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The Effect of Air Pollutants on Paper Stability

by P. BÉGIN, S. DESCHÂTELETS, D. GRATTAN, N. GURNAGUL, J. IRACI, E. KAMINSKA, D. WOODS & X. ZOU

INTRODUCTION

Literature evidence shows that acid-catalyzed hydrolysis of cellulose is the primary cause of paper embrittlement[1,2]. The sources of acidity in a sheet result mainly from the use of acidic additives (e.g. alum) during the papermaking process and from the absorption of atmospheric pollutants during natural ageing. Historical evidence indicates that atmospheric pollution can be detrimental to the integrity of books. For example, Kimberley and Emley examined a number of copies of the same books from city and country libraries[3]. They found that the paper of books kept in urban libraries contained more acid, had a higher copper number, and was more degraded than that from copies of the same edition kept in country libraries. The authors concluded that the greater deterioration was due to the absorption of sulphur dioxide (SO_2) from the atmosphere. Jarrel et al. confirmed these findings by carefully examining samples of paper taken from old books, magazines, and court records[4]. They found that portions of the paper samples that were more exposed to the air, i.e., the edges of the sheets, in general had higher acidity, a higher water-soluble sulphate content, and lower strength than the centre portions. A number of other workers in later years have come to similar conclusions[5,6,7]. More recently, a comprehensive examination of the conditions of papers in archives and libraries was conducted by Zeisler et al.[8]. Chemical analysis of 265 paper samples from 1700 to 1990 showed that the sulphate concentration of the books and archival materials was

* The following text is Part 3 of the Canadian Co-operative Permanent Paper Research Project: *The Impact of Lignin on Paper Permanence. Final Report.* Ottawa: Pulp and Paper Research Institute of Canada, Canadian Conservation Institute 1998. Some more technical data on the samples under research can be found there and, moreover, the standard deviation to any of them.

far greater than the concentration to be expected based on the measured aluminum concentration and aluminum sulphate or alum. The excess of sulphate ions could be traced primarily to the absorption of SO_2 from the air. Also, measurements of the nitrate concentration as a function of the age of the paper suggested that the nitrate content of the paper increases with the age of the samples. This can be traced to the effects of nitrogen oxides from the atmosphere.

As Jarrel noted in 1936, the examination of old books is not the ideal way to establish, with certainty, the effects of pollutants on paper permanence since the history of manufacture, and the exact conditions of use and storage, such as the degree of exposure to light, air, temperature and humidity are unknown [4]. This has led to laboratory studies using controlled, elevated concentrations of air pollutants. The air pollutants considered as the most important for paper permanence are sulphur dioxide and nitrogen oxides [9]. The published results from laboratory studies have demonstrated the effects of air pollutants on the acidification of paper [10-24]. However, some of the results are contradictory and the following key issues have not been conclusively addressed [25]:

- Effect of the absorption of air pollutants on paper permanence:
  The majority of the studies on the effects of atmospheric pollutants on paper permanence focus on the rate of absorption of SO2 and NOx into paper and its subsequent conversion into sulphite or sulphate compounds. It has often been assumed that the higher absorption of air pollutants will automatically lead to more degradation of the strength properties. However, recent results from the analysis of the mechanical properties of paper after pollution indicate that this may not be the case, particularly when the pH of the paper is in the alkaline range [23, 24]. More work is necessary to clearly establish how the absorption of air pollutants affects paper permanence.

- Role of fibre composition:
  Several workers indicate that commercial papers containing a high proportion of mechanical pulp tend to absorb more sulphur dioxide from the atmosphere [13-15, 17, 19, 22]. This has been attributed to the presence of lignin and its chemical affinity to SO_2. The absorption of SO_2 can also be affected by many other factors such as metal ion concentration, initial pH of the sheets, papermaking additives, specific surface area, and porosity of paper. On the other hand, how this higher absorption of SO_2 affects paper degradation is not clear. For example, Daniel et al. showed that acid newsprint has a larger reduction in mechanical properties than rag and fine paper after exposure to SO_2 and NO_2 [22]. However, Iversen and Kolar showed that the mechanical properties of acid-sized chemical pulp deteriorated quickly, but the mechanical properties of acid-sized wood-containing paper were unaffected by NO_2 treatment [21].

  More recently, Zeisler et al. showed that both lignin-free and lignin-containing papers suffered strength loss when exposed to high concentrations of air pollutants [23]. Therefore, more controlled experiments on pure furnishes, not containing any additives or contaminants, needed to be carried out before we could conclusively identify the role of fibre composition on the absorption of SO_2 and NO_x.

- Effectiveness of calcium carbonate:
  There is some evidence that papers containing calcium carbonate tend to absorb more sulphur dioxide, however, this work was based on a commercial paper sample and an appropriate control sample was not examined [13]. In a recent study, Daniel et al. found that papers that were deacidified and thus, had an increased alkaline reserve, absorbed more SO_2 than untreated samples [22]. This is understandable because SO_2 can preferentially react with alkaline chemicals due to its acidic nature. Therefore, the effect of SO_2 absorption on the mechanical permanence of deacidified paper cannot be directly predicted from the amount of absorbed air pollutants. In fact, the most recent work by Havermans and Zeisler et al. has indicated that an alkaline reserve may be effective in protecting paper from the negative effect of air pollutants [23, 24]. However, what is unclear is whether the alkaline reserve is equally effective in both lignin-containing and lignin-free papers and to what extent the alkaline reserve is consumed by air pollutants.

Therefore, the objective of this research project was to address the above issues and to further clarify what effect air pollutants have on the permanence of papers, particularly those containing lignin.

EXPERIMENTAL

Samples

A series of handsheets was prepared from a variety of pure pulps ranging from mechanical to rag pulps. The sheets were made with and without the presence of an alkaline reserve (2% calcium carbonate). Table 1 summarizes the different species and pulp types that were included in the handsheet study.

Four alkaline commercial paper samples were also selected for pollution and accelerated ageing using the conditions established for the handsheet experiments. Table 2 summarizes the different commercial paper samples that were examined.

Table 1: Handsheets used in the research project

Species	Pulp Type	g/m²	Moisture content (%)	cold extr. pH (0.1N NaCl)	acidity (mmols /100g)	CaCO3 (%)	Code *
Spruce	TMP	58.9	9.4	6.24	3.7		H7TS
		59.0	9.7	8.94		1.71	H9TS
	BCTMP	59.7	9.9	6.87	1.8		H7BS
		59.2	9.4	9.05		1.99	H9BS
	Bleached Kraft	60.3	7.5	6.35	0.3		H7KS
		59.8	7.0	9.47		1.91	H9KS
Aspen	BCTMP	60.8	9.0	6.65	1.5		H7BA
		58.9	9.0	9.05		1.89	H9BA
	Bleached Kraft	60.5	6.7	6.40	0.6		H7KA
		59.8	7.0	9.54		2.05	H9KA
Cotton	Rag	58.8	6.4	6.56	0.4		H7RC
		59.7	5.9	9.65		2.53	H9RC

* For the coding system cf. Ref. 2 Table 1.

Table 2: Commercial paper samples included in the research project

Sample description	g/m²	Moisture content (%)	pH*	$CaCO_3$ (%)	Code*
Alkaline fine paper: 60% softwood bleached kraft, 25% hardwood bleached kraft, 15% aspen BCTMP, 15% filler (precipitated $CaCO_3$)	72.2	6.0	9.53	13.89	C9BM
Alkaline fine paper: 85% softwood + 15% hardwood bleached kraft, 15% filler (precipitated $CaCO_3$), starch, alkyl ketene dimer sizing	70.8	6.1	9.52	10.97	C9KM
Alkaline cotton: 100% cotton, 8.5% filler (precipitated $CaCO_3$)	64.4	5.5	9.41	7.25	C9RC
Alkaline newsprint: 90% TMP + 10% bleached kraft, 7% filler (precipitated $CaCO_3$)	39.5	7.1	8.88	6.72	C9NM

* For the coding system cf. Ref. 2 Table 2.

Pollution procedure

Pollution experiments were carried out in a specially designed automated environmental chamber described elsewhere[9]. Two hundred and fifty sheets from each paper type were suspended in sheet form in the environmental chamber and exposed (one paper type at a time) to an atmosphere of 10 ppm SO_2 and 20 ppm NO_x (23°C and 50% RH). These concentrations are about two thousand

times greater than the levels that exist in indoor atmospheres. For example, based on a survey of indoor air pollutants in museums, libraries and archives[26, 27], the average ambient levels of air pollutants are about 5 ppb SO_2 and 10 ppb NO_x in indoor air, and about 50 ppb SO_2 and 200 ppb NO_x in outdoor air. Therefore, it is necessary to increase the concentration of air pollutants to study their effect on paper properties in a short period of time. The absorption rate of air pollutants by paper is linearly related to the concentration of air pollutants and a four day exposure to 10 ppm SO_2 and 20 ppm NO_x is equivalent to about 20 to 100 years of ambient levels of exposure[9]. After a four-day exposure, the samples were removed from the environmental chamber. The chamber was then evacuated to remove any traces of air pollutants. Small portions of the polluted sheets were analyzed for their SO_2 and NO_x absorption. The remaining polluted sheets were subjected to further accelerated ageing.

Accelerated ageing procedure

The accelerated ageing of the papers was carried out in controlled temperature and humidity chambers (ESPEC PRA-3GP). The samples were suspended in sheet form, in the dark, and exposed to a temperature of 80°C and a relative humidity of 65%[2]. During the accelerated ageing, specimens were removed at intervals of 5, 20, and 50 days. However, the non-buffered TMP samples were removed at 1, 5, and 12 days of ageing because of rapid degradation. After ageing, the papers were conditioned for testing according to CPPA standard A.4[28].

Analysis of physical and chemical properties

After the pollution and accelerated ageing, physical properties such as zero-span tensile strength, tear strength, stress/strain properties, folding endurance, and brightness were measured. Chemical properties such as acidity, alkaline reserve, and degree of polymerization (DP) were also determined. The relationship between the loss of mechanical properties and cellulose degradation was examined by plotting the zero-span tensile strength against the number of broken cellulose bonds. The number of broken cellulose bonds (n) is calculated as:

$$n = \frac{DP_0}{DP_t} - 1$$

where DP_0 is the initial degree of polymerization, and DP_t is the degree of polymerization at time *t*.

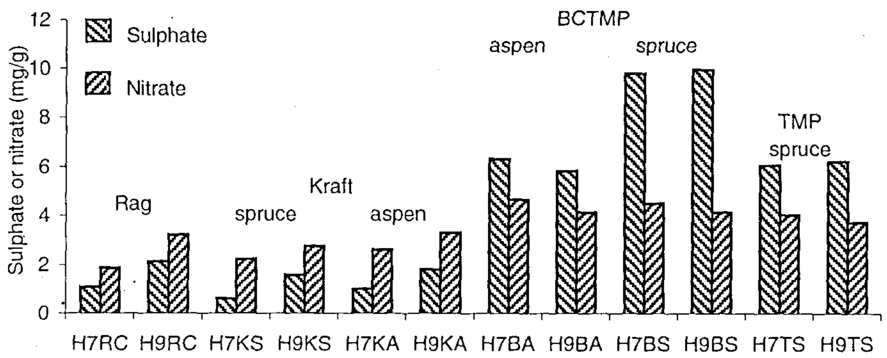

Fig. 1: Absorption of SO_2 and NO_x by buffered (2% $CaCO_3$) and non-buffered handsheets

In addition, the sulphate and nitrate contents of the samples after pollution were analyzed to get an indication of the SO_2 and NO_x absorption by the paper. Descriptions of the testing methods can be found elsewhere [9].

RESULTS AND DISCUSSION

Absorption of SO_2 and NO_x by paper

After a four day exposure to 10 ppm SO_2 and 20 ppm NO_x, the sulphate and nitrate contents of the papers were analyzed to get an indication of the amount of SO_2 and NO_x absorbed by the various papers. The results are given in Tables 3 to 5. The gain in the sulphate and nitrate content (the difference after and before pollution) was calculated and the results are shown in Fig. 1 and 2. It becomes clear that sheets from mechanical pulps (spruce TMP, spruce BCTMP, and aspen BCTMP) absorbed significantly more SO_2 and NO_x than lignin-free sheets (spruce bleached kraft, aspen bleached kraft, and rag). The mechanical pulp handsheets also absorbed more SO_2 than NO_x while sheets from chemical pulps and rag absorbed more NO_x than SO_2. Correspondingly, the pH of non-buffered sheets was substantially lowered and the total acidity was significantly increased (Table 3). We found that the higher the absorption of air pollutants, the greater the increase in total acidity.

In the case of handsheets buffered with 2% calcium carbonate ($CaCO_3$), the absorption of both SO_2 and NO_x by lignin-free sheets was increased by the presence of the alkaline buffer while for the lignin-containing sheets it remains essentially unchanged. With a 2% $CaCO_3$ addition, the mechanical pulp sheets still absorbed more SO_2 and NO_x than lignin-free sheets. The results from the four alkaline commercial papers (Fig. 2) showed the same pattern as the handsheets

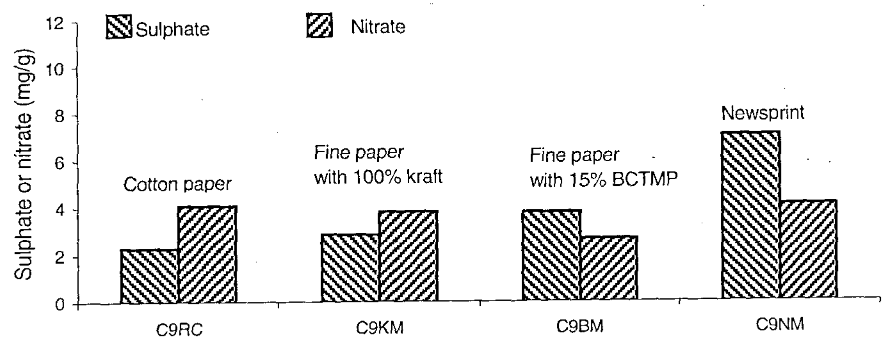

Fig. 2: Absorption of SO_2 and NO_x by alkaline commercial papers

buffered with 2% $CaCO_3$. For the handsheets and commercial papers tested, the amount of alkaline reserve consumed was 0.33 to 0.89% for the lignin-free and low-lignin (15% BCTMP fine paper) samples and 0.71 to 0.93% for the lignin-containing (23 to 27% lignin content) samples. On average, the consumption of alkaline reserve was slightly higher for the high-lignin content papers. In the case of commercial papers, there is still a significant amount of alkaline reserve left due to their higher initial calcium carbonate content.

The above results confirm the previous findings reported in the literature, i.e., lignin-containing and alkaline sheets absorb more air pollutants than non-buffered lignin-free sheets [14, 23]. However, the key question is what kind of impact do the absorbed air pollutants have on paper degradation.

Impact of absorbed air pollutants on the properties of polluted papers and artificially aged polluted papers

The effects of pollution and accelerated ageing on paper degradation were compared by the procedure shown in Fig. 3, that is, determining properties of

- untreated paper,
- paper aged for 50 days,
- paper polluted for 4 days, and
- paper polluted for 4 days and then aged for 50 days.

Fig. 4 shows the zero-span tensile strength and DP values after each treatment for rag, aspen an spruce bleached kraft, aspen and spruce BCTMP, and spruce TMP. The non-buffered handsheets were compared with those buffered with 2% $CaCO_3$.

Non-buffered handsheets (Table 3)

- *After exposure to air pollutants:* Results in Fig. 4 show that rag, bleached kraft, and TMP sheets suffered a significant loss of fibre strength, as measured by zero-span tensile strength while BCTMP sheets had a good retention of

Table 3: Properties of neutral (non-buffered) handsheets before and after pollution

Samples	H7RC	polluted	H7KS	polluted	H7KA	polluted	H7BA	polluted	H7BS	polluted	H7TS	polluted
Cold extraction pH*	6,56	3,63	6,35	3,48	6,40	3,41	6,65	3,53	6,87	3,51	6,24	3,00
Moisture content (%)	6,4	5,9	7,5	7,1	6,7	6,5	9,0	7,7	9,9	9,0	9,4	8,9
Total acidity**	0,4	4,0	0,3	5,5	0,6	7,3	1,5	19,5	1,8	24,0	3,7	24,5
Sulphate content (mg/g)	0,10	1,20	0,37	0,99	0,40	1,40	0,20	6,50	0,20	10,00	0,26	6,30
Nitrate content (mg/g)	0,13	2,00	0,10	2,34	0,08	2,70	0,17	4,80	0,16	4,64	0,18	4,20
Degree of polymerization	1932	279	2361	596	1964	663	1985	1394	1247	1088	1240	210
Number of broken bonds***		5,89		2,93		1,97		0,24		0,15		4,90
Tear index (mNm^2/g)	21,7	5,9	27,7	5,9	5,8	3,2	3,4	3,3	9,0	8,3	8,8	3,4
Breaking length (km)	3,72	3,30	4,30	3,25	4,05	3,34	3,51	3,54	4,70	4,64	4,90	3,25
Stretch (%)	2,8	1,8	3,0	1,9	2,1	1,4	1,1	1,3	2,1	2,1	2,2	1,0
TEA (mJ/g)	871	420	967	440	630	343	242	295	660	652	691	192
Zero-span tensile strength (km)	15,3	8,5	15,9	7,4	13,7	7,2	11,9	11,1	12,4	11,4	11,7	5,5
Folding endurance****	2897	35	2516	23	23	6	10	10	471	369	908	1
Brightness (%)	85,3	82,6	85,7	86,9	83,5	84,3	81,0	65,2	71,9	55,8	55,6	36,4

* 0 .1N NaCl
** mmole /100g
*** $DP_0 \times (1/Dp_{poll.} - 1/DP_0)$
**** double folds at 0.5kg

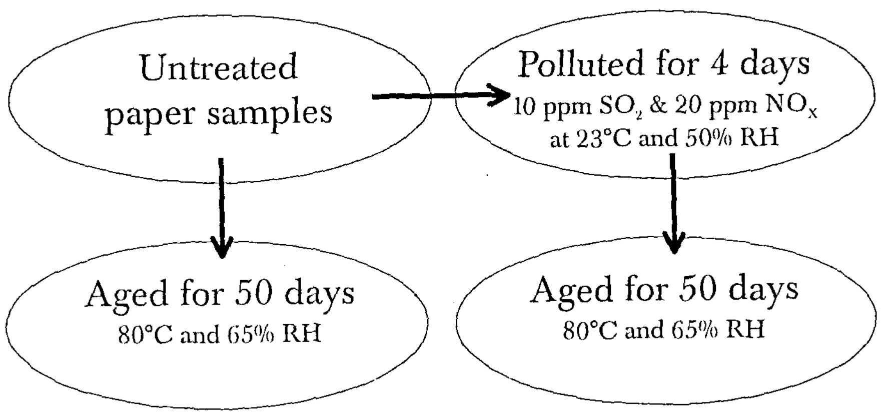

Fig. 3: Treatment used for comparing the effect of pollution and accelerated ageing

zero-span tensile strength. Other mechanical properties such as tear index and TEA followed similar trends. The DP results in Fig. 4 show a significant degradation of cellulose for rag, bleached kraft, and TMP sheets and less cellulose degradation for the BCTMP sheets. Therefore, the loss of mechanical properties is consistent with the DP results. These results indicate that there is no correlation between the amount of SO_2 and NO_X absorbed and paper degradation. For example, even though BCTMP sheets absorbed more air pollutants than the bleached kraft and rag sheets, they suffered less degradation in mechanical properties and DP before accelerated aging. In terms of optical properties, mechanical pulp sheets had a significant loss of brightness after pollution. This brightness drop is mainly due to the effect of NO_x, because NO_x is a strong oxidant and reacts with lignin.

- *After pollution and accelerated ageing:* Although the non-buffered BCTMP handsheets suffered less degradation after exposure to the air pollutants than the other non-buffered handsheets, they showed considerable degradation after accelerated ageing. The overall loss of properties after pollution and accelerated ageing was significant for all of the non-buffered handsheets (Fig. 4). This is because the exposure of the non-buffered sheets to the air pollutants

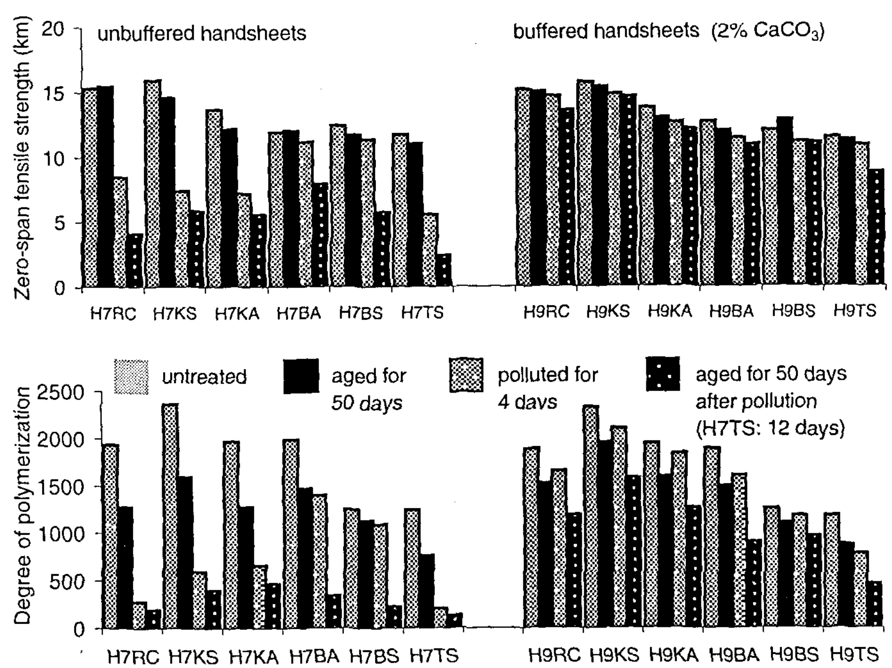

Fig. 4: Zero-span tensile strength and degree of polymerization after different treatments

Table 4: Properties of alkaline handsheets (buffered with 2 % $CaCO_3$) before and after pollution

Samples	H9RC	H9RC polluted	H9KS	H9KS polluted	H9KA	H9KA polluted	H9BA	H9BA polluted	H9BS	H9BS polluted	H9TS	H9TS polluted
Cold extraction pH*	9,65	9,02	9,47	9,33	9,54	9,24	9,05	8,49	9,05	8,34	8,94	8,02
Moisture content (%)	5,9	6,5	7,0	7,4	7,0	7,1	9,0	7,8	9,4	9,2	9,7	8,6
Alkaline reserve**	2,53	1,64	1,91	1,48	2,05	1,53	1,89	1,14	1,99	1,06	1,71	0,98
Sulphate content (mg/g)	0,20	2,32	0,34	1,92	0,42	2,23	0,20	6,00	0,14	10,10	0,11	6,30
Nitrate content (mg/g)	0,10	3,32	0,10	2,84	0,10	3,39	0,19	4,30	0,15	4,27	0,20	3,90
Degree of polymerization	1882	1648	2324	2097	1937	1830	1882	1605	1253	1179	1184	783
Number of broken bonds***		0,14		0,11		0,06		0,17		0,06		0,51
Tear index (mNm^2/g)	22,2	21,1	24,8	24,4	5,3	5,6	3,1	3,7	8,4	7,9	8,6	7,6
Breaking length (km)	3,67	3,65	3,66	3,5	3,46	3,25	2,90	3,30	4,67	4,46	4,33	4,59
Stretch (%)	2,5	2,7	2,5	2,6	1,6	1,6	0,9	1,1	2,1	1,9	2,0	2,1
TEA (mJ/g)	769	787	690	687	398	362	158	238	651	576	574	621
Zero-span tensile strength (km)	15,2	14,6	15,7	14,8	13,7	12,6	12,7	11,4	12	11,1	11,5	10,9
Folding endurance****	1866	2414	791	1178	19	17	6	8	636	506	538	342
Brightness (%)	86,1	85,1	87,5	85,3	85,3	83,6	78,4	60,4	73,8	53,2	55,0	41,9

* 0 .1N NaCl　　** % $CaCO_3$

*** $DP_0 \times (1/Dp_{poll.} - 1/DP_0)$　　**** double folds at 0.5kg

resulted in lowered pHs (between 3.0 and 3.6) after pollution. The TMP sheets, with the lowest pH (3.0) had the largest loss of strength properties. Once again, the DP changes shown in Fig. 4 are consistent with the loss in mechanical properties. In terms of optical properties, all samples, including lignin-containing and lignin-free, showed a significant brightness drop with accelerated ageing (Table 7). This may be due to the combined oxidative effect of NO_x and the thermal effect during accelerated ageing.

Handsheets buffered with 2% CaCO3 (Table 4)

- After exposure to air pollutants: Handsheets buffered with 2% $CaCO_3$ (Fig. 4) showed significantly improved ageing resistance to air pollutants even though some of them absorbed more SO_2 and NO_x (Fig. 1). This indicates that $CaCO_3$ preferentially reacts with air pollutants thus protecting cellulose from direct attack from these pollutants. As with the non-buffered handsheets, the mechanical pulp sheets had a significant loss of brightness after pollution (Fig. 5).
- After polution and accelerated ageing: After accelerated ageing, the alkaline handsheets showed a smaller reduction in zero-span tensile strength and DP than the non-buffered handsheets. The alkaline handsheets also showed better brightness retention than the non-buffered handsheets after accelerated ageing.

Alkaline commercial papers (Table 5)

Results for the alkaline commercial paper samples confirmed those obtained for the handsheets buffered with 2% $CaCO_3$, i.e., an alkaline reserve reduces the

Table 5: Properties of commercial papers before and after pollution

Samples	C9RC	C9RC polluted	C9KM	C9KM polluted	C9BM	C9BM polluted	C9NM	C9NM polluted
Cold extraction pH*	9,41	9,27	9,52	9,24	9,53	9,28	8,88	8,44
Moisture content (%)	5,5	6,1	6,1	6,9	6	6,9	7,1	7,6
Alkalin reserve**	7,25	6,92	10,97	10,18	13,89	13,30	6,72	6,01
Sulphate content (mg/g)	0,12	2,40	0,06	2,90	0,03	3,80	0,10	7,10
Nitrate content (mg/g)	0,15	4,20	0,12	3,90	0,07	2,70	0,14	4,20
Degree of polymerization	1606	1493	1262	1213	1824	1732	1728	1474
Number of broken bonds***		0,08		0,04		0,05		0,16
Tear index (mNm^2/g)	8,8	9,0	6,1	5,8	7,6	7,5	5,5	5,6
Breaking length (km)	6,94	7,08	8,37	8,17	6,53	6,32	6,91	6,80
Stretch (%)	2,6	3,1	2,2	2,3	1,5	1,6	1,1	1,3
TEA (mJ/g)	1272	1482	1175	1209	622	671	488	528
Zero-span tensile strength (km)	15,1	14,7	15,4	14,6	15,7	15,2	15,9	15,5
Folding endurance****	3797	3929	996	1112	680	716	1070	925
Brightness (%)	79,1	77,2	85,2	82,6	83,1	74,2	70,9	52,5

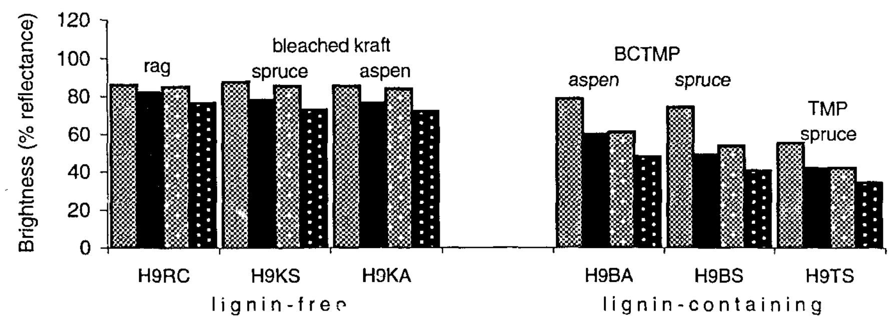

Fig. 5: Changes in brightness after different treatments (alkaline handsheets). For legend cf. Fig. 4,6,9

negative effect of air pollutants and decreases the rate of degradation of polluted samples during accelerated ageing (Fig. 6 and 7). The mechanical properties shown were measured in the machine direction. The newsprint sample showed a larger loss in brightness than the other three commercial paper samples (Fig. 8).

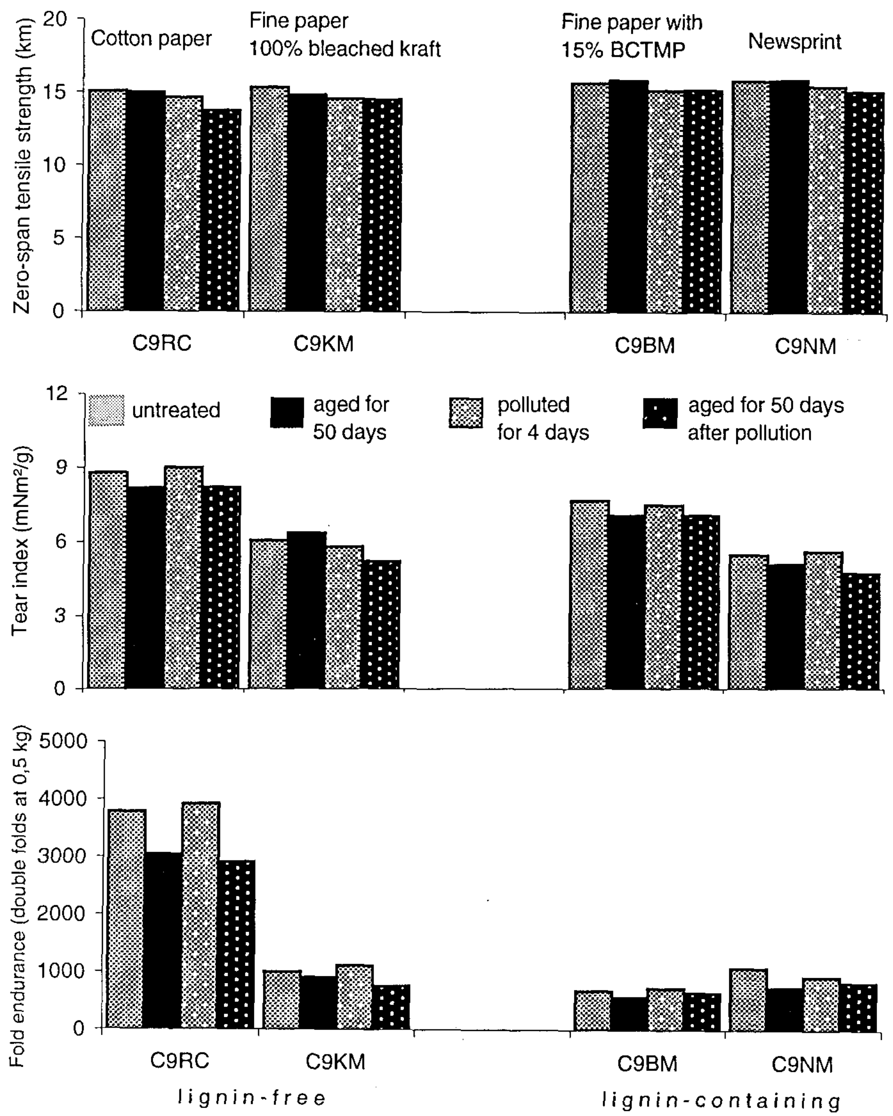

Fig. 6: Changes in mechanical strength properties of alkaline commercial papers after different treatments

Effect of lignin

Polluted alkaline handsheets

In order to isolate the effect of lignin, the stabilities of the six pulps, including lignin-containing and lignin-free, were examined in the alkaline pH range. The non-buffered handsheets contain a large amount of acid after pollution treatment and therefore are easily degraded with further accelerated ageing. Since the mechanical properties of the alkaline sheets are only slightly affected by exposure to the air pollutants, the effect of lignin is studied by comparing the ageing stability after pollution.

The bar graphs for zero-span tensile strength and tear strength (Fig. 9) show a similar stability for rag, bleached kraft, and BCTMP sheets, regardless of species and presence of lignin. TMP handsheets showed a somewhat higher loss of these properties in this experiment. This is similar to results obtained for the unpolluted samples. The larger loss of properties for the TMP handsheets may be

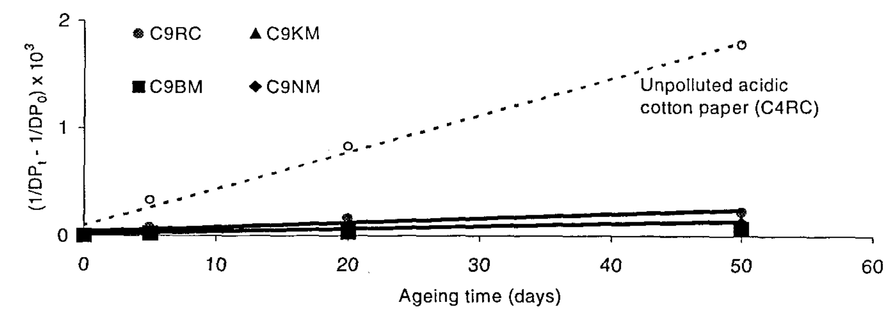

Fig. 7: $(1/DP_t - 1/DP_0)$ versus ageing time of buffered and polluted commercial papers

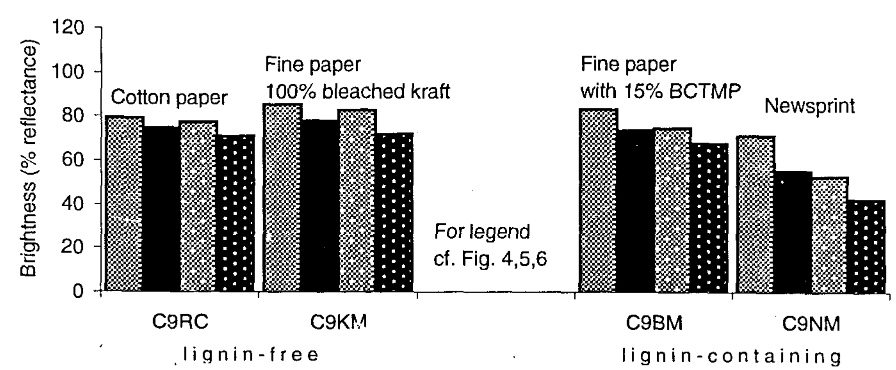

Fig. 8: Changes in brightness of alkaline commercial papers after different treatments

caused by a non-uniform distribution of calcium carbonate within the sheets as explained elsewhere (Ref. 2 p. 148–150).

The plots of ($1/DP_t$ - $1/DP_0$) against aging time (cf. Ref. 2 p. 143) show that with the exception of the TMP sheets, all of the alkaline sheets display a similar rate of cellulose degradation (Fig. 10). However, all of the polluted alkaline

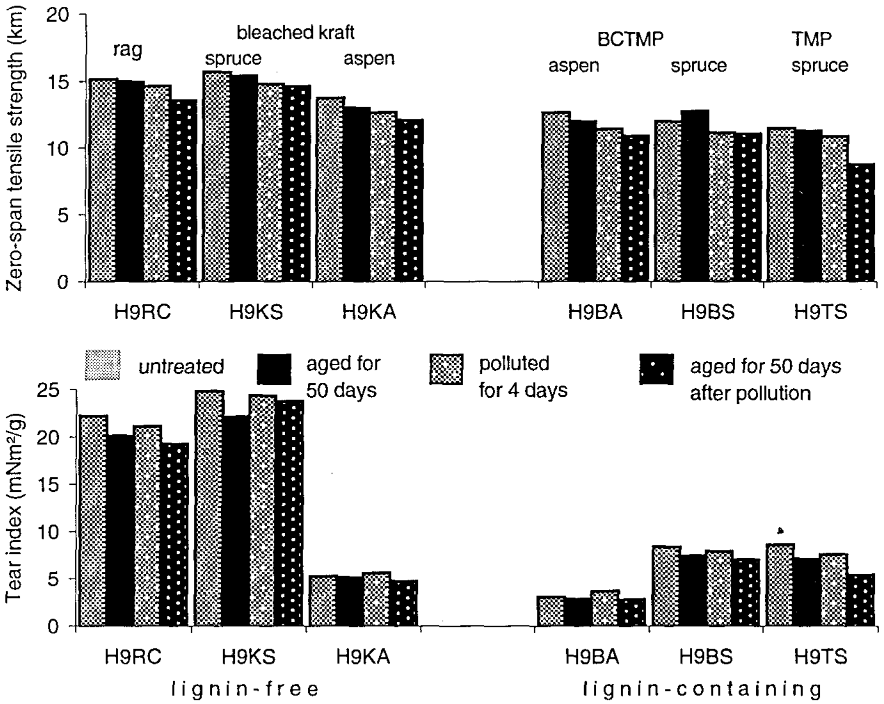

Fig. 9: Changes in mechanical strength properties of alkaline handsheets after different treatments

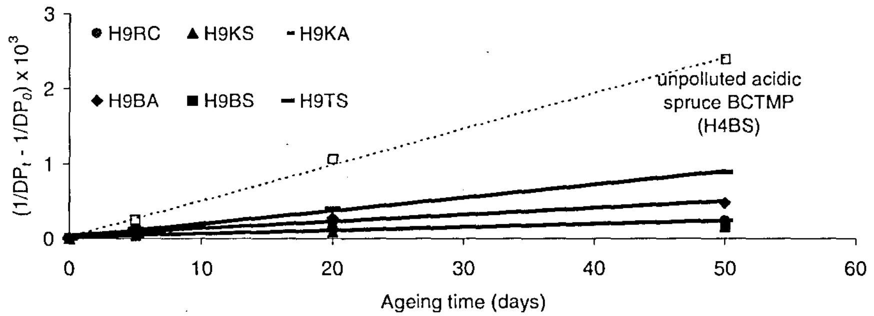

Fig. 10: ($1/DP_t - 1/DP_0$) versus ageing time for polluted buffered handsheets

handsheets have a lower degradation rate than the unpolluted acidic handsheets as shown by the slope of the acidic spruce BCTMP sample (H4BS). This is in agreement with the results from the mechanical properties (Fig. 9).

The plots of zero-span tensile strength versus the number of broken bonds n for spruce bleached kraft pulp and spruce BCTMP are shown in Fig. 11. It should be noted that these data are from acidic (with alum addition), neutral (non-buffered), and alkaline (buffered) sheets with different treatments (ageing, pollution, and pollution plus ageing). All of the data points fall on the same line, indicating that the loss of zero-span tensile strength is directly related to the cellulose bondbreakage for the same pulp, regardless of the treatments. The similar trend for lignin-containing and lignin-free sheets also indicates that the loss of fibre strength as measured by zero-span tensile is related to the cellulose depolymerization regardless of the presence or absence of lignin.

The lignin-free handsheets show a good retention of brightness after pollution while the lignin-containing handsheets show a significant loss after exposure to the air pollutants (Fig. 5). Further loss in brightness from accelerated ageing was similar for both lignin-free and lignin-containing handsheets.

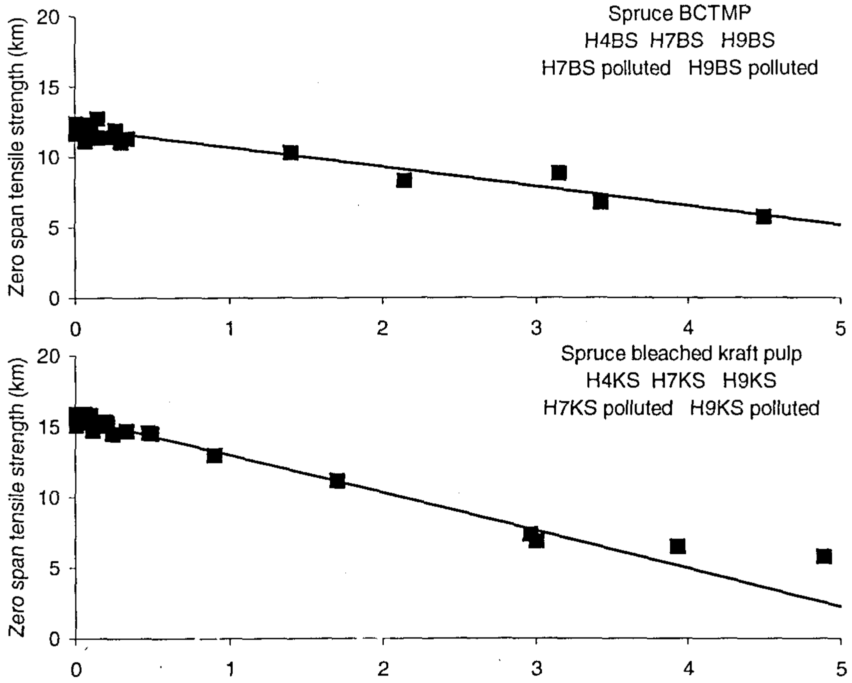

Fig.11: Relationship between zero-span tensile strength and number of broken cellulose bonds

Table 6: Testing data, part I

	Zero span breaking length (km)				Tear index (mNm2/g)				TEA index (mJ/g)			
	unpolluted		polluted		unpolluted		polluted		unpolluted		polluted	
ageing (days):	0	50	0	50*	0	50	0	50*	0	50	0	50*
H7RC	15,30	15,43	8,47	4,09	21,67	19,29	5,87	1,83	871	874	424	82
H7KS	15,94	14,56	7,38	5,83	27,71	22,61	5,90	1,76	967	801	440	131
H7KA	13,65	12,16	7,20	5,55	5,77	5,20	3,24	2,68	630	496	343	147
H7BA	11,87	12,00	11,13	7,93	3,39	3,09	3,32	2,13	242	233	295	220
H7BS	12,38	11,63	11,37	5,75	8,97	7,95	8,26	2,26	660	568	652	204
H7TS	11,72	11,03	5,53	2,38	8,82	5,98	3,43	0,68	692	543	192	30
H9RC	15,15	15,00	14,64	13,55	22,18	20,13	21,09	19,21	769	670	787	780
H9KS	15,71	15,41	14,81	14,59	24,78	22,12	24,36	23,75	690	556	687	553
H9KA	13,73	12,97	12,64	12,09	5,28	5,14	5,62	4,77	398	360	362	293
H9BA	12,67	12,01	11,42	10,92	3,07	2,91	3,67	2,81	158	143	238	227
H9BS	11,98	12,76	11,13	11,05	8,38	7,44	7,89	7,06	651	631	576	611
H9TS	11,46	11,28	10,86	8,78	8,61	7,11	7,58	5,42	574	413	621	423
C9RC	15,08	15,00	14,67	13,77	8,78	8,16	9,00	8,19	1272	1187	1482	1268
C9KM	15,37	14,82	14,58	14,55	6,05	6,35	5,80	5,21	1175	858	1209	1110
C9BM	15,69	15,89	15,17	15,23	7,64	7,05	7,46	7,06	622	569	671	572
C9NM	15,86	15,94	15,50	15,15	5,46	5,08	5,60	4,70	488	436	528	474

Table 7: Testing data , part II

	MIT Fold Number (500g)				DP				Brightness (%)			
	unpolluted		polluted		unpolluted		polluted		unpolluted		polluted	
ageing(days):	0	50	0	50*	0	50	0	50*	0	50	0	50*
H7RC	2897	1450	35	1	1932	1277	279	197	85,26	77,94	82,57	34,07
H7KS	2516	1528	23	1	2361	1588	596	401	85,69	73,71	86,91	46,53
H7KA	23	28	6	2	1964	1276	663	466	83,45	71,04	84,30	39,77
H7BA	10	9	10	2	1985	1468	1394	342	80,99	58,37	65,19	43,23
H7BS	471	259	369	1	1247	1133	1088	227	71,94	45,86	55,84	31,04
H7TS	908	200	1	0	1240	765	210	136	55,56	39,79	36,41	31,19
H9RC	1866	1541	2414	1693	1882	1522	1648	1188	86,08	81,84	85,09	76,29
H9KS	791	694	1178	503	2324	1949	2097	1578	87,47	77,89	85,30	72,57
H9KA	19	10	17	16	1937	1591	1830	1263	85,25	76,43	83,56	71,65
H9BA	6	5	8	6	1882	1488	1605	905	78,37	59,38	60,37	47,56
H9BS	636	453	506	285	1253	1100	1179	969	73,76	48,55	53,19	40,32
H9TS	538	256	342	46	1184	879	783	461	54,95	41,69	41,93	34,46
C9RC	3797	3050	3929	2911	1606	1337	1493	1119	79,12	74,78	77,20	70,79
C9KM	996	894	1112	749	1262	1227	1213	1135	85,17	77,72	82,57	71,66
C9BM	680	563	716	639	1824	1764	1732	1545	83,11	73,58	74,24	67,43
C9NM	1070	733	925	815	1728	1464	1474	1239	70,89	55,24	52,52	42,24

* 12 days for H7TS

Table 8: Changes in DP and zero-span tensile strength of polluted paper samples during accelerated ageing

		Degree of polymerization				Zero-span tensile strength (km)			
ageing (days):		0	5	20	50	0	5	20	50
Handsheets: (polluted)	H7KS	596	590	479	401	7,38	6,89	6,52	5,83
	H7BS	1088	397	282	227	11,37	8,35	6,75	5,75
	H9RC	1648	1489	1352	1188	14,64	14,77	14,06	13,55
	H9KS	2097	1930	1752	1578	14,81	15,08	14,75	14,59
	H9KA	1830	1717	1527	1263	12,64	12,90	12,66	12,09
	H9BA	1605	1343	1109	905	11,42	11,76	11,21	10,92
	H9BS	1179	1040	998	969	11,13	11,42	11,91	11,05
	H9TS	783	711	595	461	10,86	10,53	9,99	8,78
Commercial papers: (polluted)	C9RC	1493	1345	1209	1119	14,67	14,22	14,84	13,77
	C9KM	1213	1194	1169	1135	14,58	14,65	14,20	14,55
	C9BM	1732	1677	1639	1545	15,17	14,93	14,81	15,23
	C9NM	1474	1405	1315	1239	15,50	15,29	15,25	15,15

Polluted alkaline commercial papers

Four alkaline commercial papers including cotton fine paper (C9RC), fine paper with 100% bleached kraft (C9KM), fine paper with 15% BCTMP (C9BM), and newsprint with 90% TMP (C9NM), were selected for pollution and accelerated ageing experiments. The changes in mechanical properties including zero-span tensile strength, tear index and fold endurance (Fig.6; all measured in the machine direction), as well as the rate of bond breakage (Fig. 7) showed that all four alkaline commercial papers display good stability after accelerated ageing, exposure to air pollutants, and accelerated ageing of polluted samples. These results confirm the handsheet results, that is, an alkaline reserve is very effective in reducing the negative impact of air pollutants for both lignin-containing and lignin-free sheets.

The alkaline newsprint is quite stable even though it is composed largely of TMP (90%). The difference in the ageing stability of TMP handsheets and newsprint may be due to the difference in the amount of alkaline reserve (1.7% versus 6.7%). As pointed out earlier, with a 2% $CaCO_3$ addition, a non-uniform distribution of $CaCO_3$ may cause problems in protecting paper from ageing and air pollutants. Therefore, a larger amount of alkaline reserve may be needed for TMP sheets in order to improve their stability and reduce the negative effect of air pollutants.

The effect of accelerated ageing of polluted commercial papers on brightness also gives results that are similar to the ones for the handsheets (Fig. 8). There was a larger brightness loss for the lignin-containing papers with most of the loss occurring during the exposure to the pollutant gases.

CONCLUSIONS

The Canadian Co-operative Permanent Paper Research Project examined the effect of air pollutants (a four-day exposure to 10 ppm SO_2 and 20 ppm NO_x) on the ageing behavior of handsheets prepared from six pulp types and four alkaline commercial papers. The pollution results confirmed that sheets from mechanical pulps absorb more air pollutants and lose more brightness than the lignin-free sheets. The absorption of air pollutants causes a significant acidification of all the non-buffered sheets regardless of the presence of lignin. Subsequently, this causes a significant loss of both mechanical properties and cellulose DP. However, no clear correlation was found between the amount of SO_2 and NO_x absorbed and paper degradation. The addition of calcium carbonate as a buffering compound is a very effective way of reducing the negative effect of air pollutants on ageing stability of lignin-containing and lignin-free papers.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Mechanisms by which air pollutants degrade paper:
New and intriguing results on the effects of air pollutants have been obtained from this study. For example, exposure to high levels of air pollutants causes not only the acidification of paper, but also the direct degradation of cellulose. In addition, no correlation was found between the amount of air pollutant absorbed and degradation of physical and chemical properties of paper. Further work is needed to learn more about the complex degradation mechanisms of paper exposed to air pollutants.

2. Amount of alkaline reserve required to minimize paper degradation:
The results indicate that for some paper types, an amount of alkaline reserve larger than 2% may be needed to minimize the paper degradation caused by accelerated aging and air pollutants. Therefore, further research is desirable to study the effects of the amount of alkaline reserve on the permanence of paper.

3. Optical permanence of paper:
This study focused on the thermal aging stability of paper. It did not examine the effect of exposure of various types of both lignin-free and lignin-containing alkaline papers to light. Not enough is known about the optical stability of buffered

lignin-containing papers. More research is needed to determine what changes in optical properties of the "permanent" papers can be expected, what causes them, and how they could be reduced.

SUMMARIES

The Effect of Air Pollutants on Paper Stability

The Canadian Co-operative Permanent Paper Research examined, besides others, the impact of air pollutants on the permanence of handsheets from six pulp types and four alkaline commercial papers. The pollution results confirm that sheets from mechanical pulps absorb more air pollutants and show a greater brightness loss than lignin-free sheets. However, this does not necessarily result in greater deterioration of strength properties. A four-day exposure to 10 ppm SO_2 and 20 ppm NO_x causes a significant acidification and degradation of all papers containing no alkaline reserve. The addition of calcium carbonate as an alkaline reserve is very effective in reducing the negative effect of air pollutants on both lignin-containing and lignin-free sheets.

L'influence de la pollution atmosphérique sur la stabilité du papier

Le projet canadien de coopération de recherche relatif à la stabilité du papier a étudié entre autres l'influence de la pollution atmosphérique sur la résistance des échantillons de laboratoire de six types différents de fibres brutes et de quatre sortes de papier alcalin en vente dans le commerce. Les résultats obtenus par cette étude confirment que les feuilles de papier à base de pâte mécanique absorbaient davantage d'éléments polluants contenus dans l'atmosphère et qu'ils jaunissaient beaucoup plus que les feuilles de papier ne contenant pas de lignin. Ceci n'entraîne cependant pas nécessairement une détérioration plus forte de la solidité du papier. Lorsqu'on expose du papier pendant quatre jours à une atmosphère qui contient 10 ppm SO_2 et 20ppm NO_x, ceci provoque une acidification significative et une dégradation de tous les papiers dépourvus de réserve alcaline. L'addition de carbonate de calcium, comme réserve alcaline, exerce une action très efficace pour réduire les effets négatifs des substances qui constituent la pollution atmosphérique, tant sur les papiers contenants de la lignin que sur ceux n'en contenant pas.

Der Einfluß der Luftverschmutzung auf die Festigkeit von Papier

Das Kanadische Gemeinschaftsforschungsprojekt über dauerhaftes Papier untersuchte unter anderem den Einfluß der Luftverschmutzung auf die Dauerhaftigkeit von Laborproben aus sechs verschiedenen Faserrohstoffen und von vier im Handel erhältliche Papieren. Die Messungen an den Proben, die einer Verschmutzung ausgesetzt waren, bestätigen, daß holzstoffhaltige Papiere mehr Schadstoffe aus der Luft aufnehmen und stärker vergilben als holzfreies Papier. Das bedeutet jedoch nicht notwendig einen stärkeren Rückgang der Festigkeitswerte. Wenn man Papier vier Tage lang einer Atmosphäre aussetzt, die 10 ppm SO_2 und 20 ppm NO_x enthält, hat das eine

deutliche Versäuerung und einen Abbau aller Papiere zur Folge, die keine alkalische Reserve enthalten. Der Füllstoff Calciumcarbonat als alkalische Reserve reduziert sehr wirkungsvoll den negativen Einfluß der Stoffe, welche die Luftverschmutzung ausmachen, sowohl von holzhaltigen als auch von holzfreien Papieren.

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A Quantitative Measure of Borane Tert-Butylamine Complex Effectiveness in Carbonyl Reduction of Aged Papers

by MARINA BICCHIERI, MARCO BELLA & FRANCESCA SEMETILLI

Introduction

Acidity and oxidation play a very important role in paper conservation and restoration. Deacidification is a widely used method to remove acidity on aged papers.

It is important to stress that deacidification cannot be used if a large amount of carbonyl groups is present in the papers. Aldehyde or ketone groups indeed promote an alkali catalyzed β-alkoxy elimination mechanism, leading to cellulose degradation. A reduction treatment, able to reduce carbonyl groups back to alcohol groups, should be carried out, before submitting highly oxidized papers to deacidification, in order to avoid the breaking of the anhydroglucose ring in the cellulose chain. Because of the high costs of restoration procedures, it is essential to determine whether the reduction treatment is a primary need.

In the last few years borane tert-butylamine complex (TBAB) has been used in the laboratories of the Istituto Centrale per la Patologia del Libro (I.C.P.L.), Rome, as a mild reagent in reducing carbonyl groups in oxidized paper [1,2]. TBAB exerts no activity on carboxylic groups*, but is able to reduce carbonyl groups. The goal of our experimental work is to provide a simple method for the determination of these groups and to test the effectiveness of TBAB over time.

Unfortunately there is no standard method (like, for example, those used for carboxyl) for the determination of carbonyl functions in paper and, furthermore, a measure of the exact carbonyl content in aged or unaged papers is not easy to obtain. Although several methods have been reported in literature, they usually lack in complete reproducibility of measures [3,4]. Direct measure in UV-visible of carbonyl groups is impossible, due to the low molar absorptivity ε of C=O and

* It is well known that TBAB shows no activity on carboxylic groups; in fact carboxylic acids such as Fumaric and Salicylic in a 0.2 M solution of TBAB were recovered quantitatively unreacted after 3 hours.

to the insolubility of the cellulose. Blair and Cromie [5] reported the determination of carbonyl groups in Cadoxen solution of cellulose, *via* 4-nitrophenylhydrazine derivatization, but the time required for the application of this method is not suitable for a routine control.

We applied the method of Szablocs [6], with some experimental modifications; it gave reproducible results and was very easy to employ. We detected the carbonyl amount in artificially aged Whatman paper n°1 for chromatography, KIO_4 oxidized paper and KIO_4 oxidized TBAB reduced paper. Work about further characterizations of TBAB reduced papers by Raman spectroscopy, ^{1}H- and ^{13}C-NMR is in progress.

Experimental

Materials

- Whatman n° 1 for chromatography paper (pure cotton cellulose)
- Potassium metaperiodate (KIO_4) 0.015M aqueous solution
- Borane tert-butylamine complex (TBAB) 0.2M aqueous solution
- D(+) glucose 0.1% w/v aqueous solution
- Potassium hydroxide (KOH) 0.2M aqueous solution
- 2,3,5-triphenyl-2Htetrazolium chloride (TTC) 0.2% w/v aqueous solution
- Hydrochloric acid (HCl) 1M aqueous solution.

Preparation of samples and treatments:

Three sets of samples were prepared:

- untreated Whatman n°1 for chromatography paper
- oxidized Whatman n°1 for chromatography paper
- oxidized-reduced Whatman n°1 for chromatography paper.

Samples were oxidized by immersion in KIO_4 for 15 minutes, followed by single immersion in distilled water for 15 minutes. Reduction treatments for this set of samples were carried out two days after oxidation by immersion in TBAB for 60'. Papers were then washed twice with distilled water for 5 minutes.

All samples were submitted to artificial ageing in oven at 80°C and 65% R.H., drawing samples after 7, 14, 21, 28 days.

- Untreated papers (samples A) are reference sample for each ageing time.
- Oxidized papers (samples B) simulate an ancient document with different ageing degrees.
- Reduction of oxidized papers (samples C) and following ageing were executed to test the effectiveness of reduction treatment over time. These samples simulate the ageing of a restored oxidized paper.
- Another set of oxidized papers (samples D) were also treated with TBAB, after ageing, to evaluate the efficacy of the reducing product, in the case that a great amount of carbonyl groups is present in the paper.

We also chose to test the reducing power of TBAB as a function of the immersion time. For this reason two sets of aged-oxidized papers were immersed in the reducing solution for 1 hour and for 5 hours respectively.

MEASUREMENTS

UV-visible measurements were achieved using a Perkin-Elmer Lambda-5 Spectrophotometer.

The determination of carbonyl amount was performed with a modification of Szablocs's methodology. 0.5 ml of KOH and 0.5 ml of TTC were added to 5-90 mg of precisely weighed paper, placed in a flask, and the resulting suspension was placed in a boiling water bath. After 10' the solution was cooled and 0.2 ml of 1M HCl was added. If no acid was added, the red colour of the solution (especially in the case of diluted solutions) quickly disappeared and the measurement was not reproducible. Deeply red triphenylformazan precipitate was dissolved in ethyl alcohol (EtOH); the solution was filtered from residual paper and the volume sized to 20 ml with EtOH. Solution absorbance at λ=480 nm was measured. It is important to note that solutions of formazan in water or EtOH have not the same ε, but a small amount of water (<10%) does not significantly affect the solution absorbance. Further reduction of the water amount is not possible. In order to minimize this problem, all glassware used must be dry or wet with ethyl alcohol. An amount of water >40% in the solution gives a relative error of 50% or more if compared to an alcoholic solution. Fig. 1 reports the calibration straight line obtained from water/alcohol solution of glucose (water content <10%; 10 measurements for each concentration). Same results were obtained using water-alcohol solution of fructose.

To obtain the calibration line a 0.1% w/v aqueous solution of glucose was used, employing from 0.03 to 0.07 ml of the solution. After performing the reaction as explained above, the absorbance of the solution was plotted vs. moles of

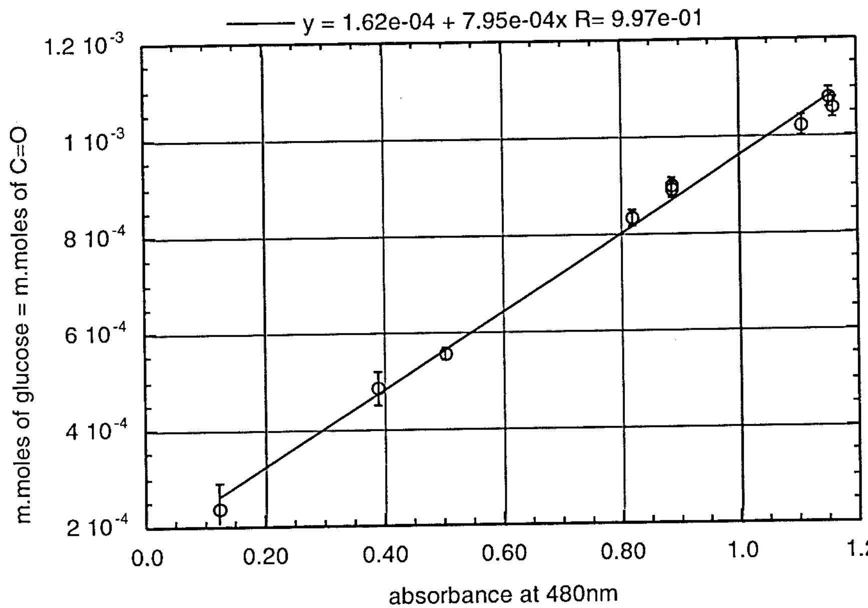

Fig. 1 Calibration line for carbonyl content in standard glucose solution at 480 nm

glucose. The amount of carbonyl in paper was measured from the calibration line, by calculating the moles corresponding to the measured value of absorbance.

RESULTS

Carbonyl groups in the paper can be present either at the end of each cellulose molecule or, by oxidation, on the anhydroglucose ring. TTC method gives a

Table 1: Total carbonyl content for untreated (samples A) ; oxidized (samples B) and oxidized reduced papers (samples C), as a function of the ageing period

Ageing days	m.moles C=O in 100g of untreated paper (A)	of oxidized paper (B)	of oxidized-reduced paper (C)
0	0.50 ± 0.03	4.25 ± 0.04	0.97 ± 0.04
7	0.67 ± 0.07	4.99 ± 0.07	1.62 ± 0.06
14	0.84 ± 0.04	7.30 ± 0.07	3.50 ± 0.16
16	0.90 ± 0.04		
21	1.09 ± 0.06	8.49 ± 0.12	4.99 ± 0.29
28	1.25 ± 0.13	8.99 ± 0.15	6.41 ± 0.30

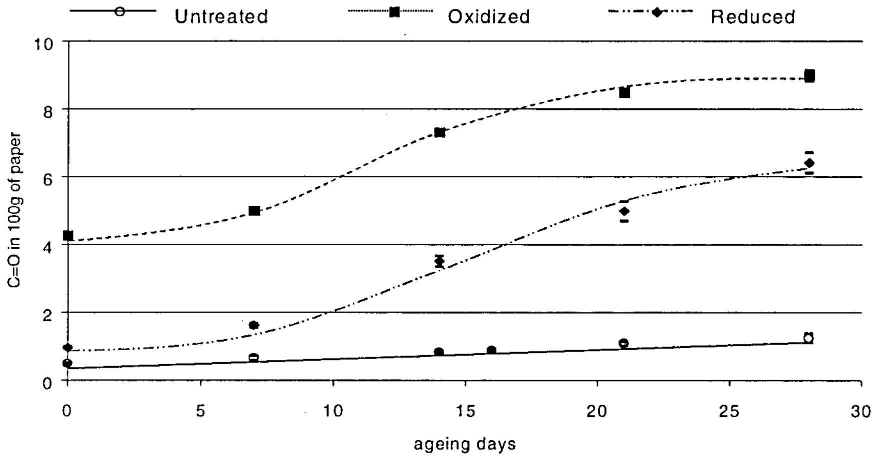

Fig. 2: Total carbonyl concentration of differently treated papers, as a function of ageing period

measure of both kinds of carbonyl groups. Table 1 and Fig. 2 show the total carbonyl content, as a function of the ageing time, related to 100 g of paper. Each value results from at least 5 measures. In Table 3 we report the total carbonyl content of aged oxidized papers, as a function of the immersion time in TBAB, related to 100 g of paper.

The experimental values of total carbonyl concentration can be fitted with a straight line for the untreated papers and with a Boltzman distribution for the oxidized and the oxidized / reduced papers. The equations and parameters, experimentally found, for the carbonyl formation in the three examined papers are reported in Table 2. In the equations y is the concentration of carbonyl groups expressed in m.moles/100g of paper and x is the ageing time in days:

$$y(\text{untreated}) = m_1 + m_2 * x$$

$$y(\text{oxidized and oxidized-reduced}) = m_2 + (m_1 - m_2) * \exp[(x-x_0)/dx]$$

Table 2 : Experimental parameters for the carbonyl content in differently treated papers

Parameters	Untreated	Oxidized	Oxidized and reduced
m_1	0.493 ±0.028	4.127 ± 0.093	0.741 ± 0.177
m_2	0.026 ±0.002	8.877 ± 0.179	6.554 ± 0.427
x_0		11.796 ± 0.424	14.855 ± 0.931
dx		3.232 ± 0.368	4.619 ± 1.633
chisq	1.041	2.159	2.462
R	0.997	0.998	0.999

Table 3: Total carbonyl content for oxidized aged papers (samples D) after 1 or 5 hours reduction, as a function of the ageing period

Ageing days	m.moles C=O in 100g of oxidized paper		
	after 1 hour reduction	after 5 hours reduction	
1	0.86 ± 0.11	0.75 ± 0.08	4.25 ± 0.04
7	2.34 ± 0.15	2.40 ± 0.25	4.99 ± 0.07
14	2.72 ± 0.33	2.62 ± 0.36	7.30 ± 0.07
21	3.67 ± 0.30	3.95 ± 0.28	8.49 ± 0.12
28	4.25 ± 0.51	4.13 ± 0.16	8.99 ± 0.15

In the second equation m_1 and m_2 are the lower and the upper asymptote respectively; x_0 is the value of the ageing time at the flex point and dx represents the slope.

As shown in Table 3 the carbonyl content is almost unchanged after 1 hour of reduction. The range of effectiveness of TBAB is 50–80%.

CONCLUSIONS

In Whatman untreated papers the plot of total carbonyl groups vs. days of ageing shows only a little increase even after 28 days: the rate of carbonyl formation is a constant over ageing time, the prevailing degradation mechanism is the scission of the glycosidic bond.

The total carbonyl groups formation in KIO_4-oxidized and KIO_4-oxidized-TBAB reduced samples follow the same law.

KIO_4-oxidized papers, after a rapid increase in total carbonyl groups, reach a limit value of ca. 9 m.moles per 100 g of paper. The prevailing degradation mechanism during the ageing is the formation of oxidized functions on the anhydroglucose ring.

KIO_4-oxidized TBAB-reduced papers show an initial amount of carbonyl groups similar to untreated paper; after several days of ageing the number of carbonyl groups increase, following a sigmoidal shape function, but the maximum value recorded after 28 days of ageing is 2/3 with respect to the corresponding oxidized-unreduced sample.

We can conclude that in all the cases the presence of oxidized groups, not completely reduced, facilitate further oxidation. We also increased the duration of the treatment by immersion in TBAB solution for a longer time, but the measurements of the number of carbonyl for samples reduced either for one or five hours remain almost the same. On the contrary, as previously reported[1], in case of ancient papers a longer immersion in TBAB is a good option to increase the effectiveness of the reducing treatment. It could also be noted that the paper will not be damaged even after a very long immersion. This is probably due to the pH 8.50 – slightly alkaline – of a 0.2 M solution of TBAB.

In conclusion, all experimental data show that the reduction treatment of oxidized papers, followed by ageing (simulating the ageing of a restored ancient paper), offers a certain level of protection compared to the oxidized paper. Obviously, TBAB is not able to impede further and intrinsic oxidation of paper, but the initial low amount of carbonyl groups retards the oxidation process. The treatment of oxidized aged papers shows an effectiveness of 50 to 80% in the reduction of oxidized functional groups.

The method used for detection of carbonyl content can also be simply applied in a qualitative manner as a micro destructive probe. A very little amount of paper could be treated with TTC and KOH at a hot temperature. The more intense the red colour appears, the more the paper is oxidized. Unoxidized papers show a pale pink colour, due to the reaction of the carbonyl terminal groups present in the cellulose molecules.

Further development of our work will involve the use of different reducing products, in order to find new applications, especially in non aqueous solutions.

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We would like to thank the CNR (Italian National Council of Research) for financial support of our work. CNR in fact set up the target oriented Special Project "Cultural Heritage". Our research group is working in the subproject "Paper Heritage: analysis, diagnosis and restoration" with the research titled "Functional groups in paper as a function of the ageing and their reduction".

SUMMARIES

A quantitative measure of borane tert-butylamine complex effectiveness in carbonyl reduction of aged papers

The goal of our experimental work is to provide a simple method for qualitative and quantitative determination of carbonyl groups, in order to evaluate when a reduction treatment is a primary need in a restoration procedure, and to test the effectiveness of borane tert-butylamine complex (TBAB) over time. Experimental data show that TBAB has an effectiveness of 50 to 80% in the reduction of oxidized functions. The modified method of Szablocs gave reproducible results and the test can also be simply applied in a qualitative manner as a micro destructive probe.

Une méthode de mesure quantitative de l'efficacité du complexe de borane tert-butylamine dans la réduction carbonyle de papiers anciens

L'objectif de notre travail expérimental consistait à trouver une méthode simple pour la détermination qualitative et quantitative de groupes de carbonyle, qui permettrait de juger quand un traitement de réduction s'impose dans la procédure de restauration du papier et qui serait adaptée pour tester l'efficacité du complexe de borane tert-butylamine (TBAB) dans le temps. Les résultats des expériences indiquent que le TBAB a une efficacité de 50 à 80 % dans la réduction des groupes oxydés. La méthode de Szablocs – modifiée – a apporté des résultats reproductibles et le test peut être aussi appliqué de façon simplifiée comme un instrument d'analyse quantitative peu dangereux.

Eine Methode zur quantitativen Messung der Wirksamkeit des Tert-Butylamin-Komplexes zur Reduktion von Carbonylgruppen in gealtertem Papier

Das Ziel unseres Versuches war es, eine einfache Methode für die qualitative und quantitative Bestimmung von Carbonylgruppen zu finden, um feststellen zu können, wann eine Reduktionbehandlung bei der Restaurierung von Papier angebracht ist, und um die zeitabhängige Wirksamkeit des Borane-Tert-Butylamine-Komplexes (TBAB) zu erproben. Experimentell gefundene Zahlen zeigen, daß TBAB eine Reduktion von 50–80% der oxidierten Gruppen bewirkt. Die Szablocs-Methode – modifiziert – brachte reproduzierbare Ergebnisse; der Versuch kann auch in vereinfachter Weise unter geringen Materialverlust zur qualitativen Analyse eingesetzt werden.

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Treatment of Deteriorated Paper with Emulsified Copolymer

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INTRODUCTION

Books and documents which are stored for long period of time are rapidly deteriorating. This deterioration is due to the low pH of the book papers [1]. The durability of this deteriorated paper should be partially recovered by deacidification. The ageing of paper sheets produces a chemical and structure change resulting in a deterioration of the mechanical properties and brightness of paper sheets [2,3]. The extent of these changes are depending on temperature, time, humidity and type of pulp, etc. [4]. Moisture and acidity of paper sheets are important factors in paper deterioration. In general, the loss in the fibre strength during ageing is due to the degradation of cellulose which is caused by acid catalyzed hydrolyses [5]. Hence, acidic papers are deacidified by washing or spraying them with a solution of an alkaline earth metal salts [6]. The use of aqueous dispersed polymer started for the restoration and preservation of books and archival documents e.g. vinyl-acetate-acrylate copolymer and styrene-acrylate copolymer [7]. The aqueous dispersion of copolymers of methyl methacrylate is highly established for conservation and restoration of archival materials [8]. The use of parylene in the conservation of artifacts and archival materials is also considered [9].

The aim of the present work is to use polyvinyl acetate polyvinyl versatate copolymer in the treatment of old paper sheets to improve their resistance to weathering conditions.

EXPERIMENTAL

- Old paper sheets delivered from the *World Stories Series (I and King of Sayam. Cairo: El-Kawmia for Printing & Publishing 1948)* were dipped in a PVAC/PV versatate copolymer dispersion of different concentrations (10–40%) for 30 seconds.

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- Some sheets were dipped in 10% dispersion for different time (10–30 sec).
- Some of the sheets treated with copolymer dispersion 10% for 30 seconds were heated at 100°C between two plate under 5 kg pressure for 5 sec.
- Some paper sheets were dipped in the copolymer dispersion containing 3% Di- octyl phthalate (DOP) as plasticizer for different time intervals.
- Some paper sheets were washed in running water before dipped in 10% co-polymer dispersion for different time intervals.

Polymer retained by the paper was determined gravimetrically by determining the difference between the weight of sheet before and after dipping (g/m^2).

The different kinds of treated paper were aged for 3 days at 80°C in a desiccator which contained saturated solution of

- $MgCl_2$ for 30%,
- $NaNO_2$ solution for 60%,
- K_2SO_4 for 94% humidity.

Some of the paper sheets were put into 94% 80°C for different time: 1–10 days.

Mechanical properties of the treated paper sheet were determined according to Tappi standard method T403/ 10.

RESULTS AND DISCUSSION

Retained polymers

Different variables which have a prior effect on the retention of polymer on the old paper sheet are studied:

Effect of dipping time

Table 1 is giving the effect of the dipping time on the amount of the polymer which is picked up with paper sheets.

From the Table it becomes clear that the retained polymer is increasing with increasing dipping time up to 60 seconds. Increasing the dipping time to more than 60 seconds is resulting in a very slight increase of the retained polymer only.

As the pH of the old paper was quite low, the sheets were washed in running stream water in order to decrease their acidity and also to remove any salts

Table 1: Effect of dipping time on the retained polymer (g/m²)

Dipping time (sec)	Untreated	Washed	DOP in copolymer
10	1.42	2.07	1,52
20	1.50		
30	1.70	2.27	1.80
40	1.90		
60	2.04	2.84	2.20
120	2.10		

formed during storage. The polymer retained by the washed paper was distinctly higher than that retained by the unwashed paper sheet. This can be attributed to increasing porosity, to salt and dirt removed by washing, and also to the decrease of paper acidity.

Also the amount of polymer retained by paper dipped in a 10% dispersion containing 3% DOP was determined. The results are shown in the last row of Table 1. It is clear that the plasticizer is slightly enhancing the retention of polymer pickup in unwashed paper, even if not in an amount comparable to the effect of washing. The positive effect of DOP can possibly be attributed to plasticizing effect, resulting in better diffusion of the copolymer dispersion into the fibres.

Effect of polymer concentration

Table 2 is giving the retained polymer as function of different concentration of the copolymer dispersion. Dipping time was 30 second.

Increasing the copolymer concentration up to 30% causes an increase in the retained polymer. Further increasing of copolymer concentration is reducing the polymer pickup by the paper. This may be due to the increased viscosity of the copolymer dispersion which decreases the diffusion into the paper.

Table 2: Retained polymer on dipped paper sheets in different polymer concentrations

Polymer concentration (%)	retained polymer (g/m²)
10	1.7
20	3.14
30	3.90
40	3.50

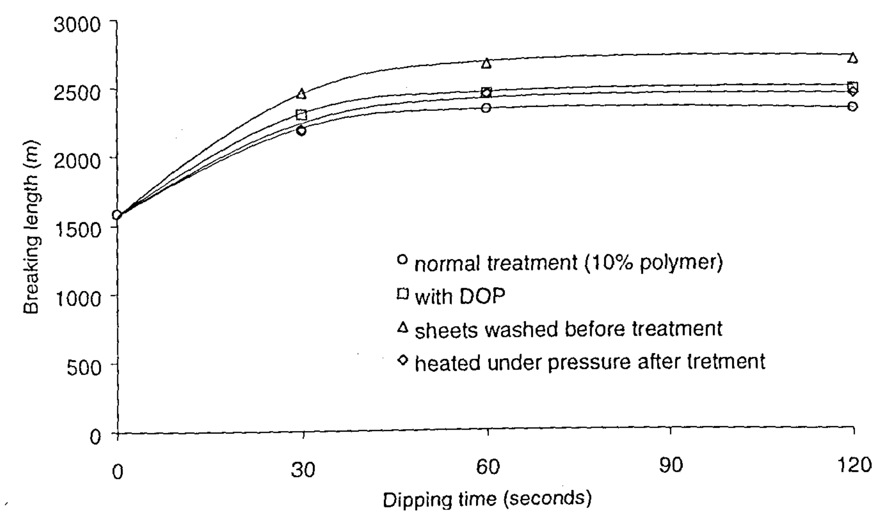
Mechanical properties of the treated sheets.

Reduced mechanical properties and increased yellowing are considered to be the most significant factors for estimating the degree of paper deterioration.

Deterioration of paper can be decreased by treating the sheets chemically or physically. In our test the treatment of the already deteriorated paper with different polymer dispersions improved their mechanical properties [15-16].

Effect of dipping time

From Table 1 it becomes evident that increasing dipping time is increasing the retained polymer. Fig. 1 shows the effect of dipping time on the mechanical properties of the paper sheets dipped in a 10% copolymer dispersion. It becomes evident that increased dipping time is increasing breaking length. This is obviously a result of the higher amount of retained polymer. Increasing the dipping time to more than 40 sec, however, and thus increasing the retained polymer to more than 1.9 g/m² is resulting in decreasing mechanical strength, only very slightly with breaking length, quite distinctly with the tear factor (Fig. 2). breaking length and tear factor. Paper containing such a high amount of polymer becomes stiff and hard.



Fig, 1: Effect of dipping time on breaking length

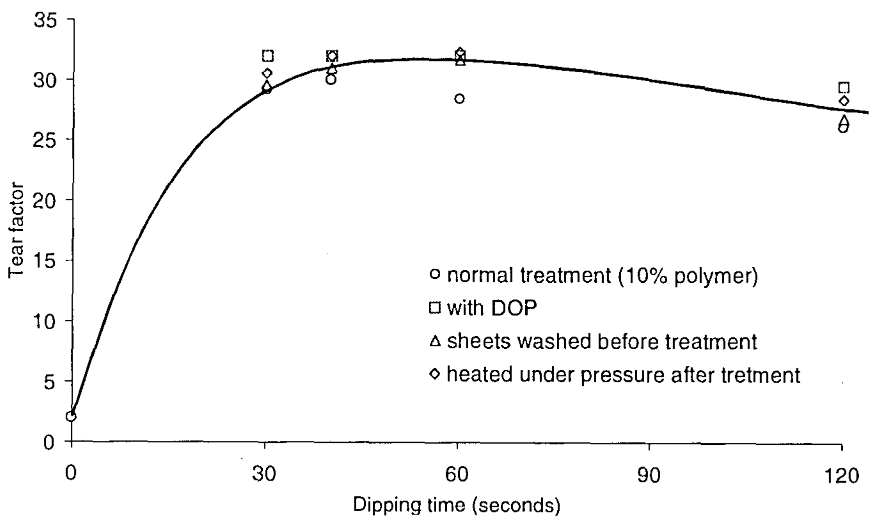


Fig. 2: Effect of dipping time on tear factor

Effect of heat pressing

In order to improve the effect of polymer treatment, the treated sheets were pressed between two plates at 100 C and 5 kg/cm^2 for 5 seconds. The mechanical properties are presented in Fig. 1a. Breaking length and tear factor of the heated sheets are higher than in unheated sheet. This can be explained by assuming that pressing paper impregnated with the polymer is forming an homogeneous film on the surface of paper and also a homogenous distribution of the polymer through fibres of paper sheets. This causes an homogeneous bonding between fibres and polymer.

Effect of DOP

Adding DOP as plasticizer has a positive effect on the mechanical properties of the dipped paper sheets (Fig.1b). The mechanical properties of the sheets dipped in the polymer dispersion with DOP are higher than those paper sheets without. The reason may be the higher polymer pickup caused by DOP (cf. Table 1 last row) and its increased elasticity, reduced rigidity, for the same reason.

Table 3: Breaking length of paper sheets aged at 80°C in different humidities for 3 days

	humidity (%)		
Treatment	30	60	94
Untreated	1420	1400	1330
Treated with 10 % Polymer	2300	2245	2180
Polymer + DOP	2470	2400	2380
Washed before treatment	2610	2520	2530
Heat pressed after treatment	2435	2420	2395

Effect of washing

The mechanical properties of the paper that has been washed before treatment are also given in Fig. 2b. It can be seen that the mechanical properties of the paper that has been washed before dipping in copolymer dispersion (10%) for 30 seconds are higher values than those of the unwashed paper: obviously a result of the higher amount of polymer pickup caused by washing. Again adding DOP is further increasing the elasticity and thus also the tear factor.

Ageing of treated old paper sheets

The differently treated paper sheets were aged at 80° C for different time [17] and at different humidity, i.e. 30, 60 and 94%. Table 3 is giving the effect of 3 days ageing on the differently treated paper.

The breaking length of all papers is affected by ageing at any humidity [18], those treated with copolymer in a smaller amount than the untreated ones. Obviously humidity has a significant influence on mechanical property reduction during ageing: the higher the humidity, the greater the deterioration. The humidity absorption reduced by the polymer treatment has a positive influence on the ageing behaviour. The highest values are obtained with the paper that has been washed before treatment: obviously a result of acidity reduced by washing. The smallest difference between the different humidities is given by the copolymer treated sheets heat pressed after treatment. The smooth surface and low porosity caused by heat pressing is reducing moisture absorption, which has a negative effect on the ageing stability, even more.

Table 4 shows the effect of ageing of the paper sheets at 94% humidity at 80°C for different time intervals. It is clear that, the mechanical properties of treated and untreated sheets are decreased by ageing. Breaking length and tear factor are decreased by increasing the ageing time. Again from this Table, it is seen that the

Table 4: Ageing paper sheet at 94% humidity for different time at 80°C

	Breaking length (m)					Tear factor				
ageing; days	0	1	3	6	10	0	1	3	6	10
untreated	1584	1490	1330	1160	1020	2	12	10	9	8
N. treated	2335	2330	2120	1980	1850	30	29	27	26	25
with DOP	2450	2465	2380	2160	1940	32	32	30	29	27
washing	2668	2670	2530	2400	2290	31	30	29	27	27
heated under press	2451	2420	2395	2340	2300	32	32	30	28	28
percentages										
untreated	100	94	84	73	64	100	600	500	450	400
N. treated	100	100	91	85	79	100	97	90	87	83
with DOP	100	101	97	88	79	100	100	94	91	84
washing	100	100	95	90	86	100	97	94	87	87
heated under press	100	99	98	95	94	100	100	94	88	88

sheets heated under pressure produce paper sheets which have a minimum loss in the breaking length and tear factor than treated one.

With longer ageing time the tear index of untreated paper is highly increasing after one day and then, with longer time, continuously reducing: obviously the result of cross linking in the cellulose molecules provoked by moist heat which is counteracted by depolymerization taking place with longer ageing time.

Breaking length as well as tear factor of the polymer treated sheets are decreasing with ageing time. but in a far less amount as with the untreated paper. The polymer treatment does not only improve mechanical strength of the paper, but this effect is also stable during ageing . The observation regarding tear index must not necessarily contradict this statement: the reducing rate during ageing (Table 4 Row 6 Column 7 to10: 600-500-450-400) is by far the highest. It can be presumed that with longer ageing time it would soon be below far below 100. There is, however, nearly no or only a very slightly reduced tear index between 6 and 10 days of ageing for the polymer treated papers.

Summaries

Treatment of deteriorated paper with emulsified copolymer

50 years old paper sheets have been treated with different concentrations of PVAc/PV versatate copolymer dispersion. The effect of different dipping time, of washing before treatment, of adding DOP to the copolymer dispersion and of heat pressing after treatment were studied. The probes were aged at 80°C and different humidities of 30 to 94% . Ageing at 80°C and 94% was also done for several time intervals. As a result it can be said that the polymer treatment is highly improving the mechanical properties of the paper and its ageing stability.

Traitement du papier abimé avec une émulsion polymère

Des feuilles de papier vieilles de 50 ans ont été traitées avec différentes concentrations de PA-acétate/PV-Versatate Dispersion Copolymère. On a étudié l'effet des différentes durées d'immersion, du lavage avant le traitement, de l'addition de DOP dans l'émulsion et de la compression à chaud après le traitement. Les échantillons ont été soumis au vieillissement accéléré à une température de 80°C et à des degrés d'humidité variant entre 30 et 94 % . Le vieillissement à 80°C et 94 % d'humidité a été effectué sur différentes périodes. Comme résultat on peut dire que le traitement au polymère a fortement amélioré la résistance du papier et sa stabilité au vieillissement.

Die Behandlung von Papier mit Polymeremulsion

50 Jahre altes Papier wurde mit PV-Acetat / PV-Versatat Copolymer Dispersion in verschiedenen Konzentrationen behandelt. Die Wirkung verschiedener Eintauchzeiten, des Wässerns vor der Behandlung, der Zugabe von DOP zur Emulsion und des Heißpressens nach der Behandlung wurden untersucht. Die Proben wurden bei 80°C und verschiedenen Feuchten zwischen 30 und 94% gealtert. Die Alterung 80°C 94% wurde über verschiedene Zeiträume durchgeführt. Als Ergebnis kann gesagt werden, daß die Polymerbehandlung die Festigkeit des Papiers stark verbessert und daß dieser Effekt alterungsstabil ist.

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Examination of Parchment in Byzantine Manuscripts

by VILENA KIREYEVA

Introduction

Our knowledge concerning the quality and texture of Byzantine parchment is based mainly on visual and tactile information. First priority is to look at its surface, which is very smooth and glossy in appearance. Namely that very quality is an important factor for the bad state of preservation of miniatures that we observe in Greek medieval manuscripts, compared to the relatively satisfactory state of preservation of West-European book painting. No historical documents on the methods to manufacture parchment in medieval Greece are known. Obviously, these methods were different from the West European practice. So scientific examination of parchment carried out during the conservation treatment of Byzantine manuscripts in the State Research Institute for Restoration (GosNIIR) in Moscow must undoubtedly arouse interest, because, during that work, some technological methods of Greek manufacturers of parchment became evident.

Observation under the electron microscope

Interesting information was obtained during the survey of the parchment of a 14^{th} century manuscript from the State Historical Museum (Acts of Apostles, mus. 3648) under the electron microscope. At the same time the examination of parchment of a Russian 13^{th} century manuscript from the same collection (Menoias, Sin. 163) was carried out. The enlargement x480 allowed to observe considerable difference in texture of both parchments. The photo of the Byzantine sample (Fig. 1) shows a poorly structured, smoothened surface, typical for Byzantine parchment, as if coated by some amorphous substance. On the second photo (Fig. 2) the texture of the surface of Old Russian parchment can be seen – distinctly structured with clearly distinguishable single fibres.

CROSS-SECTIONS

The most interesting information was obtained observing cross-sections under the electron microscope. The difference in structure of surface layer and the bulk of both kinds of the parchment can be distinguished. The surface of Byzantine parchment (Fig. 3) is covered by a thick coating, that is remarkable for its structure in layers. The border between the bulk of the parchment and the coating has a diagonal appearance. Fig. 6 shows more obviously the structure of the surface coating.

A coating of similar character can be seen on the reverse side of the same parchment leaf. Here the coating is much thinner (Fig. 5 and 6). The different thickness on both sides of the parchment is undoubtedly related to the differently irregular texture of hair- and flesh-side. For smoothing the surface of flesh-side it was necessary to use the thicker layer of coating than for the same purpose on the hair-side, which is smoother due to its nature and to the treatment during production, i.e. scraping off the epidermis.

In order to compare the Byzantine parchment with Old-Russian parchment we made cross-sections also from this material (Fig. 7). Both sides of the parchment can be seen on the photo. The cross-section is arranged vertically. The structure of each side is clearly seen and there is no trace of foreign material which in its structure would be different from the mass of collagen fibres that compose the bulk of the parchment. Also a higher magnification did not reveal the presence of any alien material on the surface of the parchment (Fig.8).

There are also differences in the basic structure of Greek and Old Russian parchment. Old Russian parchment is more friable (Fig.8), the Greek parchment is more dense. The inter-spatial distance between structural elements, i.e. collagen fibres, in the latter is smaller than in Old Russian parchment (Fig.5).

NATURE OF THE COATING

Our observations reveal that the final stage of manufacturing parchment in medieval Greece was an additional treatment for obtaining a smooth and glossy surface. We tried to find out, at least approximately, the nature of that coating by applying the method of histochemical colouring of the cross-section with P-dimethylamine benzaldehyde in a medium of concentrated phosphoric acid. The basic component of the coating turned out to be egg white [1]. Further examination by thin-layer chromatography confirmed this conclusion and specified the composition of the coating: To the egg white a mucous of vegetable origin was added, most probably linseed extract. Obviously this additive was applied be-

cause dried albumen is very fragile. Its plastification by linseed extract is giving the elasticity and strength necessary for a surface coating [2].

To confirm that this technology of parchment manufacturing is not a casual one, few samples from four Byzantine manuscripts dated from 11th to 14th centuries were investigated. The parchment samples – only tiny little pieces are necessary for that investigation – were taken from the folds of single leaves in the gatherings of several manuscripts. It became evident that both sides of all samples except one were treated with egg white with an addition of vegetable mucous. The exception was a manuscript "Akathistos to the Virgin", 14th century, that will be particularly mentioned below. Generally, the coating on the hair-side is considerably thinner and forms a less dense layer than that on the flesh-side. During the histochemical examination on transversal cross sections, this coating material filling in the canals of hair roots is clearly visible. The coating consisting of albumen and a slimy substance as described easily absorbs moisture.

The physical and chemical examination of medieval Russian and West-European parchment had not proven the presence of surface coatings or any other impregnating material. From the beginning of the 13th century the structure of Russian parchment was practically the same as that of Western Europe.

OTHER COATING

Also another kind of surface treatment was applied by Byzantine parchment makers in 14th century Constantinople. The parchment of the richly illuminated codex "Akathistos to the Virgin" (Moscow, Historical Museum, gr. 439) and two leaves inserted during the 14th century into a 12th century Gospel manuscript (Historical Museum, gr. 511) have, in addition to the treatment with albumen and linseed extract, a coating that, by histochemical and microchemical analysis, could be revealed to contain collagen glue with an addition of casein and lead white. In sections where this coating is flaked off the parchment has transparent and glass-like appearance.

ORIGIN OF THE COATING

Our investigation suggest to assume that Byzantine parchment, in contrast to that from old Russia or the Occident, was treated with organic albuminous-mucous material and sometimes was even coated to obtain a smooth and homogenous surface: possibly in order to facilitate the work of writer and illuminator. It is difficult to say whether this treatment was done on large uncut pieces, whole skins as part of parchment production, or on ruled bifolios prepared for writing as a part of this preparation. Only one manuscript was examined for this question: the 14th century Apostle mus.3548 from the State Historical Museum.

Investigation of few microsamples from diverse section of one parchment leaf, from its edges and the edges of natural and intentional holes in it, revealed that the layer of coating becomes thicker nearer to the edges of the leaf and on the borders of natural apertures. This can be explained by the high moistening effect of surface coating. This observation allows to suppose that the surface treatment was done together with cutting leaves out of the skin.

The examination of the parchment of five Greek manuscripts allows to draw a conclusion on common technological method used for preparing the parchment for writing and painting: An albuminous or albuminous-mucous coating was applied. As the examined manuscripts are dated from 11th to 14th centuries this treatment seems to have been a firm tradition.

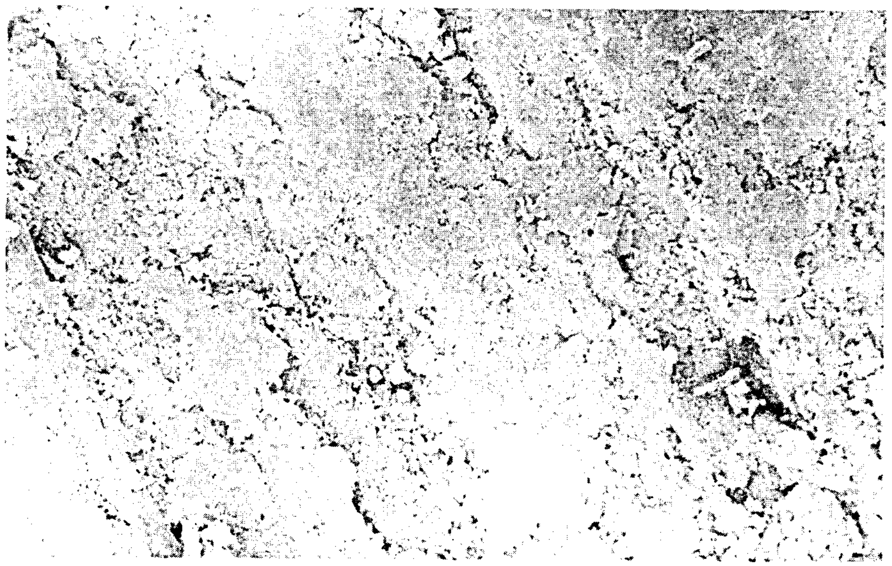

Fig. 1. Greek parchment, 14th century (x480). The surface is poorly structured and presents an amorphous appearance.

Fig. 2. Russian parchment, 12th century (x480). The surface is highly structured; single fibres are to be seen.

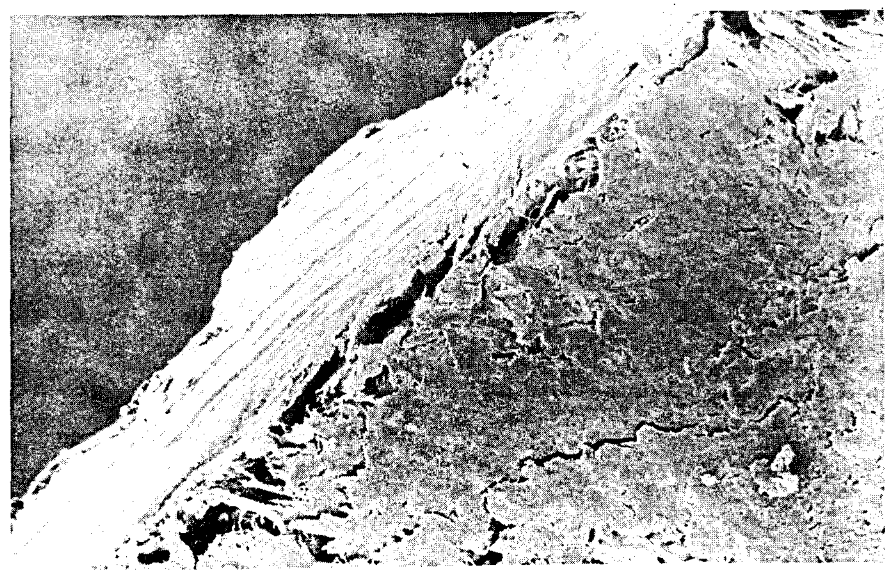

Fig. 3. Greek parchment, 14th century (x480). A layer of organic material is to be seen on the flesh-side; its structure considerably differs from the bulk of parchment.

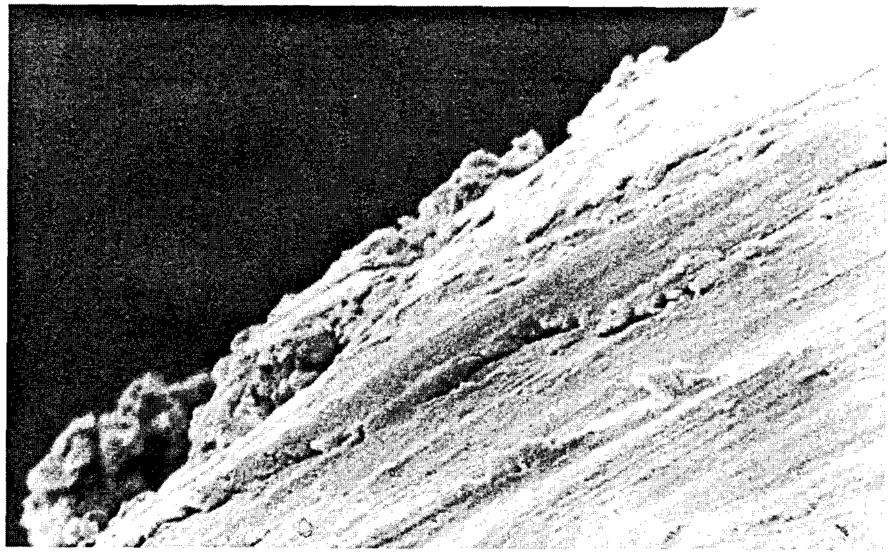

Fig. 4. Greek parchment, 14th century (x6000). This high enlargement helps to see clearly the amorphous structure of the surface coating.

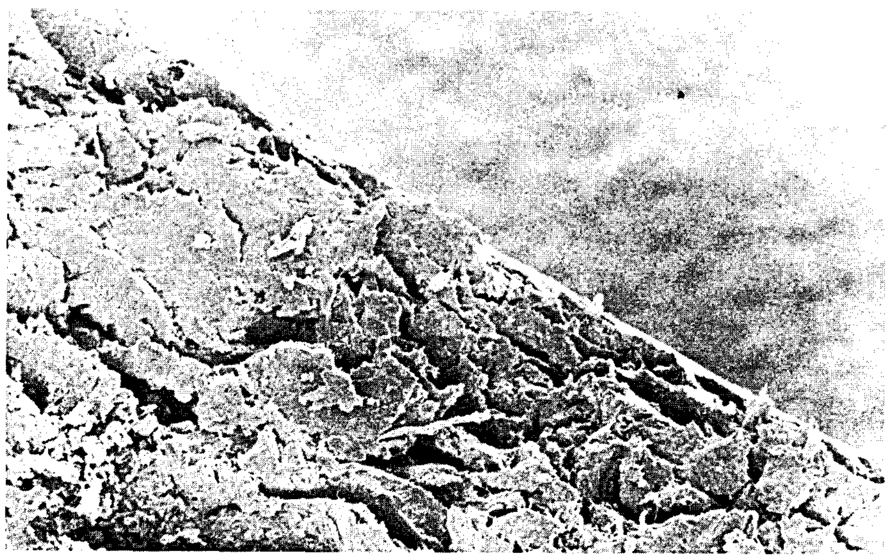

Fig. 5. Greek parchment, 14th century (x480). Hair-side with a thinner layer of coating than on the flesh side.

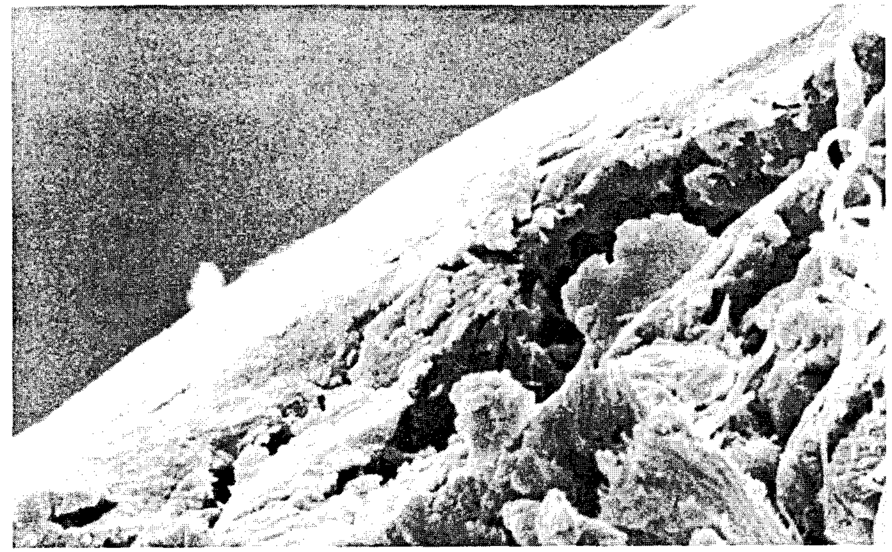

Fig. 6. Same as Fig., 5, enlargement 6000 fold. It can be seen that the coating on the hairside is analogous to that on the fleshside.

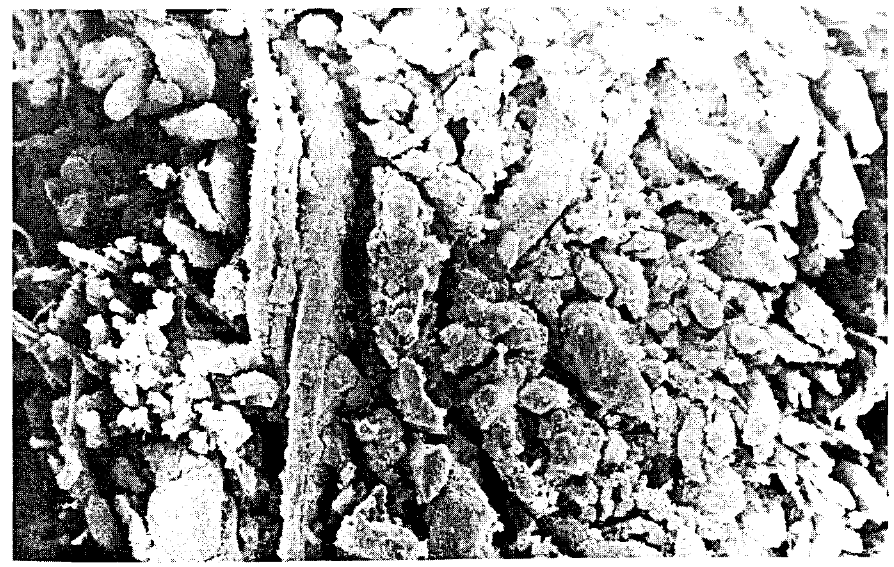

Fig. 7. Russian parchment, 13th century (x200). Cross section disposed vertically. The absence of heterogeneous coating is evident.

Fig. 8. Same as Fig. 7 enlarged 480 fold. No surface coating still is visible.

SUMMARIES

Examination of Parchment in Byzantine Manuscripts

The surface structure of Byzantine parchment, that is often glossy and smooth in comparison with the more rough or velvety surface of occidental or Russian medieval parchment, is a point of constant interest to restorers as well as to historians of Byzantine art and to palaeographers. Investigation of five Greek manuscripts dated from 11th to 14th centuries revealed the presence of thin albuminous film on both sides of the parchment leaves. By means of histochemical and microchemical analysis it was determined, that this film on base of egg white was plastisized by adding a mucus of vegetable origin, probably linseed extract. Interesting information was also obtained from the study of cross-sections of samples of different kinds of Greek parchment under electronic microscope.

Etude de parchemins byzantins manuscrits

La structure de la surface du parchemin byzantin qui est souvent brillante et lisse, en tout cas lorsqu'on la compare à la surface plus rêche et veloutée du parchemin occidental et russe, continue de susciter l'intérêt des restaurateurs ainsi que des spécialistes de l'histoire de l'Art Byzantin et des paléographes. L'analyse effectuée sur cinq manuscrits grecs datant du 11ème au 14ème siècles a révélé la présence d'un mince film d'une substance albumineuse sur les deux côtés des

feuilles de parchemin. L'analyse histo- et microchimique a mis en évidence qu'en effet ce film se compose de blanc d'oeuf qui a été plastifié en y ajoutant une substance visqueuse d'origine végétale, probablement un extrait de linette. Des observations intéressantes également ont pu être faites lors de l'analyse des coupes transversales du parchemin de manuscrits grecs.

Untersuchungen an Pergament aus byzantinischen Handschriften

Die Oberflächenstruktur von byzantinischem Pergament, das häufig einen glatten und weichen Eindruck macht, jedenfalls im Vergleich zu der rauheren und samtigen Oberfläche von westlichem und russischem Pergament, findet immer wieder das Interesse der Restauratoren wie auch von auf Byzanz konzentrierten Kunsthistorikern und Paläographen. Die Untersuchung von fünf griechischen Handschriften aus dem 11. bis 14. Jahrhundert ergab einen dünnen Film einer albuminösen Substanz auf beiden Seiten der Pergamentblätter. Histo- und mikrochemische Analyse zeigte, daß es sich tatsächlich um Eiweiß handelt, das aber durch die Zugabe einer schleimigen Substanz vegetabilen Ursprungs, wahrscheinlich Leinsaatextrakt, weichgemacht ist. Interessante Beobachtungen ergab auch die Untersuchung von Querschnitten des Pergaments griechischer Handschriften.

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2. The mixture of egg white and linseed extract for treating of parchment during manufacture is found in medieval Armenian recipes. 3 days-old linseed extract should be mixed with the egg white dissolved in water and spread on the flesh-side of the parchment. Cf. Galfayan, H.K. *Technology of parchment-making according to methods of Armenian craftsmen.* Khudojestvenoye Naslediye (=Artistical Heritage) 31 (1975): 74–79 (in Russian).

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The Development of a Universal Procedure for Archive Assessment

by JOHN HAVERMANS, PIETER MARRES & PETER DEFIZE

INTRODUCTION

Over the last decade there has been considerable concern about the condition and preservation of archive and library materials [1]. Conservation and/or restoration are highly required for several European archives and libraries, especially for those that are in a deplorable state and contain valuable information. For example, a damage survey, carried out by the Dutch State Archives, indicated that about 8% of its paper material were either brittle or weak [2]. For financial reasons a sound methodology is needed to assess the quality of archives. This makes it possible to set priorities in an objective way [3].

To get a better insight in the quality of an archive, one can carry out several measurements on some of its individual objects; however, it still turns out to be difficult to assess an archive and its over-all condition in an objective way. Such an assessment is desirable to make sound decisions about actions to be taken, e.g. conservation and/or restoration of the whole archive or parts of it and to set priorities between archives.

Our project aims for the development of a method to get a better over-all assessment for the Dutch State Archives. This method involves the development of a measurement tool, which is able to transform measurements on individual objects to objective statements about the general condition of an archive as a whole.

After preliminary research done by the Dutch State Archives in 1994, TNO started a follow-up project for the Dutch State Archives [4]. This was a pilot study to investigate the possibility of assessing archives by measuring some of its individual objects. These objects were a representative sample of the whole collection. Each of them was investigated by experts and several features of its condition were described in so called *damage forms*, especially designed for this purpose. In order to support the experts in their judgements, a so-called *damage atlas* was used as a reference. This manual contained pictures to illustrate several

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types of damage like discoloration, vermin and brittle paper [5]. From the pilot study it was concluded that for the ongoing study both, the forms and the atlas, should be revised.

Sampling objects from an archive in a representative way is not as simple as it may seem at first sight [6,7,8]. For instance, differences in size of the objects and shelves in the archive should be taken into consideration. Therefore a new sampling procedure had to be designed.

This paper presents the latest results of the Dutch Project on Archive Assessment, the new sampling procedure, types and severity of damage and accessibility profiles.

PROJECT METHODOLOGY

The whole project consists of several stages. All stages were critically reviewed and conducted by a team of Dutch experts coming from several disciplines: conservation, preservation and restoration work, mathematics, archive keepers, policy makers, physicians and chemists.

Firstly a reproducible sampling strategy was devised followed by the development of the classification model based on the evaluation of archival samples. Subsequently damages were described and classified in order to develop the new *Damage Atlas* and the new *Damage Information Forms*, serving the purpose of the project better than the previous ones. Finally tests were conducted at the Dutch State Archives in order to check the developed model and procedures.

SAMPLING IN AN ARCHIVE

Sampling in an archive is not the easiest thing to be done. We restrict ourselves to one complete collection of archival objects, received or archived by a foundation, person or a group of persons. Preferably the objects should have a unique identification within the archive to which they belong. An object can be, e.g., one document or a series of documents, bound or unbound. We also know that not all archives have identified all their stored objects, and that objects differ in size from object to object [4,9].

For the development of our management tool it is necessary that the procedure should be a general one, quite simple, applicable in many archives and also not too time consuming. Also every object must have an equal positive probability to be represented in the sample. Our present sampling procedure is based on the principles of the French statistician P. Gy who made an empirical model for particulate materials [10]. According to these principles thin objects have an equal probability to be chosen as thick objects have. We called this procedure *the trick of the meter.*

We tested the sampling strategy using several archive-employees. It was found that they were very well able to apply the procedure after receiving a short instruction. Afterwards the sampling proved to be done quite quickly: of about 200 items coming out of 1.5 km of archive shelving (approx. 20,000 items) was done within one day. In the following a short description of the procedure is given.

> *A sampling team consists of 2 persons. They make two walks through the archive. The goals of the first walk are:*
> *Firstly to define the archive as a single line of shelves by establishing rules like 'go from left to right', 'go from up to down', 'order the stacks'. Also the length of the archive is estimated.*
> *Secondly to estimate the average number of objects per meter shelving. This is done by counting, e.g., 50 radom meters.*
> *After the first walk the team goes back to the office doing some simple calculations in order to estimate the total number of objects in the archive and to determine some numbers for the second walk: sample size, archive length, average number of objects in a meter.*
> *Then the team goes for the second walk. After selecting the starting object, based on the calculations (e.g. 4th meter, 7th object in it) the team subsequently continues to count objects until the end of that first meter. Then the team will go to the next shelf meters selected for sampling, and soon until the pre-selected number (e.g. 23) is reached. The procedure is repeated until the sampling team reaches the end of the archive.*

ACCESS AND DAMAGE LEVELS

Before developing the damage survey model, again its definition should be fixed, in order to define consultability and the amount of damage. We started firstly to define 4 consultability levels. This was done by means of an expert team from several disciplines and using a pre-selected collection of over 200 objects. The consultability levels are

- Level 0: The object is in a very good condition and is suitable for consulting.
- Level 1: The object is in a reasonable condition. It may be consulted; however consulting may shorten its durability.

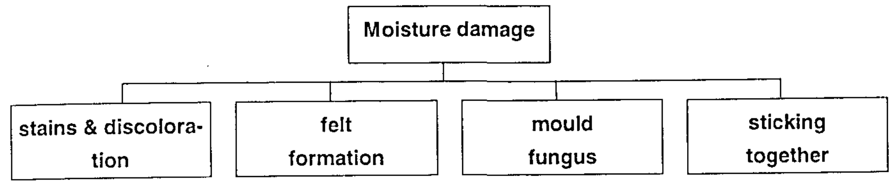

Fig. 1. An example of damage sub-categories belonging to the damage category *damage due to moisture.*

- Level 2: The object is in a bad condition. Consulting will indeed shorten its durability. The object preservation is seriously in danger.
- Level 3: The object is in a very bad condition. Consulting is not possible without endangering the preservation of the object.

Our main focus now is to calculate the consultability from data we obtain of the damage profiles of the sampled objects. A damage profile is a description of the damage in categories and sub-categories, whereby the degree of the damage is rated (damage level). Five damage categories (DC) are defined:

- Code B: Binding and book-block damage,
- Code C: Chemical damage,
- Code M: Mechanical damage,
- Code V: Damage due to moisture,
- Code I: Damage by insects and rodents.

All these categories are split up into sub-categories. An example on damage sub-categories is shown below using the damage category M: *damage due to moisture* (see Fig. 1). Here we can discriminate between:

- Stains and discoloration
- Felt-formation,
- Mould and fungus damage,
- Sticking together of several objects and/or pages within one object.

Finally, the level of amount of damage per category and sub-category is defined. This was also based on the selected collection of over 200 objects and we established three damage levels. The damage profiles to be used in the model as the input are not only related to its consultability but to its total use and are defined as:

- Low damage:
  Normal use of the object will cause no further damage to the object.

- Moderate damage:
  Carefully using the object will cause no further damage to the object, however rough use does damage it.
- Serious damage:
  Using the object causes more damage to the object.

RESULTS

Due to limited restrictions given by the State Archives, it is not possible to publish the model developed in its entirety, i.e. calculating the consultability of a selected archive based on the sampling. However the principles can be visualized as given in Fig. 2.

It should be stated that besides consultability, also a summary of the amount of damage per damage type (e.g., brittle, discoloration, mould, foxing stains) is calculated.

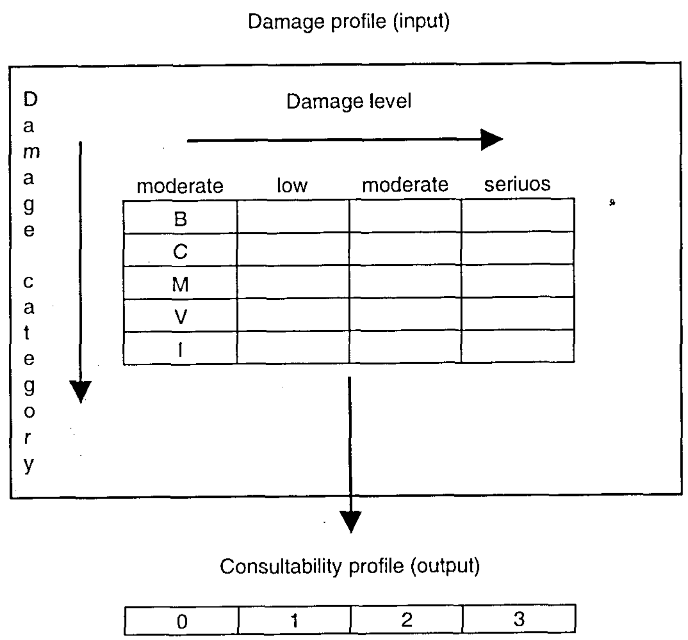

Fig. 2. The basics of the developed model. From a 4 x 5 input matrix, "the damage profile", we calculate with a special developed formula the "consultability profile".

Table 1: Results of the sampling

	Number of selected objects		Percentage f bound volumes	
	Team A	Team B	Team A	Team B
The Archive of the Council of Ministers (MR)	136	134	6	17
De Verenigde Oostindische Companie Archive (VOC)	213	220	94	94

Finally, recent results obtained from two tests at the state archives in The Hague will be showed. The archives investigated were *The Archive of the Council of Ministers (MR)* and *De Verenigde Oostindische Companie archive (VOC).* Two teams both carried out a separate sampling and object evaluation. From the results it was shown again that the sample was reliable. Table 1 shows for both teams the results of the amount of objects selected by the spot check, and the number of bound volumes within the sample.

Fig. 3 and 4 show the calculated consultability level per selected archive (x-axis), while the calculated % is given on the y-axis.

As expected, there is a slight difference between the results of both teams, however considering the reliability of a spot check and the diversity of archival materials, it can be stated that the results obtained are indeed practically useful for making policy on conservation and restoration.

CONCLUSION

From the results obtained we can conclude that consultability can be predicted from damage identification in combination with the damage level. The "classi-

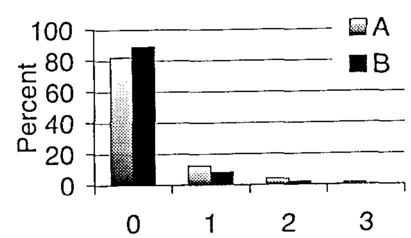

Fig. 3. The Archive of the Council of Ministers as classified by the teams, team A and team B.

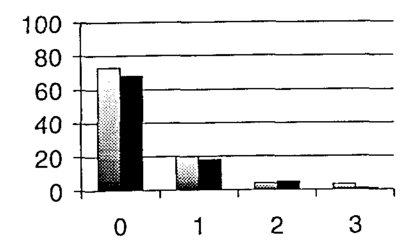

Fig. 4. The VOC archive as classified by the teams, A and B.

fier" gives a reliable overall impression on the state of the archive. The sampling model, damage classification and consultability classification can be considered as reproducible and reliable.

Acknowledgement

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Summaries

The development of a universal procedure for archive assessment

A model for calculating the assessment or consultability of archives was developed. This model includes an archive sampling procedure, defining damage profiles, damage sub-profiles and the development of a classifier. Research showed that the whole model developed is reliable and can be carried out easily.

L'élaboration d'une méthode universelle pour recenser les détériorations subies par les archives

Un modèle a été mis au point afin de recenser l'état matériel des archives et la possibilité de les consulter. Ce modèle comporte une procédure d'échantillonnage des archives qui définit les différents types de détériorations subies, établit des sous-groupes avec une classification selon les degrés. Les recherches effectuées ont démontré que ce modèle était fiable et facile à appliquer.

Die Erarbeitung einer allgemeingültigen Methode für die Erfassung von Schäden an Archivgut

Es wurde ein Modell entwickelt, wie der für die Benutzbarkeit relevante materielle Zustand von Archivgut erfaßt werden kann. Es besteht aus einem Verfahren zur Ermittlung repräsentativer Einzelstücke und der Aufstellung von Schadenstypen mit Untergruppen samt einer entsprechenden Klassifizierung. Eine versuchsweise praktische Anwendung hat die Brauchbarkeit des Verfahrens hinsichtlich Anwendung und Aussagekraft ergeben.

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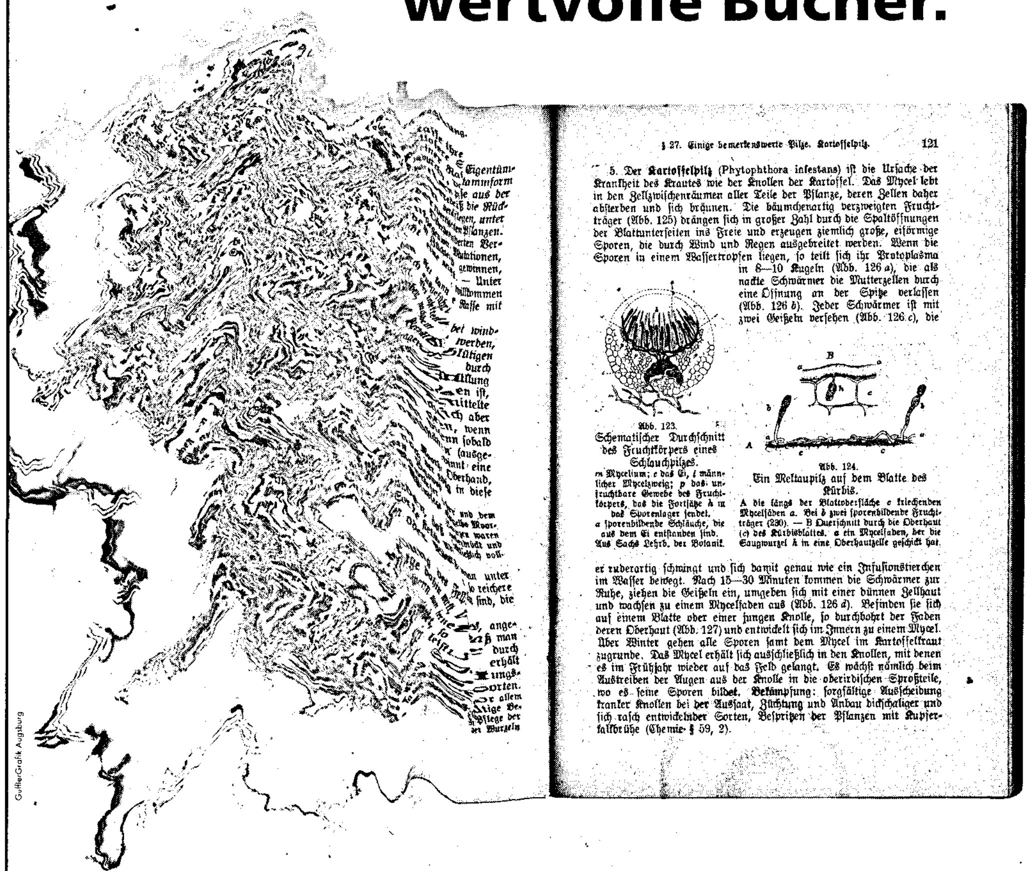

§ 27. Einige bemerkenswerte Pilze. Kartoffelpilz. 121

5. Der **Kartoffelpilz** (Phytophthora infestans) ist die Ursache der Krankheit des Krautes wie der Knollen der Kartoffel. Das Mycel lebt in den Zellzwischenräumen aller Teile der Pflanze, deren Zellen daher absterben und sich bräunen. Die bäumchenartig verzweigten Fruchtträger (Abb. 125) drängen sich in großer Zahl durch die Spaltöffnungen der Blattunterseiten ins Freie und erzeugen ziemlich große, eiförmige Sporen, die durch Wind und Regen ausgebreitet werden. Wenn die Sporen in einem Wassertropfen liegen, so teilt sich ihr Protoplasma in 8—10 Kugeln (Abb. 126 *a*), die als nackte Schwärmer die Mutterzellen durch eine Öffnung an der Spitze verlassen (Abb. 126 *b*). Jeder Schwärmer ist mit zwei Geißeln versehen (Abb. 126 *c*), die

Abb. 123.
Schematischer Durchschnitt des Fruchtkörpers eines Schlauchpilzes.
m Mycelium; *e* das Ei, *l* männlicher Mycelzweig; *p* das unfruchtbare Gewebe des Fruchtkörpers, das die Fortsätze *h* in das Sporenlager sendet. *a* sporenbildende Schläuche, die aus dem Ei entstanden sind. Aus Sachs Lehrb. der Botanik.

Abb. 124.
Ein Meltaupilz auf dem Blatte des Kürbis.
A die längs der Blattoberfläche *c* kriechenden Mycelfäden *a*. Bei *b* zwei sporenbildende Fruchtträger (230). — B Querschnitt durch die Oberhaut (*c*) des Kürbisblattes. *a* ein Mycelfaden, der die Saugwurzel *h* in eine Oberhautzelle geschickt hat.

er ruderartig schwingt und sich damit genau wie ein Infusionstierchen im Wasser bewegt. Nach 15—30 Minuten kommen die Schwärmer zur Ruhe, ziehen die Geißeln ein, umgeben sich mit einer dünnen Zellhaut und wachsen zu einem Mycelfaden aus (Abb. 126 *d*). Befinden sie sich auf einem Blatte oder einer jungen Knolle, so durchbohrt der Faden deren Oberhaut (Abb. 127) und entwickelt sich im Innern zu einem Mycel. Über Winter gehen alle Sporen samt dem Mycel im Kartoffelkraut zugrunde. Das Mycel erhält sich ausschließlich in den Knollen, mit denen es im Frühjahr wieder auf das Feld gelangt. Es wächst nämlich beim Austreiben der Augen aus der Knolle in die oberirdischen Sproßteile, wo es seine Sporen bildet. **Bekämpfung**: sorgfältige Ausscheidung kranker Knollen bei der Aussaat, Züchtung und Anbau dickschaliger und sich rasch entwickelnder Sorten, Bespritzen der Pflanzen mit Kupferkalkbrühe (Chemie § 59, 2).

Das weltweit einmalige patentierte Datukom-System sorgt für eine vollständige Entsäuerung und Konservierung Ihrer Schätze.
Gerne bieten wir Ihnen eine unverbindliche Vorführung an. Sprechen Sie mit Herrn Ass. jur. Römer

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