3-Cresol, wobei sich Dichlorophen als etwas aktiver erwies. Es ist hier zu unterstreichen, dass sich von den vielen Klebstoffen, die in unserem Laboratorium untersucht worden sind, lediglich auf der Basis von Hodroxypropyl-Zellulose hergestellter Klebstoff als fast mikrobioresistent (im Laufe von 2 Monaten eine Kolonie auf der Platte) erwies, während lösliches Nylon völlig resistent ist. Klebstoffe, die sich durch ihre mikrobiologische Resistenz auszeichnen, sind für die Konservierung von Bibliotheksmaterial besonders zu empfehlen. Auf der Grundlage der Ergebnisse unserer Tests schlagen wir vor, in die Gruppe der Pilze, die von den ASTM-Standards erfasst werden, auch Paecilomyces varioti und Aspergillus terreus aufzunehmen, da diese in allen genannten Klebstoffen nachgewiesen werden konnten (mit der Ausnahme von löslichem Nylon).

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5.2.1 Wax Seals

Old wax seals are composed of beeswax as a basic component, besides various amounts of resins, turpentine, Carnauba wax and other components.

Beeswax is composed primarily from miricin, soluble only in chloroform, other fraction-aromatic pigmented compounds, and a small amount of fatty product-cerolein, soluble in cold ethanol. Another fraction composed of cerotic acid and its homologues is soluble in warm ethanol. Bleached wax-ceresin, paraffin and Carnauba wax are the components of beeswax not soluble in chloroform.[8]

Ethanol extractable organic substances and vegetable waxes, such as Carnauba wax and others which include pieces of woodbark, undergo, as a rule, microbiodeterioration.

Dobbie and Fox[3] mention for the first time that the great acidity of the XIIIth century wax seal was probably produced by fungi. According to Fleetwood[4] Actinomycetes play an important role in the biodeterioration of wax seals. Light spots and cracking of wax seals is the resulting activity of these microorganisms. Niethammer[10] has found that wax may be the source of carbon of some fungi and Imai[7] isolated 22 fungi growing on wax and paraffin.

Well preserved wax seals have been composed of pure beeswax with 30% of pigment or beeswax with a small amount of colophony and turpentine.[1] Dobbie and Fox's data on the wax seals from the XIII-XVIth centuries indicate that there were some amounts of colophony. Microbioresistance may be attributed also to pigments-verdigris and cynober.[1]

Copper oleate for green wax seals, cynober for red ones and 2-hydroxydiphenyl or salicylanilide for white wax seals have been proposed as biocides.[1,9]

In our experiments we have used the following media with wax as a source of carbon:

Wax seals, dissolved in benzene, were placed on filter paper. Then 20 ml solution of the following salts were added to the Petri dishes:

Bushnell and Haas medium[2] composed of

NH_4NO_3 or/$NH_4/_2SO_4$	1 g
$MgSO_4$	0.2 g
$CaCl_2$	0.02 g
K_2HPO_4	1 g
KH_2PO_4	1 g
$FeCl_3$ conc.	2 drops
distilled water	1000 ml

or Iizuka and Komagata medium[6]

NH_4NO_3	2.5 g
Na_2HPO_4	1.0 g
KH_2PO_4	0.5 g
$MgSO_4$	0.5 g
$MnCl_2$	0.2 g
and traces of $CaCl_2$, $ZnSO_4$, $FeSO_4$	
distilled water	1000 ml

and wax sterilized separately, 5%. We had adjusted pH to 5.0 for fungi and 7.5 for bacteria and Actinomycetes. Cultures were maintained for 3 months at 24–26°C and 85–95% R.H. The growth of microflora was assessed every seven days and colonies of microorganisms were inoculated on sterilized agar media and identified.

We had isolated:

Aspergillus sp.
Aspergillus fumigatus, Fresenius
Alternaria tenuis, Nees
Cephalosporium sp.
Cladosporium herbarum (Persoon) Link
Coprinus sp.
Fusarium sp. (Fig. 5)
Gliomastix murorum, (Corda) Hugues
Paecilomyces varioti, Bainier
Penicillium sp. (Fig. 6)
Scopulariopsis brevicaulis var.glabra, Thom (Fig. 7)
Stemphylium sp. (Fig. 8)

and two strains of Streptomyces.

We proposed to kill the microorganisms on the wax seals with phenol derivatives:o-phenylphenol or 4-chloro-3-cresol, which are moderately strong fun-

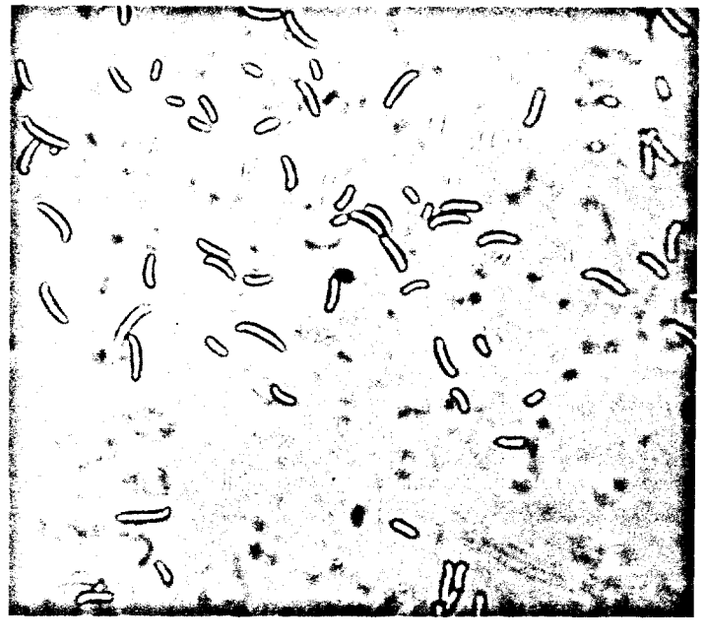

Fig. 5. *Fusarium sp.* Magn. × 500

Fig. 6. *Penicillium sp.* Magn. × 250

Fig. 7. *Scopulariopsis brevicaulis var.glabra*, Thom. Magn. × 420

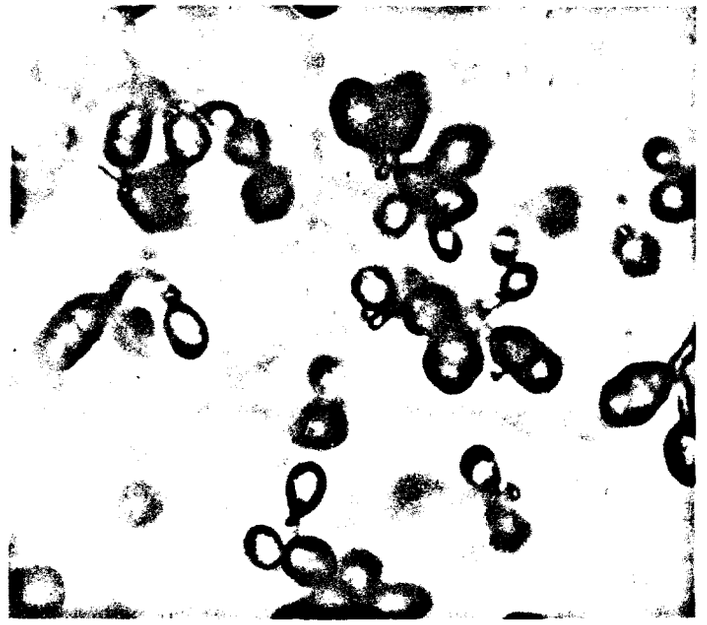

Fig. 8. *Stemphylium sp.* Magn. × 500

gicides, that don't need the use of the solvents which could damage the wax seals.

For wax-seal washing we proposed the use of distilled and sterilized water with a small addition of 0.01% of sodium salt of 4-chloro-3-cresol. The sodium salts of phenols have, however, some disadvantages because on accelerated ageing they caused yellowing of the paper, supposedly because of free sodium hydroxide produced by hydrolysis of the salt.[11]

5.2.2 Abstract

Wax Seals

Old wax seals are composed of beeswax as a basic component, besides various amounts of resin, turpentine, Carnauba wax and other components. Well preserved wax seals were composed of pure beeswax with red pigment, or with some amounts of colophony and verdigris and cynober. Wax seals with pieces of woodbark undergo microbiodeterioration.

In our experiments we have used the medium of Bushnell and Haas and the Iizuka and Komagata medium with the addition in both media of wax sterilized separately in order to isolate the microflora decomposing wax seals. Cultures were maintained for 3 months at 24–26°C and 85–95% R.H. We have isolated the following fungi: *Aspergillus sp.*, *Aspergillus fumigatus*, Fresenius, *Alternaria tenuis*, Nees, *Cephalosporium sp.*, *Cladosporium herbarum*, (Persoon) Link, *Coprinus sp.*,

Gliomastix murorum, (Corda) Hugues, *Paecilomyces varioti*, Bainier, *Penicillium sp.*, *Scopulariopsis brevicaulis var.glabra*, Thom, *Stemphylium sp.* and two strains of Streptomyces.

We propose as microbiocide for wax seals o-phenyl-phenol and for cleaning the wax seals distilled and sterilized water with a small addition (0.01%) of 4-chloro-3-cresol.

5.2.2 Résumé

Sceaux à base de cire

Les sceaux de cire anciens comportent un constituant principal: la cire d'abeille et des quantités variables de résine, de térébenthine, de cire Carnauba et d'autres constituants. Les sceaux de cire présentant une bonne conservation étaient composés de cire pure d'abeille et d'un pigment rouge ou additionnés de diverses quantités de colophane, de vert-de-gris et de cinabre. Les sceaux de cire comportant des morceaux d'écorce sont soumis à une dégradation d'ordre microbienne. Lors de nos essais, nous avons utilisé le bouillon de culture de Bushnell et Haas et le bouillon d'Iizuka et Komagata en ayant ajouté à ces deux bouillons de la cire stérilisée séparément afin d'isoler la microflore qui conduit à la décomposition des sceaux de cire. Les cultures ont été conservées pendant 3 mois à 24–26°C et à une H.R. de 85–95%. Les moisissures suivantes ont été isolées: Aspergillus sp., Aspergillus fumigatus, Fresenius, Altermaria tenuis, Nees, Cephalosporium sp., Cladosporium herbarum, (Persoon), Link, Coprinus sp., Gliomastix murorum, (Corda), Hugues, Paecilomyces varioti, Bainier, Penicillium sp., Scopulariopsis brevicaulis var.glabra, Thom, Stemphylium sp. et deux souches de Streptomyces.

A titre de microbicide valable pour les sceaux de cire, nous proposons l'o-phényl-phénol et pour le nettoyage des sceaux de cire, l'emploi d'eau distillée et stérilisé avec une addition minimale de 4-chloro-3-crésol (0,01%).

5.2.2 Resümee

Wachs-Siegel

Alte Wachs-Siegel bestehen aus Bienenwachs als Grundbestandteil und daneben aus verschiedenen Anteilen Harz, Terpentin, Karnaubawachs und anderen Komponenten. Gut bewahrte Wachs-Siegel bestanden aus reinem Bienenwachs mit rotem Pigment oder mit einem gewissen Anteil Kolophonium, Grünspan und Zinober. Wachs-Siegel, die Holzrinde-Stücken enthalten, unterliegen der mikrobiologischen Zerstörung.

In unseren Experimenten haben wir die Medien von Bushnell und Haas sowie von Iizuka und Komagata verwendet. Darüber hinaus wurde das Wachs gesondert sterilisiert, um die Mikroflora zu isolieren, die Wachs-Siegel zersetzt. Die Kulturen wurden 3 Monate lang bei 24–26°C und 85–95% relativer Luftfeuchtigkeit erhalten, wonach folgende Pilze isoliert werden konnten: Aspergillus sp., Aspergillus fumigatus, Fresenius, Alternaria tenuis, Nees, Cephalosporium sp., Cladosporium herbarum, (Persoon) Link, Coprinus sp., Gliomastix murorum, (Corda) Hugues, Paecilomyces varioti, Bainier, Penicillium sp., Scopulariopsis brevicaulis var. glabra, Thom, Stemphylium sp. und zwei Arten von Streptomyzen.

Als Mikrobiozid für Wachs-Siegel empfehlen wir O-Phenyl-Phenol und zum Reinigen von Wachs-Siegeln sterilisiertes Wasser mit einem geringen Zusatz (0,01%) von 4-Chloro-3-Cresol.

5.2.3 References

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5.3.1 Ink

Writing ink may also be subject to the attack of microoganisms, particularly by *Penicillium sp.*[1,3] Mitchell and Wood[4] report the influence of Aspergillus and Penicillium on the deterioration of a text written with ferrigallate ink. These fungi develop ammonia and acidify the text, causing yellow-brown discolouration. Conover and Stevens[1] and Peterson[5] have also described Penicillium disease of ink, and Fennel (cit. Samson 6) isolated Paecilomyces from fountain pen and Schaeffer's ink. The most resistant against fungi is alkaline writing ink of pH=8.3 composed of diammonium hydroxyferrigallate solution proposed by Roumanian workers Silbermann and Ozorowitz.[2,7] We have found that 0.1% of o-phenylphenol inhibits completely the growth of ink-decomposing fungus. For the deacidification of writing ink, methylmagnesium carbonate has been used.[8] Figures 9 and 10 present the influence of ink acidity caused among others, by fungi upon the deterioration of the text written on parchment.

5.3.2 Abstract

Ink

Writing ink may also be subject to microbiodeterioration. Several laboratories reported that Aspergillus, Penicillium and Paecilomyces may develop on writing ink. We have found that Penicillium especially may also deteriorate the text written with ferrigallate ink (Fig. 9 and 10).

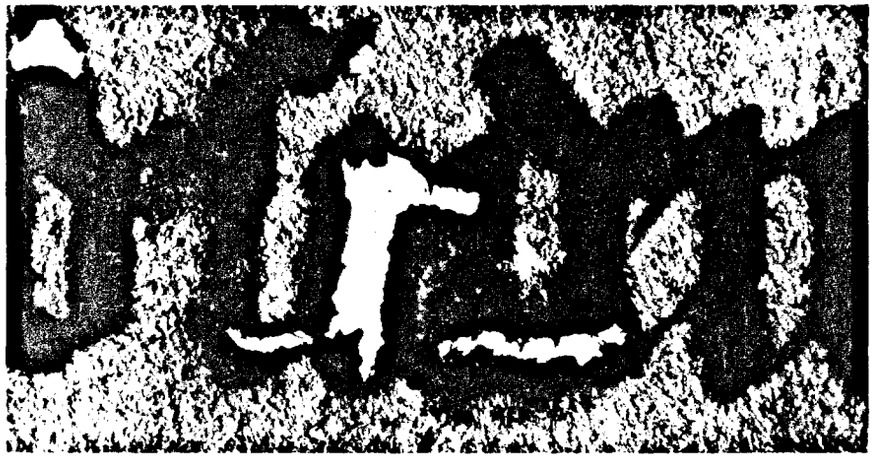

Fig. 9.

Fig. 9 and 10. The influence of ink acidity caused, among others, by fungi upon the deterioration of the text written on parchment.

Fig. 9 et 10. Influence de l'acidité causée dans l'encre, entre autre par des champignons, sur la détérioration du texte écrit sur parchemin.

Abb. 9 und 10. Einfluss des Säuregrades der Tinte, u.a. von Fungi verursacht, auf die Zersetzung des auf Pergament geschriebenen Textes.

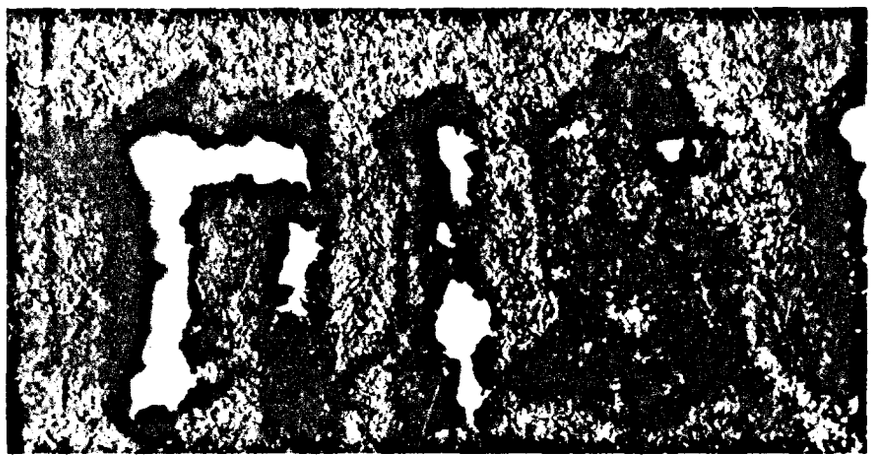

Fig. 10.

5.3.2. Résumé

L'encre

L'encre d'écriture peut aussi faire l'objet d'altérations microbiennes. De nombreux laboratoires ont reporté le fait qu'Aspergillus, Penicillium et Pascilomyces peuvent se développer sur de l'encre d'écriture. Nous avons noté que Penicillium spécialement peut aussi endommager des textes écrites avec une encre au gallate ferrique (Fig. 9 et 10).

5.3.2 Resümee

Tinte

Tinte, die zum Schreiben verwendet wird, kann ebenfalls der mikrobiologischen Zersetzung unterliegen. Verschiedene Laboratorien haben festgestellt, dass sich Aspergillus, Penicillium und Paecilomyces auf Tinte entwickeln können. Wir haben nachgewiesen, dass besonders Penicillium auch den Text zersetzen kann, der mit Ferrigallat-Tinte geschrieben ist (Abb. 9 und 10).

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5.4.1 Paints

Water-colours, pastels, chalk and other drawing materials have been used for illuminating manuscripts. Painted miniatures on parchment, vellum and paper as well as other library materials such as painted cloth, wood and metals may be vulnerable to microorganisms. Water-colours and pastels fade sometimes completely under the influence of fungi.

Paints and varnishes, which are usually polymers with other ingredients, are susceptible to three kinds of distinguishable damages: microflora can destroy paints and varnishes mechanically by breaking out the paint film; the surface of paints may be destroyed by metabolic products such as hydrogen sulphide and paints may be prone to enzymes of microorganisms.

On paint surfaces bacteria and fungi have at their disposal natural vegetable oils, fatty acids, glycerol, honey (water-colours), tragacanth gum (pastel), casein and glue. Binding agents: polymerized triglicerides, protein products, water and alien products, which adhere as dirt on pictures may also offer the nutrients for microorganisms. Theoretically, in well purified binding material, microorganisms may have only carbon, hydrogen and oxygen as the nutrient food. In pratice this degree of purification is unattainable. Moreover, under the conditions of use, dusts containing particles of soil may facilitate the contamination of paints. Soil particles, together with polymerized triglicerides, give a sufficient amount of food for microflora, and fungi hyphae help to grasp and lock the soil particles.

The most prevalent microorganisms found on paints are: *Aureobasidium (Pullularia) pullulans*, *Phoma pigmentivora*, *Cladosporium sp.*, and then the species belonging to the genus Alternaria, Trichoderma, Aspergillus and Epicoccum. As a result of producing fruiting bodies of fungi *Phoma sp.* and *Aureobasidium sp.* underneath paint films, ruptures in the form of small blisters may occur.[19,20]

Recently it was found[22] that *Aureobasidium pullulans* is unable to colonize on paint film if there are not initially other microoganisms, such as Aspergillus, Mucor, Alternaria, Cladosporium and bacteria Pseudomonas. It also reacts on the preserved paint film with phenylmercuric acetate and zinc oxide.[22] Cellulase from Aspergillus and Alternaria aid in the initial colonization of these fungi due to hydrolysis of hydroxyethylcellulose present within the paint film. Aureobasidium pullulans secreted cellulase, proteinase, esterase, phosphatase, sucrease and maltase are also able to hydrolyze extracellular polysaccharides from Aspergillus and Alternaria. The inability to grow *Aureobasidium pullulans* initially on paint film in a humidity chamber is not because of its inability to produce cellulase.[21]

70% R.H. or even less is sufficient for the growth of microorganisms, but microflora may utilize the water on the surface of film, for example the condensed water under the glass. This was observed several times, particularly on graphic works of art in the National Museum in Wrocław.

Humidity circulating in the walls caused the growth of cyanobacteria and green algae on the interior wall surfaces[10] and thus on the wall paintings.

Sometimes bacteria attack the emulsifying agent and the vehicle.[15,16] *Pseudomonas aeruginosa* and other species of the genus Pseudomonas were found in our laboratory in cases of emulsion paints. Bacteria have also been found in appreciable numbers on deteriorating paint films at the interface between wood or linen and paint. Flavobacterium is the most common, and it is suggested that this growth is a cause of the deterioration of paint films by peeling.[2]

Owing to the physicochemical characteristics required for biocides for

paints,[17] the number of fungicides and bactericides for controlling microorganisms destroying paints is much more restricted than in other fields.

Of inorganic microbiocides, zinc oxide is a white pigment formerly much used. It provides useful resistance and retards the growth of fungi but does not prevent it. This compound improves stability of paints on storage in field conditions.[13] An additional advantage of zinc oxide is the property of considerably reducing the lichens in paints.[19] Of the copper organic compounds, copper 8-quinolinolate is very effective even against algae but has a yellow-green colour.[3,18] Practice based upon considerable literature data of testing experience favours organic mercurials. In tropical conditions, however, as regards toxicity, on paints which contain too high a concentration of mercury (such as 0.3% of Hg content in the form of phenylmercury oleate, acetate or naphthenate), the loss of 75% of mercury owing to volatilization takes place.[8] Diphenylmercury dodecenylsuccinate and mercury dimethyldithiocarbamate were the least volatile of all organic mercury compounds.[8] Organotin compounds are the basis of conflicting results and the data in tropical conditions have been disappointing.[13,18] Working with our colleague, Mrs. E. Czerwińska, experiments showed that organotin compounds were effective in much higher concentration than organic mercury compounds.[5] Yoshikadzu,[23,24] however, advises spraying the walls behind the pictures in galleries with 1% ethanol solution of tri-n-butyl tin oxide.

Chlorophenols have too short a life activity, but zinc salt of pentachlorophenol, having a small amount of mercury compound, was very effective in our tests[9] and Benignus (cit. 2) was enthusiastic about zinc salt of pentachlorophenol for 3–5% of the paint. Vannoy (cit. 2) also advises the utilization of this salt for the protection of paints.

For the protection of paints containing protein and oil emulsion, the best results against fungi and algae could be obtained with dimethyldithiocarbamate compounds such as 4-chloro-2-benzyl-3,4-dichlorobenzylodithiocarbamate and nitrobenzyl derivative of dithiocarbamic acid.[7,19]

Of other organic compounds, salicylanilide-1,4-naphthoquinone derivatives, dehydroacetic acid and cyclohexylalkildimethylbenzyl ammonium sulfamate, which is more effective than mercury and tin compounds, may be mentioned. Excellent results were also obtained by using N-trichloromethylthio4-cyclohexene-1,2-dicarboximide (common name captan).[13]

Recently introduced barium metaborates has fungi- and bacteria inhibiting characteristics in field conditions,[3,20] although it was not encouraging in laboratory experiments.[20] Carter[4] suggests using benzizotiazolinone.

Dichlorophene and zinc chromate also gave good results in sulphate reduc-

ing bacteria, surface coating and corrosion.[12] Pauli[14] proposes dimethyldithiocarbamate, barium metaborate, captan and 4-chloro-3-cresol.

Damar, mastix and other varnishes used as organic coatings in the conservation of pictures may also be damaged by microorganisms. On some varnishes, such as damar and mastix, Z. Karczewski (of our laboratory) has found the following fungi: *Stachybotrys atra*, *Penicillium sp.*, *Fusarium sp.* and *Streptomyces sp.* The killing of these organisms on varnishes could be achieved only by using phenylmercury acetate (at the amount of 0.5% per weight of varnish) together with dichlorophen (0.5% per weight of varnish). It was shown[11] that varnishes may be contaminated with Penicillium, Cladosporium and Aspergillus, and metal compounds and others have been proposed as fungicides.

The resistance of paints and varnishes against microorganisms may be tested on agar (Fig. 1), on filter paper discs covered with paints,[5] on glass plates,[6] or on metallic plates covered with paints with biocides.[5] Investigations of paints can also be realized by the methods used for plastics.[5]

Degradation tests of canvas and panel paintings by using the scanning electron microscope have been made.[1]

5.4.2 Abstract

Paint

Painted miniatures on parchment, vellum and paper as well as painted cloth, wood and metals may be vulnerable to microorganisms which may destroy paints and varnishes mechanically, by metabolic products, or paints which may be prone to the enzymes of microorganisms.

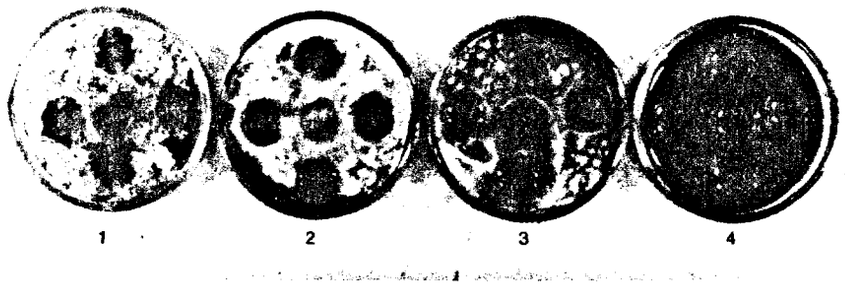

Fig. 1. Microbioresistance of synthen red: 1: sample of paste; 2 and 3: liquid samples of dye without biocide; 4: sample of dye with biocide.

Fig. 1. Résistance du rouge synthène à l'action microbienne: 1: échantillon de pâte. 2 et 3: échantillons liquides de colorant sans biocide. 4: échantillon de colorant avec biocide.

Abb. 1. Mikrobiologische Resistenz von Synthen-Rot: 1: Probe der Paste. 2 und 3: flüssige Proben des Farbstoffes ohne Biozid. 4: Probe des Farbstoffes mit Biozid.

The following genuses of fungi: Aspergillus, Alternaria, Aureobasidium, Cladosporium, Epicoccum, Phoma, Trichoderma, few strains of Streptomyces and bacteria were isolated in our experiments. Of different microbiocides, good results in our laboratory were obtained with zinc salt of pentachlorophenol and with 4-chloro-3-cresol.

5.4.2 Résumé

Peinture

Les miniatures peintes sur des parchemins, du vélin et du papier, de même que les vêtements, le bois et les métaux peints peuvent être sensibles à l'action des microorganismes qui peuvent conduire à la destruction d'ordre mécanique des peintures et des vernis par les produits de leur métabolisme. Les peintures peuvent être prédisposées à l'action des enzymes microbiennes.

Les types suivants de moisissures: Aspergillus, Altermaria, Aureobasidium, Cladosporium, Epicoccum, Phoma, Trichoderma, quelques souches de Streptomyces et des bactéries ont été isolés lors de nos essais. Parmi les divers microbicides, de bons résultats ont été obtenus dans notre laboratoire avec le sel de zinc du pentachlorophénol et avec le 4-chloro-3-crésol .

5.4.2 Resümee

Farben

Miniaturen, die auf Pergament, Schreibpergament und Papier gemalt sind sowie bemaltes Leinen, Holz und bemalte Metalle können durch Mikroorganismen beschädigt werden. Diese zerstören Farben und Anstriche mit ihren Stoffwechselprodukten mechanisch. Daneben besteht die Möglichkeit, dass die Farben von den Enzymen der Mikroorganismen befallen werden.

In unseren Experiementen wurden folgende Pilzarten isoliert: Aspergillus, Alternaria, Aureobasidium, Cladosporium, Epicoccum, Phoma, Trichoderma, einige Arten von Streptomyzen sowie Bakterien. Von den verschiedenen Mikrobioziden, die angewendet worden sind, wurden in unserem Laboratorium besonders gute Ergebnisse mit Zinksalz des Pentachlorophenols sowie mit 4-Chloro-3-Cresol erzielt.

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5.5.1 Unusual library materials: Metals

Silver was used in bookbinding and ornaments, as well as in Persian miniature landscapes to represent water.[11] Brass, copper, bronze and lead were often used for recordings as well as decorations.[5] Bronze and lead-bearing writing of the old Roman Period are in the Cairo museum.[8] Iron and steel in the form of fasteners have been often used in archives and libraries.

Corrosion of metals such as iron, steel and copper by the action of microorganisms is not only a general problem of considerable importance but also a problem regarding library materials and works of art.

In corrosion, microorganisms contribute in one of several of the following ways:

creation of corrosive metabolic products;
not uniform distribution of oxygen and its concentration on some places of metal;
cathodic depolarization;
destruction of organic coatings;
decomposition of corrosion inhibitors (such as nitric acid and sodium nitrate).

Microorganisms cannot cause corrosion by direct contact with metal if it is characterized with biocidal activity, for example, copper. Some exceptions, however, are known as Thiobacilli and Ferrobacilli which are copper resistant and some fungi such as *Penicillium funiculosum*, *Penicillium ochrochloron* and *Phoma pigmentivora* may even develop on copper sulphate and copper oxychloride solution. Thermophilic and acidophilic Sulfobolus oxidizes iron and sulphur compounds and solubilizes copper.[2] Some bacteria such as *Escherichia coli*, *Citrobacter freundii*, *Serratia marcescens*, *Aerobacter aerogenes* and *Desulfovibrio desulfuricans* attack biocidal zinc ion although at a lower degree than iron.

The most corrosive metabolic products of microorganisms are acids, which yield hydrogen and sulphuric acid. These occur as a result of metabolism of Thio- and Ferrobacilli and may decrease pH of environment to 0.7. These bacteria are the most important inorganic acid-producing organisms. Organic acids produced by microorganisms may also cause the corrosion of metals. Acids which contain one, two or four carbon in molecule are active in the vapour state. Aminoacids and aliphatic acids and acids taking part in Krebs cycle (biochemical transformation of decomposition's products of sugars, fats and proteins), as pyruvic and citric acids are active in deep water conditions. Sometimes acid metal complexes are formed as typical formic acid-copper complex by Penicillium sp.[3,4,6,7,9,12,13,14]

Fungi such as *Aspergillus niger*, *Aspergillus amstelodami*, *Penicillium cyclopium*, *Penicillium brevi-compactum, and Paecilomyces* are able to produce acids and cause the corrosion of steel, copper and aluminium.[1]

The corrosion of metals in oxygen-free environments is caused as a rule by the activities of the sulphate-reducing bacteria Desulfovibrio desulfuricans, especially in heavy clay of about neutral pH, containing sulphates. In this case corrosion has been traced to the presence of sulphate-reducing bacteria, which act in a two-fold manner: firstly, converting the sulphates to sulphides which attack the iron or the inorganic material and secondly, breaking down the hydrogen film and thus making it possible for corrosion to continue. When

corrosion takes place under such circumstances the surface of the iron is found to be covered with a black crust of iron sulphide and the clay surrounding the object is also stained black. Corrosion made by Desulfovibrio desulfuricans is very prevalent and is a common cause of the destruction of iron pipes buried in clay. Hydrogen is utilized by these organisms due to the presence of enzyme hydrogenase. This enzyme is directly associated with the ability to bring about cathodic depolarization. Sulphate reducing bacteria have been found in Europe, Asia, Africa, North and South America, Australasia and Antarctica and they have been encountered at a depth of 71 m in clay. Certain features of their metabolism suggest that they are one of the most primitive of ancient creatures and many of the species of living things on our planet could originate from sulphate-reducing and silicate decomposing bacteria.[10] Numerous bacteria, apart from the mentioned Desulfovibrio, such as *Clostridium aceti*, *Hydrogenomonas facilis*, *Micrococcus denitrificans* and *Methanobacterium omelianski* containing the enzyme hydrogenase are active in catalyzing the oxidation of hydrogen. Desulfovibrio desulfuricans may initiate the activity of another different group of microbes which produce acids, mineral and organic, with well known corrosive effects. Desulfovibrio desulfuricans form thick clumps which allow differential aeration and concentration cells to arise. Moreover it breaks down protective coatings and thus allows electrochemical corrosion (pure or microbially induced) to occur.

Mercaptans and ammonia produced by some microorganisms may also cause metal corrosion.

For the protection of steel, copper and iron against activity of microorganisms:phenylthiourea, tetramethylthiram monosulphide as fungicide and panacide (dichlorodiphenylmethan), citrimide (trimethylcetylammonium bromide), lauryl pentachlorophenate, benzylalkonium chloride, sodium tetrachlorophenate as bactericide were used. Squire[12] suggests using non-corrosive rust remover containing sodium benzoate as biocide.

5.5.2 Abstract

Metals

Brass, copper, bronze, lead and silver were often used for recordings and as ornaments and decorations. Iron and steel in the form of fasteners have been used in libraries. Therefore the corrosion of metals by fungi and bacteria may be seen and it may often cause problems in libraries. The activity of particular bacteria and fungi and their metabolic products in the process of metal corrosion are discussed. Fungi and bacteria inhibitors are proposed.

5.5.2 Résumé

Métaux

Le laiton, le cuivre, le bronze, le plomb et l'argent ont été souvent utilisés pour les inscriptions et ont servi d'ornements et de décorations. Sous forme de fermoirs, le fer et l'acier ont été utilisés dans les bibliothèques. La corrosion des métaux par les moisissures peut donc être observée et peut souvent poser des problèmes dans les bibliothèques. L'activité de bactéries et de moisissures spécifiques et les produits de leur métabolisme agissant dans le processus de corrosion des métaux sont présentés. Des inhibiteurs bactériens et fongques sont proposés.

5.5.2 Resümee

Metalle

Messing, Kupfer, Bronze, Blei und Silber wurden oft für Aufzeichnungen, als Ornamente und für Verzierungen benutzt. Eisen und Stahl wurden in der Form von Schrauben und Muttern in Bibliotheken verwendet. Eine Korrosion der Metalle, hervorgerufen durch Pilze und Bakterien kann deshalb auftreten und dann in Bibliotheken zu problemen führen. Hier wird die Tätigkeit bestimmter Bakterien und Pilze sowie ihrer Stoffwechselprodukte im Prozess der Korrosion der Metalle näher beleuchtet, entsprechende Hemmstoffe gegen Pilze und Bakterien vorgeschlagen.

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5.6.1 Unusual library materials: Glass

Glass surfaces in graphic works of art and glass enclosed bookcases are vulnerable in libraries,[5] archives and museums. Damage caused by microorganisms may be observed on the glass which covers water-colours and other media. Glass does not protect the pictures from dust and changes of R.H. It has been found that moisture condenses between linen and glass quicker than when air can circulate freely. Serious problems were dramatically emphasized during WWII when optical instruments such as magnifying glasses, telescopes, photographic apparatus and measuring instruments became completely unusable.

Microorganisms do not obtain nourishment from the glass itself but from organic dust and greases, especially from dead insect bodies, some impurities, and sizes.[1,3,7,10]

The activity of microorganisms may be attributed as a rule to their metabolic products:organic acids that etch the glass surface or an alkali etching on lime-silicate glasses by maintaining the correct water supply to produce a concentrate solution of alkali carbonates.[2,6] This action produces a characteristic channelling on the glass surface which, in the case of fungus *Monilia crassa*, can etch boro-silicates glasses in about four months. Some bacteria such as Thiobacilli excrete sulphuric acid which may damage the composition of glass.[1] Other organic acids such as oxalic and acetic acids produced by fungi may also frost and etch the glass.[7]

On glass without added nutrient the growth of *Penicillium funiculosum, Aspergillus vitricolae, Penicillium capsulatum, Aspergillus glaucus* and *Eurotium tonophilum* was observed.[12] The organisms infesting glass in India included *Aspergillus niger, Aspergillus fumigatus, Aspergillus candidus, Penicillium sp., Sepedonium sp., Curvularia sp., Paecilomyces sp., Monilia sp.*, and *Cladosporium sp.*[11] and Hendey[6] has reported fungi belonging to the genus Aspergillus and other species such as *Stachybotrys atra, Sporotrichum roseum, Monilia crassa* and *Penicillium sp.* which develop on glass surfaces. Ohtsuki[9] has described only one Aspergillus variety, designated as *Aspergillus glaucus var. tonophilus.* Taking into consideration the protection of glass against microflora, storage in low humidity is proposed,[3,4,11] but the chemical method appears to be the most satisfactory. Best control for a short period was given with metacresyl acetate (cresatin) = $CH_3C_6H_4OOCCH_3$-volatile fungicide employed by mixing with an equal quantity

of ethylcellulose resin[3,4,13,14] or ethylmercuric thiosalicylate $C_2H_5HgOOC.C_6H_4SH$ incorporated to the extent of 0.2% in lacquer.[8] The use of copper naphthenate and pentachlorophenol in lacquers is also suggested.[11] For pictures, the glass should be sterilized before it is replaced by cleaning with cotton-wool that has been moistened at least with ethanol or cotton-wool soaked in 1% of ethanol solution of 4-chloro-3-cresol and left until the ethanol evaporates.

5.6.2 Abstract

Glass
Damages caused by microorganisms in libraries and museums have been observed on glass which covers water-colours and other picture media. The activity of fungi may be attributed to their metabolic products. Several genuses of fungi which damage the glass are reported. Protection of glass against microflora is also suggested.

5.6.2 Résumé

Verre
Les dommages causés par les microorganismes dans les bibliothèques et les musées ont été observés sur les plaques de verre recouvrant les aquarelles et divers autres tableaux. Plusieurs types de moisissures endommageant le verre sont observés. Proposition de protection des verres contre l'action de la microflore.

5.6.2 Resümee

Glas
Durch Mikroorganismen hervorgerufene Schäden sind in Bibliotheken und Museen auch auf dem Glas festgestellt worden, das Aquarelle und andere Bildmedien schützt. Die Tätigkeit der Pilze ist auf deren Stoffwechsel-Produkte zurückzuführen. Verschiedene Pilzgattungen, die Glas zerstören, werden genannt. Schliesslich wird auch vorgeschlagen, wie Glas gegen die Mikroflora geschützt werden kann.

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6.1 Methods of Testing the Microbioresistance of Particular Library Materials

Considering library materials and the protection of works of art against microorganisms, it is of essential importance to standardize procedures not only in the laboratory of one country, but also in international interlaboratory studies. Only microbial resistance of plastics is based on an international standard, as a result of the coordination of the ISO Task group "Biological Attack".[6] For textiles, only a few standard methods exist in particular countries and each of them varies, at least on the assortment of microorganisms. Table 3 presents the species of fungi used in the standard tests of resistance of textiles in different countries[1,4,5,11,13,14,15,16,17] and Table 4 presents the species of fungi in the standard tests of resistance of plastics.[1,2,3,4,6,10] Microbiological corrosion of metals is evaluated on metal samples which may be placed in jars containing the medium with deionized water and the samples (cit. 4). Closed jars with metal samples and medium are sterilized at 120°C and inoculated with the following microorganisms: *Cladosporium resinae* (Lindau) de Vries, *Aspergillus niger*, van Tieghem, *Pseudomonas sp.*, *Desulfovibrio desulfuricans*, (Beijerinck) Kluyver and van Niel, and the mixture of microorganisms taken from suitable environments. The assessment is made after 2 and 4 weeks, and after 4 and 6 months of culturing at 20°C and 85–100% R.H. For the standardization of procedures that are applied in the studies of resistance of paper, cardboard and adhesives against fungi and bacteria, only USA methods for industrial purposes exist.[1]

Screening tests of various biostatic agents that are offered to the pulp and paper industry are sometimes carried out using two species of fungi as test

organisms: *Aspergillus niger*, van Tieghem and *Penicillium expansum*, (Link) Thom and two species of bacteria: *Aerobacter aerogenes*, Kruse (Beijerinck) and *Bacillus mycoides*, (Flügge) Smith.

Table 3. The species of fungi used in the standard tests of resistance of textiles in different countries.
Table. 3. Types de moisissures utilisées dans les méthodes standard d'essai de résistance des textiles appliquées dans divers pays.
Tabelle 3. Pilzarten, die bei Standardtests der Beständigkeit von Textilien in verschiedenen Ländern verwendet werden.

Fungus species	France	Netherland	India	West Germany	Poland	USA	Swiss
Acremonium cinnabarinum (Link)							•
Acrothecium sp.					•		
Alternaria tenuis (Nees)							•
Aspergillus amstelodani (Mangin, Thom i Church)	•						
Aspergillus flavus (Link)	•						
Aspergillus fumigatus (Fresenius)			•		•		
Aspergillus niger (van Tieghem)	•			•		•	•
Chaetomium globosum (Kunze)	•	•		•	•	•	•
Chaetomium indicum (Corda)			•				
Curvularia lunata (Walker, Boedijn)			•				
Memnoniella echinata (Rivolta, Galloway)	•				•		
Myrothecium verrucaria (Albertini i Schweinitz Diftmar)	•	•			•		•
Paecilomyces varioti (Bainier)	•				•		
Penicillium funiculosum (Thom)	•				•		
Penicillium rubrum (Stoll)			•				
Penicillium wortmanni (Kloecker)			•				
Phoma pigmentivora (Fries, Desmazieres)					•		
Stachybotrys atra (Corda)	•				•		•
Torula sp					•		
Trichoderma viride (Persoon ex Fr.)	•	•		•	•		

The most important factors in selecting a method are the determination of appropriate testing conditions and the estimation of a suitable range of microorganisms. Special attention should be paid to the composition and the pH

Table 4. The species of fungi used in the standard tests of resistance of plastics.

Table. 4. Types de moisissures utilisées dans les méthodes standard d'essai de résistance des matières plastiques.

Tabelle 4. Pilzarten, die bei Standardtests der Beständigkeit von Kunststoffen verwendet werden.

Fungus species	Great Britain	USA	CSR	France	ISO	SSSR
Acrostalagmus cinnabarinus (Link)	•			•		
Alternaria tenuis (Nees)			•			
Aspergillus amstelodami (Mangin, Thom i Church)			•	• •		•
Aspergillus flavus (Link)	•	•	•	• •		
Aspergillus sydowi (Bainier i Sartory, Thom i Church)			•			
Aspergillus versicolor (Vuillemin, Tiraboschi)			•			
Chaetomium globosum (Kunze)		•	•	• •	•	•
Cladosporium herbarum (Persoon, Link)			•			
Memnoniella echinata (Rivolta Galloway)				•		
Myrothecium verrucaria (Albertini i Schweinitz, Diftmar)			•			
Neurospora sitophila (Montagne, Saccardo)			•			
Paecilomyces varioti (Bainier)	•	•	•	• •	•	•
Penicillium brevicompactum (Dierckx)			•	•		•
Penicillium cyclopium (Westling)			•	•		•
Penicillium funiculosum (Thom)	•	•		•	•	
Penicillium luteum (Zukal)			•			
Stachybotrys atra (Corda)			•	• •		•
Sterigmatocystis nigra (Aspergillus niger) van Tieghem		•	•	• •	•	•
Trichoderma viride (Pers. ex Fr.)	•	•		•	•	
Aureobasidium (Pullularia) pullulans (de Bary Berkhout)		•				
Pseudomonas aeruginuosa (Migula)	•					

of the media, the temperature, relative humidity, oxygen and carbon dioxide.[17,18,19,20] When selecting microorganisms it should also be taken into consideration those which do not destroy tested material but which, in certain conditions may develop on it or can tolerate the proposed fungicide.[4] Also, the estimation of results is a great influence on the value of testing. Some methods recorded in literature are based on visual determination. They are certainly not sufficient and should be completed with other data, as descriptions of tear,[7] mechanical and optical resistance. It was assumed that weight losses were the result of microbial dissimilation of plasticizer from the formulation of plastics, often used as library materials. Studies of microbial resistance should be examined in all possible aspects with two or three methods, especially when considering new means of protection for basic or auxiliary library materials against microflora.

The resistance of paper and cardboard against the activity of microorganisms may be estimated according to ASTM[1] methods in Petri dishes on agar mineralized medium. The samples of paper to be examined are placed on the surface of the hardened medium and they are inoculated with particular species of fungi: *Chaetomium globosum*, Kunze, *Aspergillus niger*, van Tieghem, *Aspergillus terreus*, Thom. Cultures are incubated for 14 days at 28–30°C and 85–95% R.H. The lack of growth of fungi on samples of paper or cardboard proves the paper to be fungi-resistant.

Paper and cardboard protectants may also be evaluated by burying in standard soil: the tested paper samples are placed in a wooden box (height 150 mm) and filled with the active soil for two weeks in an incubator at 28–30°C and 85–95% R.H. After this period of time the strength of samples is determined.

The resistance of adhesive preparations and adhesive bonds with and without biocide may be determined on samples of adhesives contaminated in sterilized jars with 1 ml of each suspension of the following species of fungi: *Aspergillus niger*, van Tieghem, *Aspergillus flavus*, Link and *Penicillium luteum*, Zukal. After 3, 7, 14, 21 and 28 days of incubation the viscosity of samples is determined.

The samples may also be examined for bacterial growth after inoculation of adhesive with 0.6 ml of each of these inoculae of the following bacteria: *Pseudomonas fluorescens*, Migula, *Bacillus subtilis*, Cohn and *Proteus vulgaris*, Hauser.

Besides examining the viscosity, we check the growth of microflora at frequent intervals on potato dextrose agar (fungi) and on nutrient agar (bacteria) and in regard to odour, discolouration and gas formation of the contaminated adhesive.

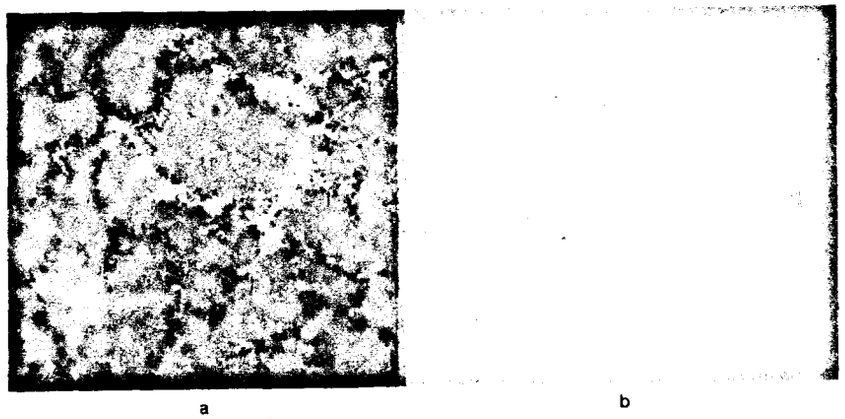
The microbioresistance of leather was determined in our laboratory by ap-

plying the following methods: Samples of leather were moistened with sterilized distilled water and placed both face and back to the surface of agar with distilled water and agar of Czapek/Dox in Petri dishes. These samples were then sprayed with spore suspension of the following fungi: *Penicillium claviforme,* Bainier, *Aspergillus niger,* van Tieghem, *Trichoderma viride,* (Persoon) Harz, *Streptomyces coelicolor,* Waksman and Henrici. Petri dishes with hardened medium and samples of contaminated leather were incubated for 4 weeks at 24–26°C and 85–95% R.H. Microbioresistance of leather and fungicidal activity was determined visually or on the basis of mechanical properties.

The resistance of parchment was estimated in a similar way using, however, parchment-preferential fungi such as *Fusarium orthoceras,* Appel and Wollenweber, *Cladosporium herbarum,* (Persoon) Link, *Scopulariopsis brevicaulis,* Bainier and *Streptomyces sp.* These microorganisms were incubated for only 3 weeks at 24–26°C and 85–95% R.H.

Determination of resistance of plastics to microorganisms was carried out according to ISO Task group "Biological Attack".[12] Five species of fungi: *Chaetomium globosum,* Kunze, *Paecilomyces varioti,* Bainier, *Penicillium funiculosum,* Thom, *Aspergillus niger,* van Tieghem, *Trichoderma viride,* (Persoon) ex Fries and some species of bacteria: *Pseudomonas aeruginosa,* Migula were used in our laboratory. It seems to me that Actinomycetes should be included because they decompose plastics and plasticizers under various conditions.[8, 9] The samples were sprayed with the spores of fungi and bacteria suspension in distilled water and placed in the humidity chamber for 28 days at 30 ± 2°C and 95–100% R.H. For evaluation, the following scale was used: no growth (plastic is resistant), growth visible under microscope (satisfactory), growth visible with naked eye (unsatisfactory). The resistance of plastics on agar medium and the soil burial test was also proposed. (Fig. 1).

The resistance of textiles and wood has been carried out, as reported in chapters 4.1.1 and 4.2.1, on artificial media and by using the soil burial method. This method is, in my opinion, the most drastic and convincing although it is difficult to standardize. In this test, treated cloth or stakes are buried in soil containing degrading fungi and bacteria for varying periods of time, after which they are removed and graded for deterioration. Data are recorded either on the amount of decay per unit of time or on the time required to obtain a certain amount of decay. With textiles, tensile strength of the cotton fiber has been a popular criterion of measurement for deterioration. The resistance of paints or varnishes was carried out on agar, filter paper discs and on metals covered with paints or varnishes.



a b

Fig. 1. The activity of microflora on polyvinyl chloride in soil burial test during 4 weeks (a), control (b).

Fig. 1. Activité de la microflore sur le chlorure de polyvinyle lors d'essai d'enfouissement pendant 4 semaines. (a), contrôle (b).

Abb. 1. Tätigkeit der Mikroflora auf Polyvinylchlorid bei Erdabfallagerungs-Tests im Verlauf von vier Wochen (a), Kontrolle (b).

6.2 Abstract

Polish and other standard methods and projects of testing fungicides and bactericides to protect various library materials are described.

6.2 Résumé

Description de méthodes polonaises et autres méthodes standard, projets d'essai des fongicides et des bactéricides destinés à protéger divers types de matériels de bibliothèque.

6.2 Resümee

Politur, andere Standardmethoden sowie Projekte zum Testen von Fungiziden und Bakteriziden, die zum Schutz von verschiedenen Bibliotheksmaterialien eigesetzt werden können, werden beschrieben.

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7.1 Methods of Testing Fungi- and Bactericides

Of the numerous methods recorded in the literature of testing fungi- and bactericidal activity in our laboratory, the following have been selected:

A. Determination of the inhibiting concentrations of biocides against mycelium growth on an artificial medium:
A suitable amount of fungicides dissolved in acetone is added to potato dextrose agar (200 g of sliced potato, 20 g of agar and 20 g of dextrose, pH approximately 5.0) at 60–70°C. In strictly measured amounts poisoned medium is added to the Petri dishes. After drying at 37°C the agar medium in the Petri dishes is inoculated in the centre with an equal amount of spore suspension. Fungi are incubated at 24–26°C. Every 24 h for ten days, diameters of fungi colonies from the bottom of the dish are measured. The concentration of the compound which does not allow the growth of fungi is the completely inhibiting concentration.

B. Evaluation of the influence of chemical compounds on spore germination is carried out in our laboratory in polystyrene microbeakers:

Polyethylene rings 2mm high and 9.5 mm internal diameter are placed on glass slides and filled completely with the polystyrene solution in benzene. After evaporation of the benzene at 30°C for about five days, the microbeakers are filled with 0.1 ml of spore suspension in distilled water or in 0.2% solution of sucrose and added.

Glass slides with microbeakers are placed in Petri dishes on glass sticks. In order to prevent drying, filter paper discs imbibed with glicerol dissolved in water (20:80) are placed on the bottom of the Petri dishes. The culture temp. is 25°C and the time of incubation depending on the fungi (18–48 h). Uniform deposition of the fungicide on the bottom of the microbeakers may be secured due to the use of the surface active agent Triton X-100. When the spore suspension is prepared, some addition of the surface activity agent is also required. The evaluation of the biostatic or biocidal compound is carried out on the basis of the amount of germinating spores.[5]

C. An investigation of the vapour action of fungicides is carried out on agar medium in Petri dishes or test tubes:

Slopes of hardened medium are inoculated with conidia of representative fungi, for example *Aspergillus niger*, van Tieghem. Loosely fitting cotton wool plugs are put inside the test tubes a little above the hardened medium. On the surface of the cotton plug, filter paper imbibed with tested fungicide is placed. The test tube is then closed with a rubber plug. If the vapour of the compound under test is fungitoxic the zone of inhibition of fungal growth in the test tube may be observed. Vapour activity of fungicides may also be investigated in Petri dishes as follows: potato dextrose agar in 100 mm Petri dishes is inoculated at predetermined points with abundant fruiting fungi. The fungicide under test is dissolved in acetone and is pipetted onto discs of filter paper, which are fastened with scotch tape to the Petri dish lids. After evaporation of the solution from the filter paper the lower parts of the Petri dishes containing inoculated agar are inverted over lids and sealed in place by pouring molten paraffin into the space between the base and the lid. Absence of growth of fungi proves that the tested compound is fungitoxic by vapour action.[3] Laboratory test on artificial media determine merely the fungicidal activity of chemical compounds, but more than that, the evaluation of potential usefulness for the protection of a particular material is needed.[1,3]

Libraries and archives have not only to cope with the most complicated macromolecules but also with other compounded problems. Library materials and especially books are very often contaminated with microorganisms which

may cause typical serious diseases, and disinfection of these materials is needed. For evaluating the effectiveness of germicidal preparations we pay respect to pathogenic bacteria that show biochemical differences. Methods therefore must be used for determining the effectiveness of bactericides against G+ and G– bacteria and tuberculocidal, sporicidal and fungicidal activity. For this purpose *Escherichia coli*, (Migula) Castellani and Chalmers, *Staphylococcus (Micrococcus) aureus* Rosenbach, *Pseudomonas aeruginosa*, Migula, *Proteus vulgaris*, Hauser, *Bacillus subtilis*, Cohn as also fungi *Candida albicans* and *Trichophyton gypseum* and *Mycobacterium tuberculosis*, (Zopf) Lehmann and Neumann (these last tests were made in the Institute of Tuberculosis, Warsaw) were studied. Since the activity of bactericides of some chemical compounds (such as quaternary ammonium compounds) are reduced in the presence of organic matter, the efficacy of disinfectants were evaluated on two substrates: water and nutrient broth. The tests were made in test tubes, to which different dilutions of disinfectants and suspension of bacteria were added. After 5, 10 and 15 min of exposition, one loopful of culture of bacteria were transferred to a corresponding subculture tube with a nutrient broth. The loss of growth of bacteria on this medium after 24, 48 and 72 h expressed that this dilution of disinfectant is capable of killing the bacteria. These experiments were performed in our laboratory by Mrs. E. Czerwińska.

The essential importance for the evaluation of disinfectants may be attributed to the methods, using carriers, which determine the maximum dilutions that would be effective for practical disinfection. The USA method[2] uses as carriers polished stainless steel cylinders of the length of 10 ± 1 mm, and porcelain penicylinders of the same length. After contamination with bacteria or fungi, carriers are treated with different dilutions of disinfectant and after transferring to a second test tube with nutrient broth, the growth of microorganisms is determined (bacteria after 48 h and fungi after 7, 14, and 21 days). The German standard method[4] uses as carriers squares of batiste 1× 1 cm, which present some advantage over steel and porcelain carriers, because they are for single use only and seem to be more suitable from a physicochemical point of view. Additionally, the disinfectants may be tested in practical conditions, for instance book storerooms or reading rooms. (Fig. 2 and 3).

Disinfection was carried out in 5 library and archive storerooms; in the National Museum in Cracow after an exhibition of some graphic works of art in tropical conditions; and from previous cencentration camps of Oświęcim and Majdanek (3 times). The experiments were carried out with a Formulsin Aerosol Generator Zelenka-Austria and afterwards with Aerosol Fogs Microsol 202 from Italy, producing droplets of about 10 microns. We could observe in

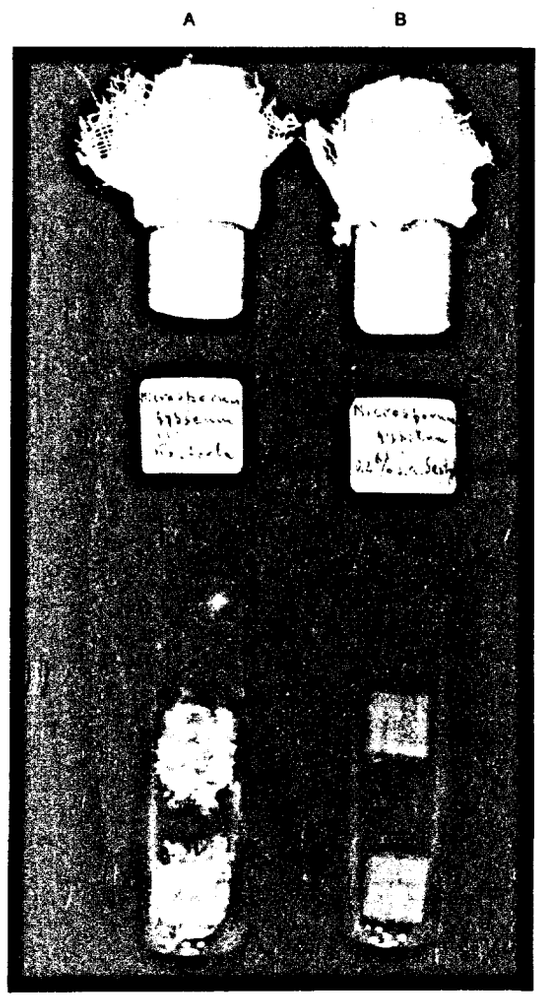

Fig. 2. The activity of Septyl on Microsporum gypseum tested according to the German method: A: control, B: 0.2% of active agent.

Fig. 2. Activité du Septyl sur Microsporum gypseum testée selon la méthod allemande: A: contrôle. B: 0.2% d'élément actif.

Abb. 2. Tätigkeit von Septyl auf Microsporum gypseum, getestet nach der deutschen Methode: A: Kontrolle, B: 0,2% ige aktive Agens.

our laboratory that disinfectant 4-chloro-3-cresol is fungicidal but only bacteriostatic and it does not kill the spores of *Bacillus subtilis*.

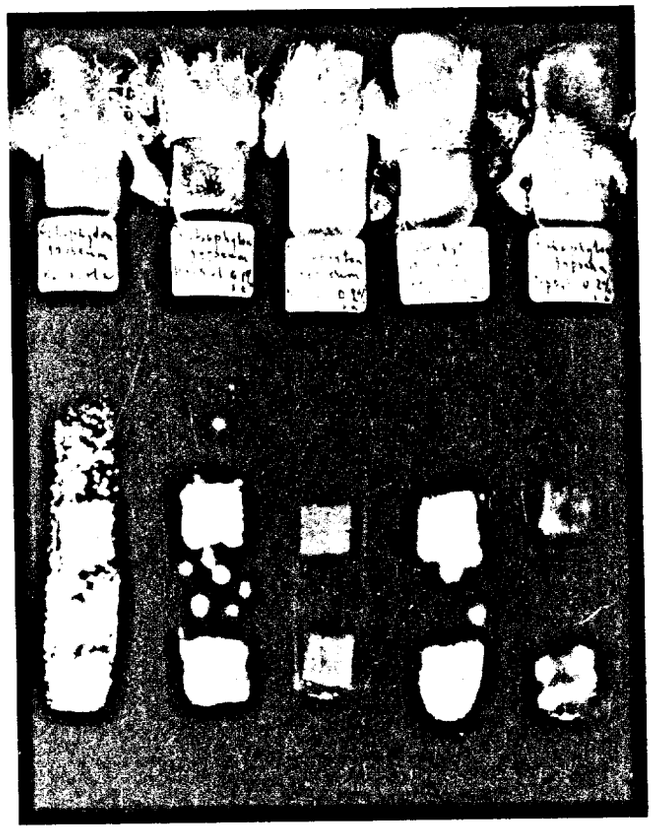

Fig. 3. The activity of Septyl with comparison to Gevisol on Trichophyton gypseum: A: control, B: Gevisol 0.1% C: Gevisol 0.2% D: Septyl 0.1%, E: 0.2% of active agent.

Fig. 3. Activité du Septyl comparée au Gevisol sur Trichophyton gypseum. A: contrôle. B: Gevisol 0,1%. C: Gevisol 0,2%. D: Septyl 0,1%: E: 0,2% d'élément actif.

Abb. 3. Tätigkeit von Septyl im Vergleich zu Gevisol auf Trichophyton gypsesum: A: Kontrolle, B: Gevisol 0,1%, C: Gevisol 0,2%, D: Septyl 0,1%, E: 0,2%ige aktive Agens.

7.2 Abstract

Determinations of the inhibiting concentrations of biocides against mycelium growth on artificial medium, evaluations of the influence of chemical compounds on spore germination, investigation of the vapour action of fungicides and evaluation of the effectiveness of germicidal preparations are described.

7.2 Résumé

Détermination des concentrations de biocides inhibant la croissance du mycellium sur milieu artificiel, évaluation de l'influence de produits chimiques sur le développement de spores, essai de l'action des vapeurs de fongicides et évaluation de l'efficacité des préparations à effet microbicide.

7.2 Resümee

In diesem Artikel werden folgende Problemstellungen beschrieben:
- Bestimmungen der Konzentrationen von Bioziden, die gegen Mycelium-Wachstum auf künstlichen Medien notwendig sind,
- Beurteilung des Einflusses chemischer Verbindungen auf die Sporenkeimung,
- Untersuchung der Dampftätigkeit von Fungiziden,
- Beurteilung der Effektivität von Germizid-Präparaten.

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8.1 The Problems of Toxicity of the Biocides used in Document Protection

At the present time the counteraction for microbial deterioration of library and archive materials may be considered vital. But when selecting fungi- and bactericides we are obliged, above all, to take care that they should not be deleterious upon these materials. Simultaneously, they should inhibit effectively the microorganisms that damage these materials and additionally kill pathogenic microflora which may infect custodians, superintendents and readers. Moreover, fungi- and bactericides should offer sufficient safety margins to human beings and mammals and they cannot be seriously degradable to the environment. Of the great amount of existing bacteri- and fungicides only a few may be selected for the preservation of valuable materials and even these raise some objections. Therefore cooperation between custodians/curators, scientists, conservators and restorers should be continued to seek suitable compounds to provide longevity for library materials. Microbiologists should standardize their methods and all people responsible for the preservation of library

and archive materials should be obliged to standardize, among others things, disinfection treatments in libraries and archives.

The great problem in using bacteri- and fungicides is the knowledge of their mechanism and action and their toxic effects to man and other mammals.[4,5] The majority of bacteri- and fungicides act by linking up with the sulphydryl groups in glutathione and cysteine present in microorganisms and by linking with the lipoproteins group in cell membrane.[7,22,23,30] This kind of behaviour is a characteristic of metallorganic compounds and chlorophenols. Salicylanilide changes the cytoplasmic membrane and inhibits activity of cysteine and oxydase and dehydrogenase of microorganisms.

Ethylene oxide, which is used most often together with carbon dioxide or fluorinated hydrocarbons as gaseous bacteri- and fungicide, eradicates but does not immunize the materials against all biological agents and the mechanism in this case is that it reacts to the active groups of the proteins of microorganisms and cause their degradation. Like methyl bromide and formaldehyde it is an alkylating agent which is more effective against spores than other fungi- and bactericides.[31] Ethylene oxide, in addition to ionizing radiation effects, causes mutagenic changes on various microorganisms.[7] Beta-propiolactone reacts with the -SH groups of the enzyme proteins.[29]

At present, fungi- and bactericides are as a rule not innocuous to humans and mammals and therefore there are some efforts to improve the pesticides over available ones without costing inefficacy.[33] The toxicity of biocides against warmblooded organisms with doses LD_{50} is standardized. It determines the amount of substance (the most often in mg on kg weight of body), causing the mortality of 50% of one species of animal. The studies of toxicity should be carried out on different species of animals applying various methods of administering the biocides: oral (p.o.), intravenous (i.v.), intraperitoneal (i.p.), subcutaneous (s.c.), cutaneous (c.t.) and by inhalation. Toxicological studies are most often carried out on rats. The tested compound or formulation is given orally. On the basis of these studies (DL_{50}) for rats, p.o biocides were divided into five classes of toxicity. Substances in which DL_{50} amounts to 50 mg/kg of body weight are highly toxic; 51–500 mg/kg are toxic, 501–5000 mg/kg slightly toxic. The DL_{50} beyond 5000 mg/kg to 15,000 mg on kg of body weight denotes a practical nontoxic, for the health beyond 15,000 mg/kg of body weight substances are harmless.[7,26]

All organic and inorganic mercury compounds applied to library and document materials are strongly toxic, and phenylmercury acetate in the amount of 31.25 mg/kg of body weight of mouse resulted in death in 4–5 h. The sudden death of people working with mercury compounds has been recorded[6] and the population of birds was decreased owing to the use of mercury compounds.[27] In

1972, 6,530 human beings were poisoned with methylmercury compounds.[12] Some amount of mercury compounds may be bound to the proteins of fungi and in this way become dangerous to man.[20] The organomercury compounds concentrate probably in lipid phase.[10] Phenylmercury acetate is slowly degraded in sewage, giving inorganic mercury compounds,[30] probably methylmercury.

Bis-tri-n-butyl tin oxide, often used in paper production, is much less toxic than mercury compounds and DL_{50} of 10% suspension of this compound in water amounts to 194 mg/kg rat's body weight (cit. 23). According to J. E. Elsea and O. E. Paynter (cit. 29) acute toxicity of bis/tri-n-butyltin/ oxide amounts to 148 mg/kg to rats and the minitoxic level was determined by Y. Shirazu (cit. 29) as 3.5 mg/kg per day to rats. This compound is absorbed by the skin.

o-Phenylphenol which inhibits the glycolysis and dehydrogenase of citrate and succinate is slightly toxic. Its toxicity for rats ranges 2,480 mg/kg. The toxicity of dichlorophen is one of the same order and DL_{50} of this compound is 2,000 mg/kg. A lethal dose of thymol for humans ranges probably 50–500 mg/kg and, in concentration, more than 2% is skin irritant; 2,4,6-trichlorophenol belongs to the group of moderate toxic compounds and DL_{50} for rats ranges 820 mg/kg. Phenolic compounds are degraded in sewage after a short period of time, for instance o-phenylphenol is completely degraded in 24 h. The adaption of 4-chloro-3-cresol is somewhat longer, but the further addition is also degraded in 24 h. Dichlorophene is degraded more slowly.[30] Pentachlorophenol possesses a higher toxicity and its DL_{50} ranges 210 mg/kg. This compound is easily absorbed by skin. Its dehalogenated compounds as 2,3,4,5-,2,3,4,6-, and 2,3,5,6-tetrachloro,2,4,5-,2,3,5-trichloro,3,4-, and 3,5-dichloro and 3-monochlorophenols are microbioresistant[1,2] (cit. 23), and may cause prolonged pollution. Microbiologically methylated compounds of penta and tetrachlorophenols carried out by Penicillium, Aspergillus and Scopulariopsis also create some troubles (cit. 23). However, sunlight caused quick decomposition of pentachlorophenol at pH 7.3 and slow decomposition at pH 3.3 in aqueous environment.[37] Technical pentachlorophenol contains dibenzodioxins (octachlorodibenzodioxin and hexachlorodibenzodioxin)[21] and, according to the Environmental Protection Agency 18 October 1978, 43/202/ 48443–617 pentachlorophenol is too hazardous to man and to the environment to allow continued use.[17] Pentachlorophenol undergoes almost no degradation in the sewage.[30] The toxic data for zinc and lauryl salts of pentachlorophenol could not be found but they are probably less toxic than pentachlorophenol.

Comparatively low mammalian toxicity is possessed by zinc dimethyldithiocarbamate and DL_{50} of this compound for rats ranges 1,400 mg/kg of body

weight.[7,13,18] It causes the inhibition of thyroid gland function[16] and as other carbamates it is a recognized carcinogen.[3,14,19,24,28,32] Carbamates have been causing ataxia and paralysis[25] and liver cancer.[36]

LD_{50} for Irgasan DP-300 is low and ranges 2.9 g/kg. The urine contained metabolite glucuronide of Irgasan DP-300. This product is absorbed by skin.[9]

Formaldehyde, sometimes used, causes, in concentration of a few ppm (part per million), irritation of the mucous membranes of eyes and nose and admissible dosis in the air ranges from 1 ppm (DBR, Swiss) to 3 ppm (USA).[15]

Ethylene oxide (1,2-epoxyethane) caused strong irritation of the mucous membranes of eyes and nose and respiration tract. Concentrations above 3,000 ppm are dangerous if inhaled for 30 min or more[7,13,18] and 50 ppm is given as the maximal concentration permissible during long usage.[31] The majority of deaths in animals occur after exposure for 7 h to 2,000 ppm or higher from respiratory irritation and injury. Ethylene oxide has a direct effect on renal hemodynamics in the rat.[38] The permissible limit for short term single exposures of not more than 1 h is probably near 500 ppm.[8] Ethylene oxide probably causes a general disruption of biological processes.

Ten years of contact of workers exposed to the activity of 5–10 ppm of ethylene oxide did not cause a chronic toxicity. Acute toxicity, however, caused by ethylene oxide was observed. Vomiting, confusion of thinking and skin irritation are the symptoms of toxicity of ethylene oxide.

Methyl bromide, used in the fumigation of tents at the concentration of 11,000 ppm caused severe intoxication.[34]

Admissible doses of borax and boric acid ranges for the rat at 350 ppm.[35]

Recommendation for the safe use of bacteri- and fungicides has been perfectly described in literature. The areas of greatest absorption of biocides is the scrotum, upper back, shoulders and forearms. The preventive recommendation at present is the use of plenty of soap and water. If a person should feel ill while working with biocides he should stop work at once and get medical attention. When pesticide is used in accordance with widespread and commonly recognized practices, it will not generally cause unreasonable adverse effects or risk to man or the environment, considering the economic, social and environmental costs and benefits of the use of any pesticide.[11]

8.2 Abstract

The mechanism of the action of bacteri- and fungicides used for the protection of library materials and the toxic effects on man and animal are discussed.

8.2 Résumé

Présentation du mécanisme d'action des bactéricides et des fongicides utilisés pour la protection des matériels de bibliothèque et les effets toxiques sur les personnes et sur les animaux.

8.2 Resümee

Der Tätigkeitsmechanismus von Bakteriziden und Fungiziden, die zum Schutz von Bibliotheksmaterialien verwendet werden, und die damit verbunden giftigen Wirkungen auf Menschen und Tiere werden hier behandelt.

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9.1 The Problems of Toxicity of Microorganisms Causing Damage to Library Materials

Books circulate in homes, schools, hospitals and churches, and very often they are contaminated with microorganisms which may cause typical serious diseases.[5,9,20,23,40,49,61] In cases of scarlet fever, diphtheria, poliomyelitis, typhoid

fever smallpox, anthrax, meningitis and kindred ailments, books found in the rooms of patients so suffering are invariably burned. The reason is obvious, for the sputum from such individuals may contain the virulent microorganisms.[5,9,20,31,61] The organisms that remain for long periods on the surfaces of pages include the spore bearers, Mycobacteria and fungi. Soft crude dirty paper appears to be capable of holding more microbial growth than the partially or highly glazed paper.[9] Particular individuals may be infected by the agency of a book by the usual routes of inhalation, ingestion, contagion or through the skin or mucous surfaces. Psocids or book-lice may also convey disease. Clothes (blankets) may remain infective for about two weeks.[5,20] In Lansing, Michigan, twenty personnel in the hospital office died of tuberculosis owing to the filthy habit of wetting their thumbs in order to turn over pages.[31,61] In this way they had spread infection by minute droplets of tuberculous sputum. Analogical cases were observed before the first World War in Petersburg and Kharkov in Russia and in the Berlin Municipal Library.[48,53] We know that tuberculous sputum sprayed in the act of coughing, sneezing and speaking may be preserved as dried sputum for 9–10 months (cit. 48) and Peterson[53] had found that tubercle bacteria as dried sputum could be preserved on walls, floors and handkerchiefs for 8 years (from 1898 to 1906), but they had lost virulence after 2–3 months. *Eberthella typhi* may survive 8 days, *Escherichia coli* 20 days, *Staphylococcus aureus* 45 days, *Bacillus anthracis* 60 days and *Streptococcus scarlatinae* 28 days. Bryan[9] recommends "that the books used by people suffering from colds, sore throat, influenza, measles, scarlet fever, diphtheria, meningitis, infantile paralysis, whooping cough, pneumonia, tuberculosis and books read while convalescing, should be stored for a safe period of time before redistribution. When child epidemics occur in schools, books from sick children should not be redistributed until several days have elapsed". Ethylene oxide seems to be effective against dangerous bacteria and especially tubercle bacterium.[46] Consistent toxicity of ethylene oxide with carbon dioxide on these bacteria in a small volume of moist sputum and somewhat less consistent toxicity in dried sputum was found.[46] Disinfection of contaminated books is necessary.

The most dangerous for library and archive collections are undoubtedly fungi.[22,23,32,33,40] Although on the one hand several fungi for instance *Penicillium camemberti* and *Pennicillium roqueforti,* tickle the palate of gourmandizers and are needed for the manufacture of bread and beer (kein Pils ohne Pilz), on the other hand they destroy valuable materials and are innocuous to human health[1,3] and especially extreme care should be emphasized for custodians, curators, superintendents, and other workers in libraries, archives and museums. When considering fungi (popularly called moulds or mildew) as

pathogens, it is important to distinguish between "mycotoxicosis" and "mycosis".[12] Mycotoxicosis provokes activity against different organs: liver, kidneys, lungs, nervous system. Mycosis refers to a generalized invasion of living tissue by growing fungi and their metabolites. Owing to the relative stability of mycotoxins to heat, they may remain for long periods and may also cause the troubles for workers in libraries and archives. Mycotoxins[4,6,54,58,63,65,66] may exhibit both acute and chronic effects and although we need not provoke panic, when fungi exist in abundance in libraries they may produce serious problems.

The genus Aspergillus represent some of the most prevalent mycotoxin-producing fungi.[8,13,14,16,19,26,34,38,39,44,45,56,58,62,64] In human infections of the lungs and other viscera, the species most frequently encountered is by far Aspergillus fumigatus,[1,58,63] which is above all the inhabitant of cellulosics, collagenics and sound recording materials followed by *Aspergillus flavus, Aspergillus niger, Aspergillus terreus, Aspergillus versicolor, Aspergillus clavatus* and *Aspergillus chevalieri*, which damage different library objects and works of art. It is generally understood that particular species of the genus Aspergillus cause diseases with symptoms similar to tuberculosis and some of them are injurious to the mucous membrane; besides this they are etiological agents of the inflammatory state of particular membranes; the eye globe, the conjunctiva and the tear duct. Aspergillus fumigatus produces, among others, strong fungitoxic fumigaclavin A and C and tremorgenic products[14] and fumitoxins A,B,C and D. Fumitoxin A is steroid, having molecular structure $C_{31}H_{42}O_8$.[19] In ear and skin infection the most frequent species is *Aspergillus niger*.[4] *Aspergillus flavus, Aspergillus Wentii, Aspergillus amstelodami* and *Aspergillus terreus*, deteriorating different library and archive materials including plastics, have been shown to be lethal to many animals, in which post mortem revealed a fatty degeneration, necrosis of the liver and congestion of the liver.[55,64] *Aspergillus terreus* produces also territrems A and B.[38,39] *Aspergillus ochraceus* and *Aspergillus flavus* cause liver degeneration and its necrosis.[56,62] Besides liver and kidney damage Aspergilli and Penicillia cause neurotoxic influence and therefore some antibiotic substances, territrems, deriving from these fungi and causing tremors and convulsions, have not been accepted as antimicrobial agents in medicine.[12,38,39] In general aspergillosis, abscesses are formed in lungs, kidneys, liver, heart, muscle, spleen, brain and meninx and attack the central nervous system. Apart from this, members of the genus Aspergillus produce metabolites, which are heavily pathogenic. For example, cancerogenic aflatoxins from *Aspergillus flavus* especially frequent the inhabitant of adhesives. Some Aspergilli, as *Aspergillus versicolor, Aspergillus nidulans* and others,[14,26] contain cancerogenic metabolite sterigmatocystin, which as aflatoxins has in its molecule the benzofuran ring

system responsible for carcinogenicity. Ochratoxins A and C, the most toxic derivatives of *Aspergillus ochraceus* and isolated also from *Penicillium viridicatum* contain the chlorine atom at position 5 of the ochratoxin molecule.[14] The second toxic metabolite of *Aspergillus flavus* and *Aspergillus ochraceus* is 3-nitropropanoic acid. Cytochalasin E from *Aspergillus clavatus* and *Aspergillus chevalieri* and Helminthosporium caused human mortality from ingestion of these fungi.[14,44,45,59] Terreic acid from *Aspergillus terreus* is highly toxic to mammals and LD_{50} of this metabolite to mice ranges 71–119 mg/kg p.o.

Penicillia cause ulcers, damage of mucous membranes on the oral cavity and an inflammatory state of bronchi. Penicillium rubrum causes liver damage[34] and fatal intoxication of mammals.[62] *Penicillium viridicatum* causes degeneration of the heart muscle, disease of kidneys & atrophy of the spleen.[10,29,34] Metabolites isolated from Pennicillium viridicatum include, among others, very toxic ochratoxins, viridicatin, cyclopenic and xanthomegnin and viomellin, causing hepatic alterations.[10] Mycotoxin-citrinine was found in Penicillium chrysogenum.[57] Huang and Harris (cit. 32) described a rare example of disseminated penicilliosis. The patient had acute leucemia complicated by pulmonary and cerebral penicilliosis. Penicillium commune was cultured from the pulmonary lesions at autopsy and observed within and around blood vessels. Mycotoxins are produced also from *Penicillium frequentans, Penicillium notatum*, the inhabitants of magnetic tapes and motion picture films. *Penicillium janthinellum*, often observed on nylon produces penitrem A, tremorgenic toxin, and *Penicillium nigricans, Penicillium raistricki* and others produce tremorgenic toxin X-indol derivative, identical probably with fumitremorgen B isolated from *Aspergillus fumigatus*.[51] *Penicillium islandicum*, Sopp produces cyclochlorotine, which causes necrosis, vacuolation of liver cells and development of blood lakes. The second metabolite of this fungus, simatoxin, causes jaundice and retarded growth of newborn rats.[24] *Penicillium cyclopium* and *Penicillium crustosum*, the inhabitants of leather, produce tremorgenic toxin tremortin.[28] *Penicillium stoloniferum, Penicillium brevicompactum, Penicillium białowiężense, Penicillium roqueforti*[47] produce very toxic mycophenolic acid, which causes anemia in rats and after several weeks after oral administration of daily dosis 30 mg/kg death follows.[35,36] Twenty-three identified metabolites from various Penicillia were studied extensively.[51] It is worth mentioning that the Manchester physician, Blackley,[7] tried inhalation experiments on himself with Penicillium and Chaetomium spores which caused an attack of bronchial catarrh. According to him this experiment was too unpleasant to repeat.

Mucous membranes and the whole organism may be contaminated with Stachybotrys atra, a frequent inhabitant of library and archive materials. Stachybotrys atra produces mycotoxin-12,13-epoxy-delta[9]-trichothecenes and

causes stachybotryotoxicosis.[21] This fungus causes necrosis in the mucosa of the mouth, pharynx and intestinal tract.[8,42,43] *Cladosporium cladosporioides* given to mice caused their death due to hemolytic jaundice and disease of the kidneys.[17] Moreover *Cladosporium herbarum* and *Trichoderma viride* damage the oral cavity and *Stysanus stemonitis* and *Alternaria sp.* damage the respiratory tract and cause asthmatical diseases. Alternaria species and, among others, *Alternaria tenuis* were believed the source of toxicosis in man in the USSR during WWII[10,25] and 90% of Alternaria strains were lethal to rats when fed in a corn-rice mixture,[11] causing, at the beginning, neuropathic disturbances, changes in blood, marrow and liver degeneration.[11] Out of 212 Alternaria strains 60% were lethal to mice at the concentration 300 mg/kg after peritoneal injection and to rats p.o. (cit. 33). Many metabolites of Alternaria may be toxic[52] and the major mammalian toxin is believed to be tenuazonic acid.[18] Tenuazonic acid is a tetramic acid derivative produced by many species of Alternaria, as Alternaria alternata and Alternaria tenuissima and also the genus Aspergillus. LD^{50} of tenuazonic acid ranges 266 mg/kg to rats.[18] *Alternaria tenuis* and *Alternaria sp.* may cause superficial mycoses of skin, hair and nails.

Toxicity to rats has been found in such fungi representatives of the genus: Penicillium, Fusarium, Aspergillus, Chaetomium and Alternaria and the most toxic were some species of the genus Aspergillus, Penicillium and Chaetomium. Certain toxins isolated from these genuses were chemically characterized.[12,25,43,45] Toxic metabolites scirpenes are produced by: Trichothecium, Trichoderma, Fusarium, Cephalosporium, Myrothecium, and from these fungi such metabolites as trichodermol, trichodermin, trichothecin, verrucarol, diacetoxyscirpenol, crotocin and toxin T_2 were isolated.[12,43,51] They have dermatoxic and alimentary toxic activity. *Cephalosporium acremonium* may infect skin, mouth, tonsils and pharynx and may cause chronic meningitis and neurologic and psychiatric disturbances.

It was found that *Cephalosporium acremonium* and *Paecilomyces varioti*, observed very often on library materials, play a part in causing inflammation of the stomach, ulceration and cancer diseases, and *Chaetomium globosum* caused disease in the central nervous system and was lethal to experimental animals.[27,30,37] Trichothecium roseum also causes skin diseases and abscesses of the stomach,[62] as well as fatal accidents to animals.[55] *Fusarium oxysporum* has been associated with cutaneous, corneal and urinary tract infections and has been observed in diseases of the nails and abdominal diseases. This fungus probably caused cancer of the teat.[60] *Fusarium monilliforme* revealed mutagenic activity[15] and it produces toxin, and *Fusarium monilliforme*, *Fusarium roseum* and *Fusarium culmorum*, isolated many times from library materials, produce emetic

and rejection factors.[37,62] Evidence exists of Helminthosporium in human pulmonary tissue. Metabolites of Helminthosporium contain polyhydroxyantraquinone toxic to animals.[27,59] *Scopulariopsis brevicaulis*[41,50] and Aureobasidium cause disease of the skin that are difficult to cure. Rhodotorula has generally been regarded as nonpathogenic, but it has been cultured from numerous sources in human patients including skin and nails, bronchial secretions, urine, blood aortic valve, ascites fluid, vulvovaginal area, cerebrospinal fluid, pharynx and faeces.[4]

All the above mentioned fungi were found on library, archival, ethnographical and other valuable materials. Fungi may cause pulmonary irritation in certain sensitive humans. Symptoms of asthma and skin irritation, as well as other more dangerous diseases have often been observed in our laboratory. Allergies due to an intensity of symptoms occurring during hot and damp weather have been clinically studied.[1,4,63,65] Allergies may be modified in various countries owing to geographical differences. In some regions of Europe the symptoms of allergy may be more acute due to the high relative humidity. More physically sensitive persons, and especially miners, children and old people,[3] are susceptible from May to November; the less physically sensitve from July to October. The numbers and types of fungus spores will vary depending on the time of day, season and location, as well as humidity. During respiration, particles which are larger than 10 microns are deposited in the nose and pharynx, and those smaller than 5 microns reach the alveoli. The allergic response may even be immediate as in the case of Cladosporium herbarum, producing metabolite 3,4-dihydro-6,8-dihydroxy-3-/6-methylhydropyran-2-ylmethyl/ isocoumarin or cladosporin,[2] Alternaria tenuis and Aspergillus fumigatus, and asthma is produced as a rule by Epicoccum, Cladosporium and Alternaria.

For a long time fungi were regarded as harmless, because usually toxins of ingestion of fungi did not produce dramatic symptoms. Fungi, however, as particular climatic sequences may cause out-breaks of mycosis and may favour toxin production, especially in heavily contaminated libraries, archives and museums.

9.2 Abstract

Books and archives as germ carriers of typical serious diseases such as tuberculosis, scarlet fever, diphtheria, poliomyelitis, typhoid fever, meningitis and others, are discussed. Special attention is focused on fungi, the most dangerous for library and archive collections.

9.2 Résumé

Présentation des livres et des archives comme supports bactériens de maladies graves typiques telles que la tuberculose, la scarlatine, la diphtérie, la poliomyélite, la fièvre typhoïde, la méningite etc . . . Une mention particulière est faite des moisissures, micro-organismes les plus dangereux des collections de bibliothèques et d'archives.

9.2 Resümee

Bücher und Archive als Keimträger typischer ernsthafter Erkrankungen, wie zum Beispiel Tuberkulose, Scharlach, Diphterie, spinale Kinderlähmung, Typhus, Meningitis und andere werden hier diskutiert. Besondere Aufmerksamkeit wird den Pilzen gewidmet, die für Bibliotheks- und Archivsammlungen am schadhaftesten sind.

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