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„Determining the influence of water on the 19th and 20th-century papers subject to certain mass conservation treatments”

INTRODUCTION

Mass deacidification technologies are applied to save the library and archive collections around the world because of bad condition of many 19th- and 20th-century papers. Paper structure during the deacidification treatment is filled with alkaline substance which reacts with acids to the form of salts. The deacidification treatments change some paper properties. One of the most important question is how water influences the properties of deacidified papers. It is very important in the face of floods which happen more and more often because of climate changes, and the climate is unpredictable.

MATERIALS AND METHODS

A) Samples preparation

Paper samples from the 19th- and 20th-century books were deacidified with the use of four mass deacidification treatments: Bookkeeper, Libertec, Battelle and DAE (table 1). A part of paper properties were tested ten months after the deacidification. The following tests were carried out: capillary rise, dyes changes in direct contact with water, microbial susceptibility. The deacidified as well as not deacidified papers (controls) were tested.

Table 1. Basic specifications of four chosen mass deacidification technologies.

Names of mass deacidification treatments	Localization of installations	Chemicals used in treatments
Bookkeeper	Preservation Technologies, L.P., 111 Thomson Park Drive, Cranberry, Township, PA 16066, USA	magnesium oxide suspension in perfluoroheptane
Battelle	Zentrum für Bestandserhaltug GmbH, Mommsenstraße 7 D-04329 Leipzig, Germany	magnesium titanium ethoxide in hexamethyldisiloxane
DAE (**D**ry **A**mmonia and **E**thylene Oxide)	Nippon Filing Co., Ltd. Shin-Ohanomizu Urban Building 8F 3-2, Kanda Surugadai, Chiyoda-ku, Tokyo, 101-0062, Japan	dry ammonia and ethylene oxide react to form: monoethanolamine, diethanolamine, triethanolamine and a certain quantity of other compounds can appear.
Libertec	Libertec Bibliothekendienst GmbH Kilianstraße 86 90425 Nürnberg, Germany	magnesium oxide and calcium carbonate mixture in air stream (fluidization process)

B) Capillary rise test (fig. 1)

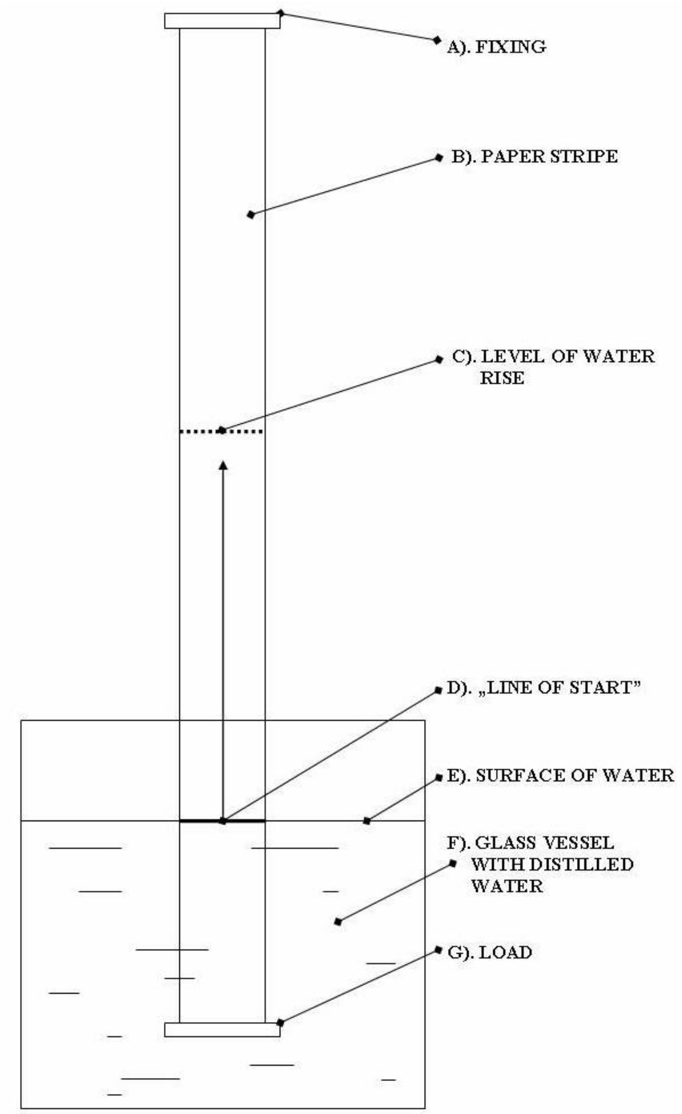
Definition

Standard-sized long paper samples (stripes) are fixed at the top, slightly loaded at the bottom and partially immersed in water. The water starts to rise during a specific period of time. The level of water rise is measured in millimetres after removing the stripes from water.

Conditions of measurement

According to PN-ISO 8787 (Klemm method), the capillary rise methodology was used for performing tests. Samples of machine made papers from books issued in 1851, 1860, 1870, 1892, 1914 and 1921 were investigated. The width of samples was 15 mm. Immersion time in fresh distilled water (23º C) amounted to 30 minutes. After this time, the level of rise of water in paper samples was measured in millimetres at the distance between the line of paper immersion in water (“the line of start” - drawn by pencil before the test) and the top of the wet area of paper. The results were calculated as the average of five measurements.

Fig. 1. The scheme of capillary rise test

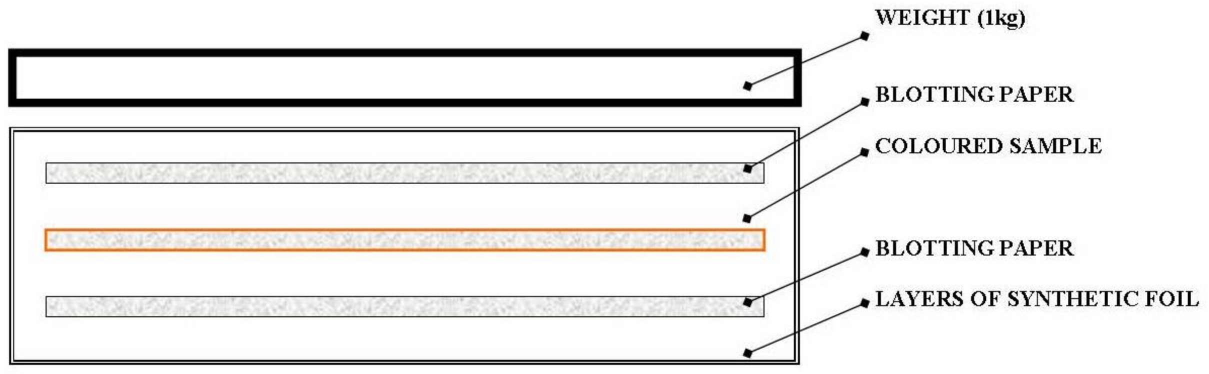


C) Test of the influence of water on dyes on paper (fig. 2)

Definition
The influence of water on dyed, surface coloured, printed and written papers is estimated after a long contact with wet blotting paper under the standardized load.

Conditions of measurement
Different machine-made and coloured paper samples from the 19th- and 20th-century papers were tested. These were samples from books, writings, maps etc. Blotting papers (Herlitz) were immersed in fresh distilled water and the excess of water was removed by flowing away of the samples during the period of approximately two minutes.
The samples of maximum size of 60 × 90 mm were put between two wet blotting papers (without the excess of water) and then such "covered" samples were put between two glass plates (60 × 90 mm). Such prepared samples were wrapped with synthetic foil and pressed under the load of 1 kg. After 24 hours of storing the samples at ca. 23°C, they were removed and dried in normal conditions. All changes which appeared as a result of the test were observed by visual examination in daylight. During the observations, the samples were put on a black paper serving as a background in order to remove some negative optical effects of transparency of coloured matters). The tests were carried out twice.

Fig. 2. The scheme of the test of the influence of water on dyes on paper



D) The test of microbial susceptibility (fig. 3)

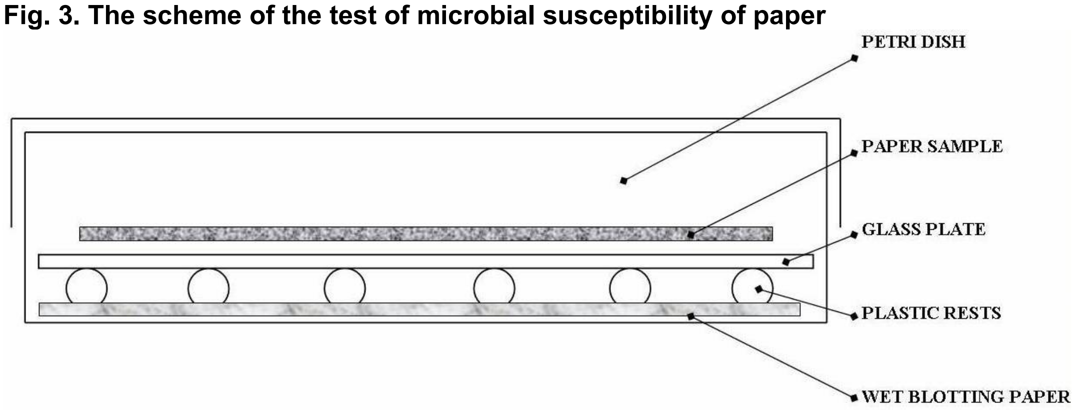
Definition

Microbial susceptibility of paper is tested on paper samples stored in high humidity and slightly higher temperature. The moment of the first appearance of a microorganism and the speed of its growth are observed during the tests.

Conditions of measurement

Machine-made paper from the book issued in 1897 was used for the test. The size of samples was 5 × 5 cm. The tests were carried out on wire and felt sides of paper. These sides are characterized by slightly different properties and structure between them. The crossing lines dividing the surface of samples into four parts were drawn in pencil on every sample. Before the test, the samples were stored in room conditions for six days. It allowed their natural infection because there are lots of fungal spores in dust. Then, the dusty samples were put on sterilized glass plates in the Petri dishes. The water added to the bottom of Petri dishes allowed to obtain high humidity (RH = 95-100%). Small plastic rests were added as isolators between the glass plates with samples and water at the bottom. The Petri dishes with samples were stored in incubator at 28ºC for ninety days. Because of continuous evaporation of water, it had to be regularly replenished. The surfaces of samples were observed in the light of the stereoscope microscope every two days. The growth of microorganisms, such as fungi, slimy bacterial colonies, and streptomyces was observed in four stages: (±) the initial growth of microorganisms (visible in the stereoscope microscope); (+) skimpy growth of microorganisms (visible in the stereoscope microscopy); (++) growth of microorganisms visible with the naked eye; (+++) growth of microorganisms distinctly visible with the naked eye. This division depended on the size of colonies (measured during the tests) and the intensity of their growth. The microbial growth was observed within four marked areas of all samples. The days on which microorganisms reached a certain stage of growth were noted. The result of the test was the average of the number of days during which a certain stage of growth was achieved on each of the four areas of the sample.
The fungal colonies which appeared on the samples during the tests were inoculated into the culture mediums (malt extract agar, czapek yeast agar, glycerol nitrate agar). Fungal species were identified by Joanna Karbowska-Berent (Ph. D) from the Department of Paper and Leather Conservation.

Fig. 3. The scheme of the test of microbial susceptibility of paper

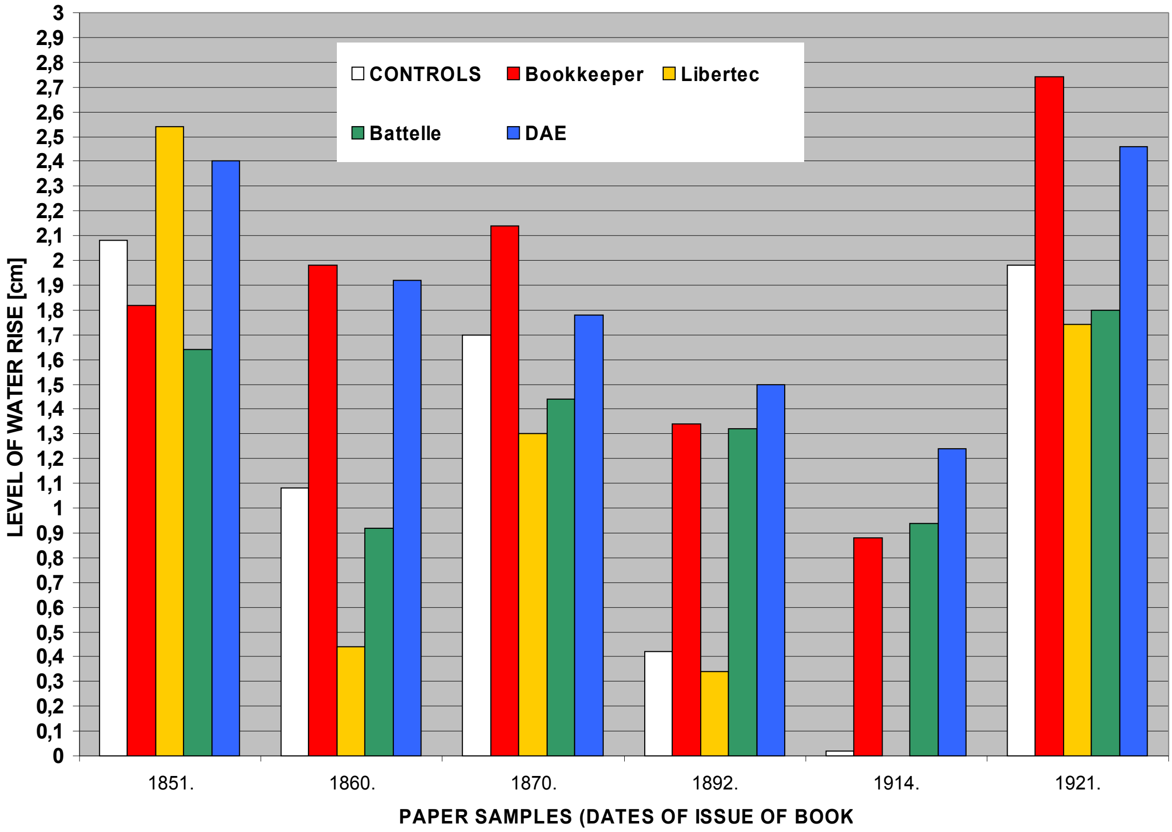


RESULTS

A) Capillary rise (fig. 4, table 2)

The level of water rise in paper samples was different and depended on the deacidification treatment applied.
The highest water rise was only 2,8 cm (Bookkeeper, 1921). Tested controls had different affinity to water but the applied mass deacidification treatments caused additional changes in paper properties. Papers deacidified with the use of DAE and Bookkeeper treatments had the biggest affinity to water. In case of papers deacidified by the DAE treatment, the main cause of papers affinity to water was the presence of water-soluble ethanolamines, which dissolve quickly and easily in water. In case of papers deacidified by the Bookkeeper treatment, a possible cause for a faster water rising might be the presence of a small amount of surfactant, which is an organic compound added to chemicals.

Fig. 4. The results of capillary rise tests of deacidified and not deacidified papers (controls)



In comparison to controls and other deacidified papers, a brownish weeping was distinctly visible on papers deacidified with the use of Bookkeeper and, especially, DAE treatments. A weeping was less visible in case of papers deacidified with the Battelle treatment and almost invisible in case of papers deacidified with the use of the Libertec treatment.
It was only in one case that papers deacidified by the Libertec treatment showed a higher capillary rise in comparison with the controls! It was the paper sample from 1851. The other part of papers deacidified with the Libertec method was characterized by a little affinity to water in comparison with controls and other deacidified papers. Papers deacidified with the use of the Battelle treatment showed such affinity to water similar to papers treated with the Libertec method.

Tab. 2. The results of capillary rise tests of deacidified and not deacidified papers (controls)

Deacidification method	Year							
	1851	**1860**	**1870**	**1892**	**1914**	**1921**	**Number of times when water rise was higher than controls**	**Number of times when water rise was lower than controls**
Bookkeeper	-	+	+	+	+	+	**5**	**1**
Libertec	+	-	-	-	-	-	**1**	**5**
Battelle	-	-	-	+	+	-	**2**	**4**
DAE	+	+	+	+	+	+	**6**	**-**

+ higher, - lower

B) The influence of water on dyes on paper (figs. 5-8)

Almost no changes were observed in printing inks on papers. Only red dyes used for making of printing inks were in some cases slightly more sensitive to water. This fact was observed both in case of controls and deacidified papers. On the contrary, the dyes used for pulp dying and writing inks on controls were in many cases very sensitive to water and some mass deacidification treatments caused their sensitivity to increase. The most visible changes could be detected on papers treated with the DAE and Bookkeeper methods. Some negative but less visible colour changes were also observed on papers deacidified with the Libertec and Battelle treatments.

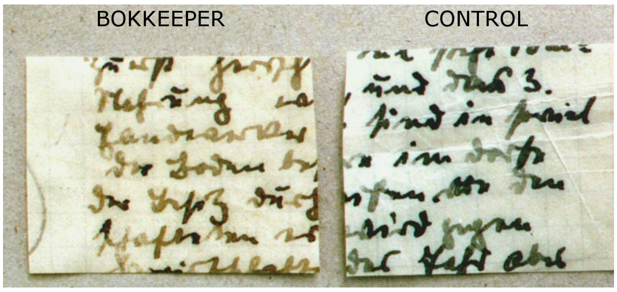


Fig. 5. Changes of writings after 24 h contact with wet blotting paper. Control (on the right) and paper deacidified with the Bookkeeper treatment.

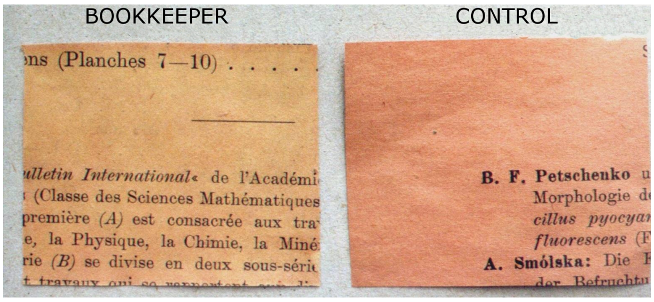


Fig. 6. Changes of dyes on paper cover after 24h contact with wet blotting paper. Control (on the right) and paper deacidified with the Bookkeeper treatment. Samples from 1928.

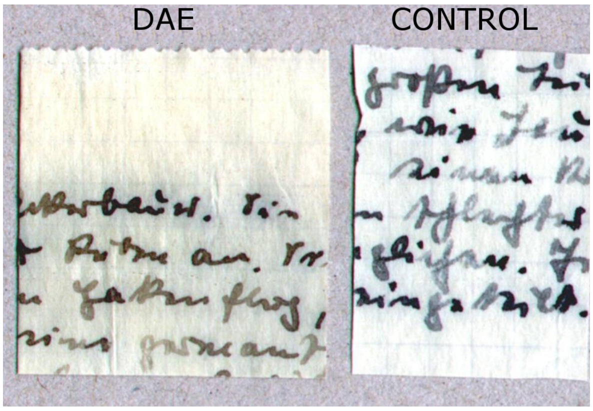


Fig. 7. Changes of writings after 24 h contact with wet blotting paper. Control (on the right) and paper deacidified with the DAE treatment.

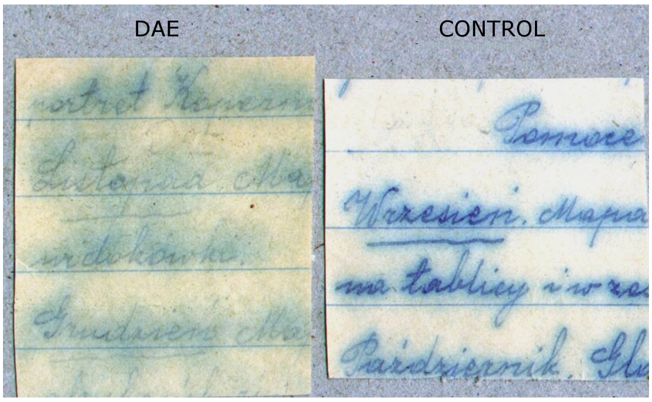


Fig. 8. Changes of writings after 24 h contact with wet blotting paper. Control (on the right) and paper deacidified with the Bookkeeper treatment.

Additional and very simple tests were carried out on the samples. One drop of distilled water was added on the surface of paper quarters and then, every minute (up to six minutes) the behaviour of water was observed. Paper deacidified with the Bookkeeper and DAE treatments absorbed water more easily and quickly than the controls. Paper deacidified with the use of Battelle treatment absorbed water more slowly than in case of the two above-mentioned papers. On the contrary, the drops of water added on the Libertec-deacidified papers were absorbed very slowly and in small quantity.

C) Microbial susceptibility (fig. 8, tables 3 and 4)

The chosen method to determine the speed of microbial growth on deacidified papers in high relative humidity allowed to observe different tendencies in microbial susceptibility.
All methods of mass deacidification increased the microbial susceptibility of paper (both on the felt and the wire side) especially in the first stages of microbial growth (±, +, ++). An exception was the 3rd stage (+++) of the microbial growth on the wire side of paper deacidified with the Battelle treatment. Papers deacidified with this method were distinctly less susceptible on the wire side during the 2nd (++) and the 3rd (+++) stages of microbial growth. This could be attributed to the presence of titanium dioxide, which is created in the paper during a deacidification process. This substance is slightly antiseptic and allows to slow down, or sometimes stop, the growth of microorganisms. During the 3rd (+++) stage of microbial growth, the difference between some deacidified papers and the controls faded. *Penicillium citrinium* and another unidentified fungus were identified on the controls. More fungi species were identified on deacidified papers. Except fungi, other kinds of microorganisms, such as slimy bacterial colonies and streptomyces, were also observed.

Through visual observation, the applied method allowed to generally estimate the microbial susceptibility. In the future, it would be very interesting to investigate the microbial susceptibility of deacidified papers infected with single species of fungi. This method is proposed by a Polish scientist Bogdan Filip Zerek.

Fig. 8. The results of the tests of microbial susceptibility of deacidified and not deacidified papers (controls)

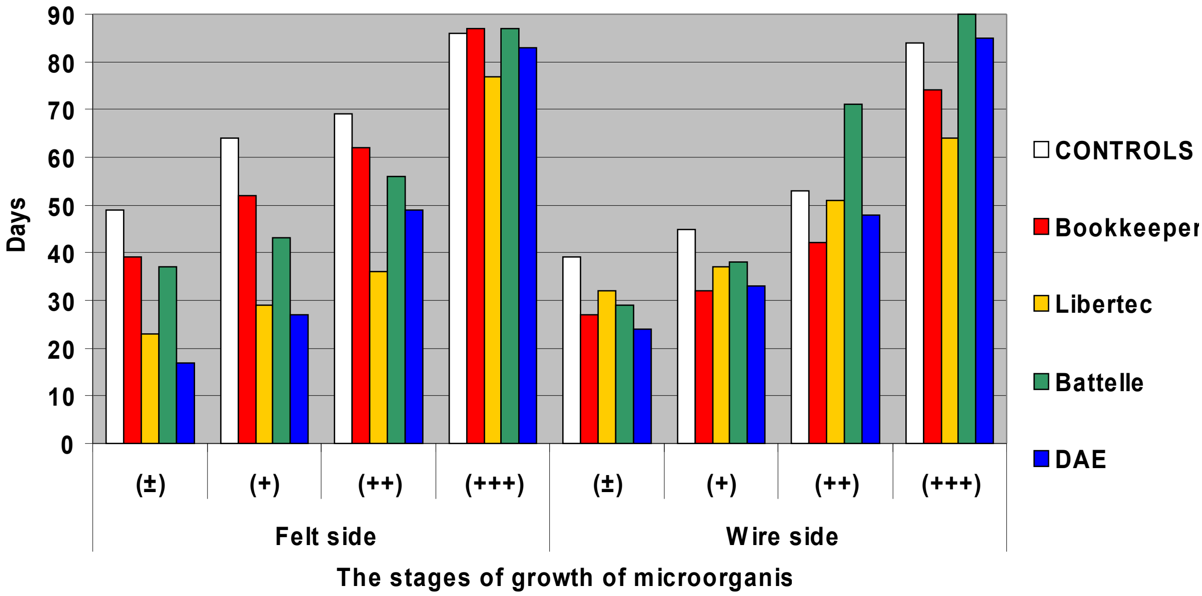


Table 3. The results of the tests of microbial susceptibility of deacidified and not deacidified papers (controls)

Deacidification method	Stages of microbial growth									
	Felt side				Wire side				Number of times when samples were more susceptible than controls	Number of times when samples were less susceptible than controls
	(±)	(+)	(++)	(+++)	(±)	(+)	(++)	(+++)		
Bookkeeper	+	+	+	-	+	+	+	+	**7**	**1**
Libertec	+	+	+	+	+	+	+	+	**8**	**0**
Battelle	+	+	+	-	+	+	-	-	**5**	**3**
DAE	+	+	+	+	+	+	+	-	**7**	**1**

+ more susceptible, - less susceptible

Table 4. Identified species of fungi (by Joanna Karbowska-Berent)

Deacidification method	Felt side	Wire side
Controls	• *Penicillium citrinum*	• *Penicillium citrinum* • not identified fungus species of the *Dermatiaceae* family
Bookkeeper	• *Aspergillus Flavipes*	• *Penicilluium chrysogenum*
Libertec	• *Penicillium chrysogenum* • *Cladosporium cladosporioides* • *Scopulariopsis candida*	• *Penicillium glabrum*
Battelle	• *Aspergillus versicolor* • *Penicillium decumbens*	• *Cladosporium sphaerospermum* • *Scopulariopsis chartarum* • *Penicillium citrinum*
DAE	• *Cladosporium sphaerospermum* • *Penicillium waksmanii*	• *Penicillium waksmanii*

CONCLUSIONS

1. **In direct contact with deacidified papers, water causes various side effects.**

2. **The kinds and the intensity of side effects depend on the mass deacidification method applied.**
3. **The use of deacidification treatments is absolutely necessary to protect the 19th- and 20th-century papers against acid deterioration. However, special attention should be paid to eliminate side effects which can appear on deacidified papers after a possible damping or flooding.**
4. **Special attention should be paid to monitor the microbial condition of deacidified collections which were damped.**

5. **It seems probable that the speed of microbial growth on deacidified and flooded collections could be faster than on undeacidified papers. The speed and the intensity of microbial growth could depend on the applied method of mass deacidification.**

6. **It is necessary to continue and develop methodology as well as to continue the investigations related to the influence of water on deacidified papers in order to better protect the deacidified collections.**