The Effect of Alkaline Boxes and File Folders on the the Accelerated Ageing of Paper by Air Pollution

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Introduction

The effect of air pollution on ageing paper has been the topic of several studies during the last years. A major study has been carried out in the framework of an european program, the STEP project CT 90-0100[0]. It has become clear that SO_2, NO and NO_2 accelerate the natural ageing of cellulose. In combination SO_2, NO and NO_2 act as synergists.

To prevent this accelerated ageing, filtering systems have been added to the climate control units in museums, archives and libraries. Since most of the collections containing paper artifacts (prints, drawings and archival material) are stored in boxes, the question has been raised to which extent boxes with an alkaline reserve ("buffered" boxes), are able to protect paper artifacts from air pollution.

A research program is set up in which the protective properties of an "acid-free", but not buffered box and a "buffered"box, are investigated. Each box contains stacks of three types of paper, a bleached sulphite softwood cellulose paper, a groundwood containing paper and a permanent paper grade without optical brightners. In a first experiment the boxes were exposed to 20 ppm NO_2 and 10 ppm SO_2 at a flow of ca. 800l/h during three months. Before and after the exposure pH, alkaline reserve and sulphur content (by non destructive x-ray fluorescence spectroscopy) were measured. In a second experiment three boxes were investigated an ordinary office box was added. In the boxes two types of file folders were placed. One file folder was an ordinary office folder, the other a lignin free, buffered folder. The exposure was continued for 10 weeks and paper samples were withdrawn from the exposed boxes and file folders weekly and analyzed for sulphur content.

Experimental materials

Document storage boxes

Two identical document storage boxes were chosen. The boxes are of the type which is one piece, self locking and made of corrugated board. The corrugated board is a B-flute single wall board comprised of two facings adhered to one fluted medium with fluting perpendicular with the spine of the box. The assembly does not include adhesive or metal fasteners.The self locking assembly is made as such that the tabs fit snugly into incisions cut in the top and bottom of the box. A shallow thumb cut is centered on two outside edges. The thumb cut is 3 cm in height.

One box was made of "acid free", lignin containing corrugated board with an alkaline starch sizing. The other box was made of lignin free corrugated board with an alkaline reserve in facing papers and the flute of the corrugated board. In the second experiment an ordinary office document storage box made of groundwood containing recycled board is added.

Papertypes

Three types of paper were chosen for the experiments. A bleached sulphite softwood cellulose paper, a groundwood containing paper, rosin sized with alum and a permanent paper grade without optical brighteners which meets the Dutch standard for permanent paper (NEN 2728)[1], [2].

File folders

Two type of file folders were chosen. One is an ordinary office file folder[3], the other a file folder which meets the requirements of the CL-Kwaliteitseis no. 2 [4].

Test methods

The aim of this study was to investigate the function of a document storage box as a protection against air pollution. The major acid pollutants- sulphur dioxide and nitrogene oxide are ubiquitous in urban air worldwide with typical ambient concentrations of 5-50 ppb for SO_2 and 50-200 ppb for NO_2 [5]. To be able to measure the effects of pollutants on relatively short notice the concentrations chosen are much higher than the ambient levels. The concentration of SO_2 and NO_2 are chosen at the same level of the concentrations in the STEP Project CT 90-0100 [6]. Thus the results from that study could possibly be compared with the study described here.

Previous studies on the degradation of paper by air pollutants showed that in particular SO_2 is absorbed and that the uptake is accelerated by the presence of NO_2 [7].

The analytical methods chosen for the research were concentrated to measure the direct effects of the uptake of sulphurdioxide. No effort was made to measure the degradation of the mechanical properties.

pH cold extract

This method was used to determine the hydrogen concentration of paper extracts to obtain an impression of the amount of H_2SO_4 in the paper formed by the uptake of SO_2. The cold extraction is carried out after NEN 2151.

Alkaline reserve

This method is used to determine the alkaline reserve of the paper. The alkaline reserve stand for the presence of materials such as calcium carbonate in paper, that are capable of absorbing acidic gases from the environment. Through this method the amount of calciumcarbonate present in the paper can be measured before and after exposure and thus give an impression of the amount of SO_2 absorbed. The alkaline reserve is carried out after ISO 10716.

X-ray fluorescence spectroscopy (Omega 5)

The Omega 5 is an nondestructive x-ray fluorescence spectrometer(XRF). The elemental composition of places on the surface of objects, both qualitative and quantitative are obtained rapidly and accurately. A surface of at least 2 mm^2 can be analyzed without the need of a sample taken. The exact place to be analyzed is marked with the guidance system of two laser beams which intersect on the object when it is in the right position. Using the system for paper the beam is

directed in such a way that the total amount of the elements present in the paper is measured. The reliability of the method for this purpose had to be established in advance. Samples of paper with the same weight per square meter were impregnated with a known amount of an iron sulphate $(Fe(SO_4)_2(NH_4)_2 * 6 H_2O$. The amount of sulphur per square cm was introduced into the software of the Omega 5. So as to make the calculations, the paper weight was introduced. The reproducibility of the method was good, the relative standard deviation being less than 5%.

Exposure chamber

The testchamber is made of plexiglass and placed in a climate chamber. The chamber volume was 165 l. Purified (with activated carbon) dry air is added to the ENET GGSK 220 climate chamber. A mixture of SO_2 and NO_2 is added using mass flow controllers in order to obtain a continuous concentration of 20 ppm NO_2 and 10 ppm SO_2 in the test chamber. The temperature in the test chamber was 23°C and the relative humidity 50%.
The floor through which the humidified air mixed with the air pollutant gases enter was perforated and a fan was used to circulate the polluted air in the chamber. The exchange was 5 times per hour. The sulphurdioxide was obtained from a bottle with ca. 1,25% SO_2 in nitrogene and the nitrogen oxide form a bottle with ca. 2,5% NO_2 in nitrogene. The first dilution with dry air takes place in a mixing chamber, the second dilution takes place in the climate chamber.

Exposure experiments

First experiment
The document storage boxes were filled with stacks of ca. 200 sheets of the three test papers. The stacks were kept upright by folded sheets of acid free museum board. Two boxes are placed upright in the middle of the exposure chamber. The exposure is continued for 12 weeks with 20 ppm NO_2 and 10 ppm SO_2.
After the exposure pH, alkaline reserve and sulphur content was measured from the three test papers. Measurements were made separately form the margins and the center of the paper sheets. The stacks of paper were divided in three parts and from every part twosheets were taken for the measurements. The average of these analysis were calculated. The sulphur content was measured using XRF. Twelve points at the margins and five points in the center of each sheet were measured. The first three sheets of each stack were separately measured. This was done because the groundwood containing paper showed an overall yellowing of the first pages whereas the next sheets were only yellowed at the margins.
The cold extraction pH and the alkaline reserve of the three layers of the corrugated board of the boxes were measured separately.

Results and discussion

Measurements of the boxes after exposure
After exposure a considerable difference between the condition of the two boxes could be observed. The results of the measurements before and after exposure are listed in table 1.
The pH of the "acid-free" document storage box had dropped from 6.2 to 3.0, the pH of the alkaline document storage box was reduced from 9.0 to 7.7. More than 50% of the original alkaline reserve was still left. The pH of the flute and the inner facing of the corrugated board from the "acid-free" box dropped from 8.1 to 6.4 and from that of the alkaline box from 9.0 to 7.9.

Table 1

Testmethod	Corrugated board	***alkaline* document storage box**		**"acid-free" document storage box**	
		***before* exposure**	**after exposure**	***before* exposure**	**after exposure**
pH	outside box	9.0	7.7	6.2	3.0
	flute	9.1	7.8	8.1	6.3
	inside box	9.0	7.9	8.1	6.4
Alkaline reserve in % $CaCO_3$	outside box	8.29 %	4.75 %		
	flute	7.86 %	6.02 %		
	inside box	7.86 %	6.37 %		
Surface pH*	outside	7.7	6.7	4.8	2.9
	inside	8.4	6.6	7.2	4.7

* *The surface pH is measured separately from the outside and the inside of the first layer of the corrugated board. As the measurement of the surface pH is not very accurate the results can only give an indication* [8]. *The measurements were carried out to get an impression of the diffusion of SO_2 through the board.*

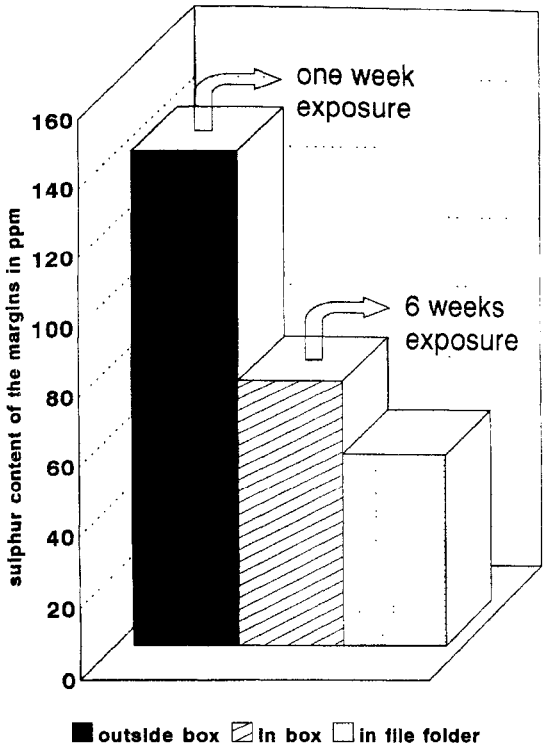

Figure 1. Effect of the box and file folder on the sulphur content of the paper. Outside the box is measured after one week exposure, inside the box after 6 weeks exposure.

Measurements of the testpapers inside the boxes after exposure

The influence of the pollution on the three types of paper in the two boxes varied. In both boxes the colour of groundwood containing paper changed into yellow-brown. The first sheets of the stacks were completely brown and deeper down the stack only the margins of the sheets were discoloured. The paper had become "brittle paper". The results of the measurements of the test papers before and after exposure are listed in table 2.

The discolouration of the groundwood containing paper coincided with the sulphur content. The permanent paper grade paper showed no significant colour change and no physical damage. The pH of the groundwood containing paper and the bleached suphite softwood paper dropped from resp. 5.6 to 3.0 and from 6.3 to 3.5, where as that of the permanent paper grade paper dropped from 9.2 to 8.3. The sulphur content was the highest in groundwood containing paper, considerably lower in the permanent paper grade paper and the bleached sulphite softwood paper.

There was no significant difference in condition of the test papers in the two boxes. These results may have been caused by the design of the boxes which had two thumb cut holes. Another possibility is that differences in absorption which might appear in an early stage of the experiment could disappear after long term exposure to high concentrations of SO_2 and NO_2.

Second experiment

Experimental parameters

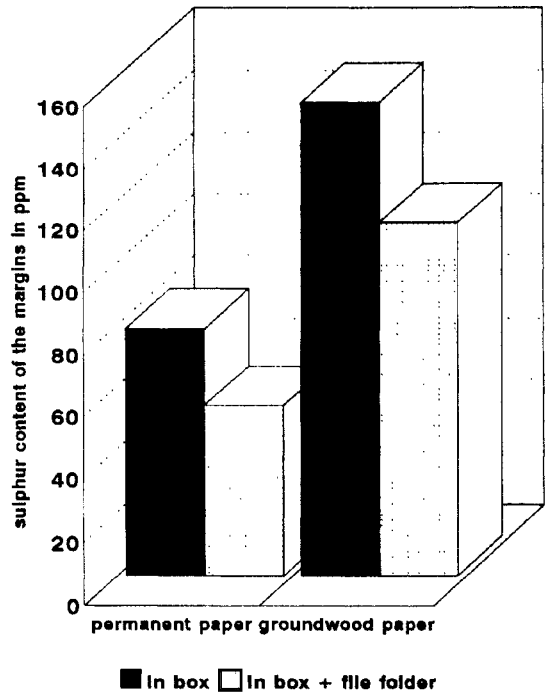

Figure 2. The absorption of SO_2 by respectively permanent paper and groundwood paper after 5 weeks exposure

A new experiment is set up with three boxes; an ordinary document storage box made of groundwood containing recycled cardboard, the "acid-free" document storage box and the alkaline document storage box. The thumb cut holes of the boxes are closed with alkaline board. Each box contains two stacks of paper, the permanent paper grade paper and the groundwood containing paper. Beside that the boxes contain two file folders, an alkaline file folder and a neutral file folder, both filled with a stack of the two test papers. Additional two stacks of the test papers without any protection are placed in the exposure chamber.

The boxes are exposed to the same concentrations of SO_2 and NO_2 as in the previous experiment. The exposure is continued for 10 weeks and a sheet of paper from the middle of each stack of paper was withdrawn from the unprotected stacks, from the exposed boxes and file folders weekly and were analyzed for sulphur content. Since the measurements are non destructive yet very indicative of the amount of penetration of the pollution they will give an insight in the process of accelerated ageing of the paper inside the boxes

Results and discussion

Measurements of the testpapers inside the boxes after exposure

After 10 weeks exposure the results were comparable with the results of the first experiment. The first sheets of the groundwood containing paper had yellowed significantly. The papers further inside the stack were yellowed only at the margins. The sulphur content of the margins of both test paper increased almost linear during the exposure. The sulphur content in the center of both papers increased only slightly.

Table 2

groundwood containing paper				
Test method	*Alkaline document storage box*		*"acid-free" document storage box*	
	before exposure	*after exposure*	*before exposure*	*after exposure*
pH	5,6		5,6	
margin		3,0		3,1
center		3,7		3,6
Sulphur content	67(10)	in ppm	67(10)	in ppm
margin		292 (14)*		249 (31)
center		71 (16)		87 (9)
bleached sulphite softwood cellulose paper				
pH	6,3		6,3	
margin		3,4		3,5
center		4,9		4,6
Sulphur content	<40	in ppm	<40 ppm	in ppm
margin		72 (12)		92 (11)
center		<40		<40
Permanent paper grade paper without optical brighteners				
pH	9,2		9,2	
margin		8,1		8,3
center		8,6		8,6
% $CaCO_3$	5,62	in %	5,62	in %
margin		5,02		4,18
center		5,34		4,66
Sulphur content	< 40ppm	in ppm	<40 ppm	in ppm
margin		130 (15)		154 (24)
center		<40		66 (18)

* *The standard deviation of the average of the sulphur content is given between brackets.*

There was almost no significant difference between the three boxes in relation to the sulphur content of both test papers. It seems that the construction of the box has a dominant effect in relation to the protection against air-pollutants. There was not much difference between the boxes with a thumb cut hole and the closed boxes

A comparison between the unprotected stack of test papers and the test papers in the document box showed that the sulphur content of the paper in the box after 5-6 weeks reaches the same level of one week exposure outside the box.

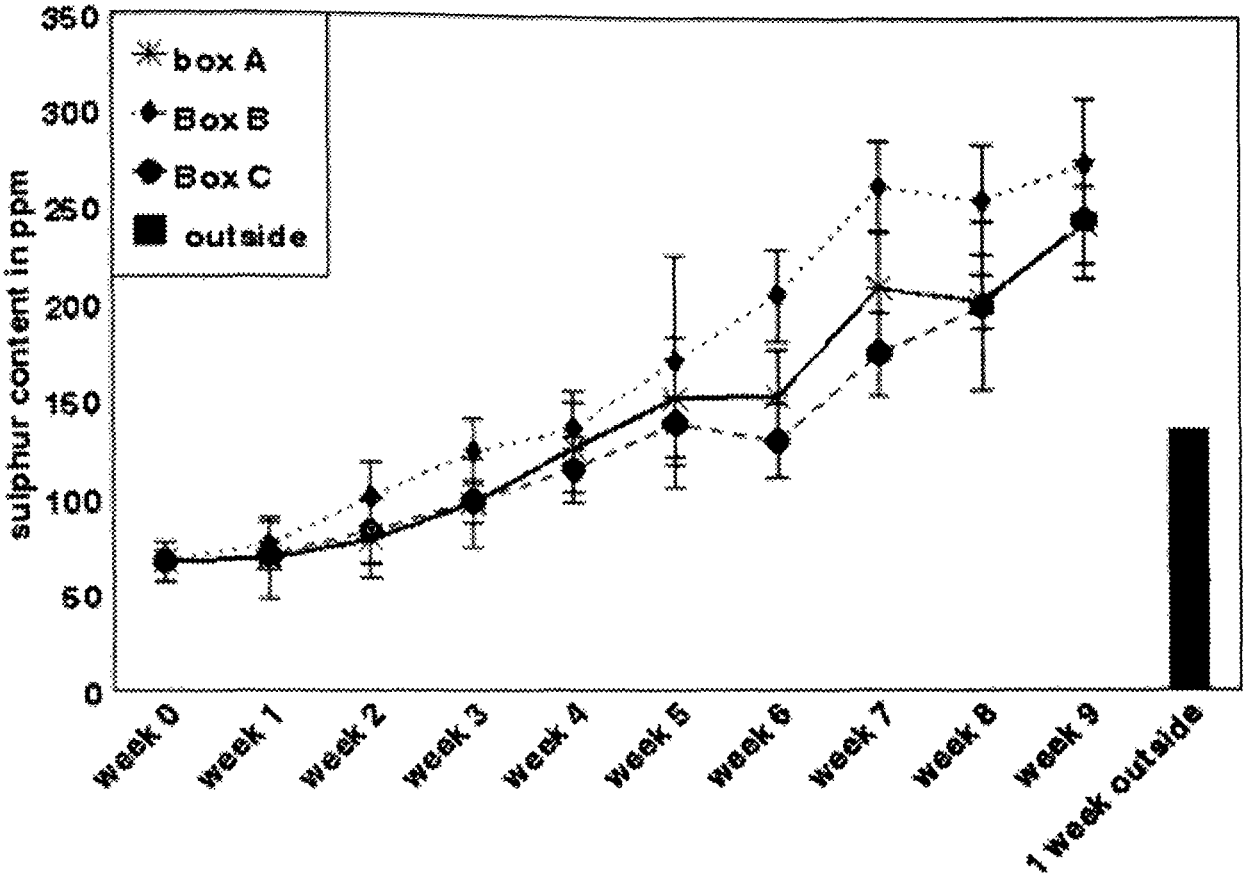

Figure 3. The sulphur content of the margins of groundwood-containing paper in three boxes. A: "acid-free" box, B: alkaline box, C: office box.

Measurements of the testpapers inside the file folders

Between the two file folders no difference in sulphur content of the test papers was analyzed. However there was a significant positive effect in relation to the stacks of paper without file folders in the box.
As in the document storage box the first pages of a stack of groundwood containing paper inside the file folder showed an even discolouration whereas deeper in the stack only the margins were yellowed.

Conclusions

The sulphur content of the margins of the paper sheets increases during exposure almost linear with the exposure time. The sulphur content in the center of the paper sheets increases more slowly.
The use of a storage box has a positive effect against the uptake of air pollutants by the documents stored inside. The level of sulphur at the margins of paper sheets after 5-6 weeks reaches the same level as paper sheets without protection of a box. To prevent the damage by air pollution the construction of the box seems to have more effect than the type of cardboard from which the box is made.
The use of file folders gives an extra protection.

Suggestions for further research

The investigation of the effectiveness of boxes made of board which contains activated carbon or zeolite is worth to be studied further. Another topic will be the investigation of the effect of alkaline boxes on the air quality inside the box in which acid documents are stored.

Acknowledgement

This research was conducted at the Central Research Laboratory for Objects of Art and Science in Amsterdam. The Dutch Ministry of Education, Culture and Science provided financial support as part of the program entitled "Verzuring Cultuurgoederen"

My special thanks goes to my colleagues, Wilma W. G. Th. Roelofs and Henk van Keulen, for their continuous support. The brainstorming sessions with Agnes Brokerhof, Rob Crèvecoeur, Raymond Heesters, Thea van Oosten and Wolter Kragt provided a multi disciplinary input. René Sinkeldam, student of the Technical College Amsterdam carried out hundreds of measurements. Without his help we could not have obtained the results in a relatively short time. The TNO Centre for Paper and Board in Delft provided us with well defined test material which was very useful.

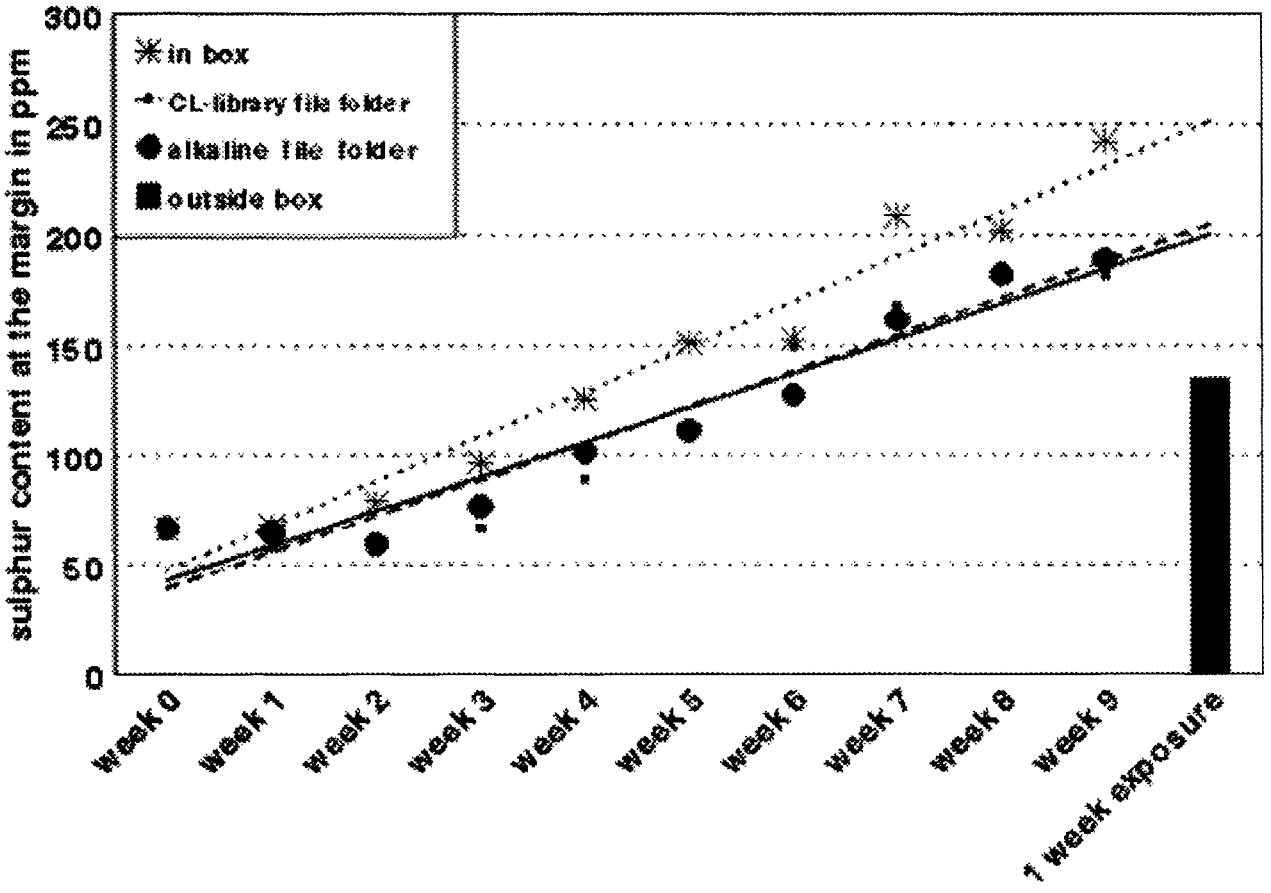

Figure 4. Protection against air pollution of the documents by a box and by two different file folders

Notes

0. Havermans, J. et al, The effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials-Paper. STEP Project CT 90-0100, Delft 1994

1. NEN 2728, Permanent houdbaar papier, Eisen en beproevingsmethoden. Nederlands Normalisatie Instituut, 1993

2. The three test papers were specially produced for the STEP Project CT 90-0100 and are decribed in the report as respectively paper-1, paper-3 and paper-5. The paper were kindly placed at our disposal by TNO Delft.

3. Although the file folder was taken from the office administration and thought to be acid an investigation into the properties showed that the file folder was made of alkaline paper.

4. The Central Laboratory has formulated a number of standard specifications for storage materials for museums and archives. CL-Kwaliteitseis no. 2 contains the specifications for an alkaline, lignin free file folder.

5. Bennett, B.G., J.G. Kretschmar, G.G. Akland, and H.W. de Koning, Urban Air pollution world wide, Enviromental Science and Technology, 19 (1985) 298-304

6. Havermans, J. et al, chapter 6.

7. Havermans, J. et al, chapter 9

8. Karreman, M.F.S., H.J. Porck, W.J.Th. Smit, J.H. Hofenk de Graaff, P. Vlasveld, De oppervlakte pH meting van papier: Een vergelijking van standaard methoden. De Restaurator 20 (1990), 5-7