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The Effect of Different Strengthening Methods on Different Kinds of Paper

by HELMUT BANSA & RITSUKO ISHII

INTRODUCTION

Within the wide range of means to preserve our cultural heritage stored in archives and libraries, as far as it is endangered by chemical or biological decay, preserving the original format is without doubt the noblest. But, as soon as the originals have suffered decay in an amount that they can no longer be handled as it is necessary for reading, this noblest means is also the most expensive one – possibly with one exception, see below. Generally it must be stated that, if a sheet of paper has reached that state of decay that it can no longer be handled, the only means to preserve it is to combine it with another sheet-shaped object. Any other method, resizing, defined as bathing the sheets in the solution of a film-forming compound or spraying them with such a solution, or graft polymerization or such else, do not really give the necessary stability to a sheet decayed to this extent. Honestly, to use a term that might be construed as somewhat too sharp, the stability effected by these methods is only measurable on sheets not needing to be strengthened.

The methods to combine a sheet of brittle paper with another, a strengthening sheet-shaped object, differ in how this other sheet-shaped object is produced and how it is integrated into the original. The oldest and considered classic, but antiquated method is laminating another paper, mostly Japanese tissue, onto the surfaces of the decayed one using starch paste or methyl cellulose as adhesive. In the variant that a thermoplastic, mostly poly methyl methacrylate[1], is used, this laminating is widely used and possibly indispensable for water sensitive objects, in the case of corrosive ink in an advanced stage, e.g.. To avoid the aesthetic alteration at the surface of the original, the second, the strengthening sheet can be brought into the interior of the decayed paper after having split it[2]. In order to achieve better adaption or to speed up the process, the strengthening sheet can be produced directly for the decayed one and in combination with it, either using fibres for paper, i.e. leafcasting[3], or a plastic monomer for a synthetic coating, i.e. the

Parylene-process[4]. It is discussed that, regarding the cost, this process could possibly compete with microfilming.

Regarding the strengthening effect of the different methods and its ageing stability little information can be found in technical literature. Until now, relevant studies done have been limited to paper splitting[5], even this not taking into consideration the ageing behaviour of sheets treated for strengthening. The object of this study[6] is to get an idea of comparative results of the other methods in question, and mainly of their impact on ageing. We were interested in not only the strengthening effect of the different methods, but also in their impact on the aesthetic appearance. We excluded any resizing methods, for reasons given above, and we excluded the classic lamination with starch paste or methyl cellulose: it is highly inferior to splitting and leafcasting regarding aesthetics and does not give any advantage (with the exception that it needs little equipment). It should be considered to be obsolete.

Another request of our study was to test the different methods not only on new paper or laboratory handsheets, chosen in conservation research because they are well defined, but also on old papers, preferably those really needing to be strengthened or at least near to that state, as they are the usual objects of practical work.

PROJECT

Five different papers were chosen for treatment according to four different strengthening methods, one of them in three variations, and submitted to accelerated ageing. For evaluating the strengthening effect we chose only one, i.e. tensile strength after one defined fold, as it has been proved to be apt just to describe the usability of old papers[7], the more common MIT-folding test being too harsh for really brittle material. We excluded definitely the conventional tensile strength test, as for strong papers it gives the same results as tensile post fold and as it does not give sufficient distinction for weak ones. A totally brittle paper that breaks when simply folded and that therefore can not be handled without a support, can have a tensile strength of, say, 2 or 3 N: the same as a very thin, but flexible and therefore usable paper. We also explicitly abstained from the usual ph checking after treatment and after ageing. All strengthening methods can be done in a way to raise the pH or at least, if it is initially low, they can be combined with one of the usual methods of deacidification. Furthermore, the pH goes down in any way during accelerated ageing. Relevant tables would hardly give any other information than supporting this platitude. To evaluate aesthetics - a field very hard to evaluate - we chose thickness, stiffness and colour change, and additionally we submitted the treated sheets to a subjective assessment of 15 observers.

Table 1: The papers

Paper	Origin	Fibre	ash (%)	pH [a] (surface)	g/m²	thickness (mm)
filter	produced by J.C.Binzer Papierfabrik, Hatzfeld, Germany, 1994.	100% chemical pulp	0,26	5,8	60	0,13
coated [c]	produced by Scheufelen Papierfabrik, Lenningen, Germany, 1994	10% rag, 85% chem., 5% mech. pulp	28,2	7,4	127	0,13
groundwood 19th cent.	Bibliotheca Döllingeriana. München 1898	20% chem., 80% mechanical .pulp	11,9	4,4	70	0,07
groundwood 29th century	Kojinbetsu chinginchosa kekkahoku. Tokyo 1948	40% chem., 60% mechanical. pulp	11,9	3,1	49	0,08
rag 17th century [b]	Caspar Klock: Conciliorum tom.II. Nürnberg 1649	100% rag	1,15	6,7 (margin) 5,8 (print)	78	0,10 to 0,13
rag light [b]	Caspar Klock: Conciliorum tom.II. Nürnberg 1649	100% rag	1,15	5,5 to 6,5 (margin) 4,7 (print)	78	0,10 to 0.13

a. surface
b. The sheets of paper A are from the same book, but there is a difference regarding pH and yellowing. Two groups can be formed. Light: CIE L*= ca. 84 - a* = ca. 2,5 - b* = ca. 14. Dark: CIE L* = ca. 74 - a* = ca.5 - b* = ca. 17. The reason for this difference might be different sizing or different storage immediately after production. This difference is corresponding to the behaviour during accelerated ageing (see below).
c. coating: calcium carbonate and china clay; starch, styrene, butadiene.

THE PAPERS

As just stated, we had good reasons to do our research not only on new and well defined papers, but also on old ones, representing those which are really treated according to the conservation methods in question. Using old papers has some risks: there is only a limited amount which may not be enough for all desirable tests and which may run out when, in the course of progressing research, additional tests might become desirable. The paper of an old book, apparently throughout the same, may prove to be different in the course of progressing research, mainly during accelerated ageing, and this in qualities hardly to be manifested in terms of the usual paper analysis. Generally, old papers, and particularly those from the hand-making period, are much more different than modern ones, as well one sheet from the other as also the sheets within themselves. Nevertheless, it should be considered imperative to base research projects on conservation treatments on true old paper. Realistic results which can be used for choosing the method best apt for a certain damage and a certain old object can only be expected under this condition. The papers chosen for the project reported here are given in Table 1.

Strengthening Treatment

The strengthening treatments to be examined for their effect were the following:

- Paper splitting. As this method is quite new[3 5 8 9 10 11], i.e. not fully experienced in all its possibilities and variants it has been executed using three different adhesives for the core (Japanese tissue, 0,05 mm [a])
  - Wheat starch paste
  - Methyl cellulose [b]
  - Acrylic emulsion
  - Leafcasting, i.e. an extremely thin paper in the leafcasting machine and couching it wet-in-wet forming onto the paper to be treated
- Laminating, i.e. sealing the commercial product "Filmoplast R™" [d], a Japanese tissue coated with an acrylic, onto the paper in question
- Parylene, i.e. coating the paper in question with a thin film of Parylene. This method is the only one among those checked here which can be defined to be a mass method as the books must not be unbound for treatment.

a. product no. 611140 as delivered by JAPICO Feinpapier GmbH, Frankfurt, Germany; 0,05 mm

b. type MH 300; product of Hoechst AG , Höchst, Germany

c. Plextol P565, poly acryl acid butyl ester, product of Röhm AG, Darmstadt, Germany

d. produced by Hans Neschen GmbH & Co. KG, Bückeburg, Germany

Leafcasting, splitting and lamination was done in the restoration institute of the Bavarian State Library in Munich, Germany (Institut für Buchrestaurierung: IBR); Parylene was applied by the company offering this method, i.e. by SCS Speciality Coating Systems, Inc., Nova Tran™ Parylene Coating Services, Clear Lake, 54005, USA. For leafcasting and paper splitting, the papers were previously

washed, as it is usually done in conservation practice. For laminating with a heat-set tissue and for the Parylene process this pre-treatment is not necessary. On the contrary: laminating as described is preferably done when a wet treatment is not possible, because the object to be restored is highly water sensitive.

Leafcasting

As the method to strengthen paper in the leafcasting machine seems not yet to have been described enough in detail, at least not in the English language[12], to bring the conservation world to take notice of it as a commended method ousting traditional lamination using starch paste or MC and claiming to compete with paper splitting, possibly being superior to this modern method from the aesthetic viewpoint, such a description shall be given here.

Leafcasting for paper strengthening is done in the context of traditional leafcasting, i.e. to fill in missing parts. A special machine is necessary, and to do the process in a high aesthetic quality it should be a machine which allows an accurate work: zero or negligible loss of fibre, adjustable suction, adjustable working area. Moreover, for high quality leafcasting accurate computing is necessary: how much fibre is needed to produce a sheet of a certain thickness down to 0,01 mm of a certain colour to be mixed out of predied fibre. As third condition for results of high aesthetic quality, a certain relation between size of the aspired paper, its thickness and concentration of the fibre suspension shall be observed. All these requirements for optimum results, mainly based on experience and depending to some extent on the size of the machine, can only be met if the data are accurately computed, with the use of a PC[13], allowing reasonable time. For accurate computing specific data are necessary: numbers correlating to the mixture of pre-dyed fibre to gain a certain colour, i.e. exactly or as near as ever possible to that of the sheet to be treated, and numbers for the size of the missing parts. For both a machine should be available: for colour measurement, relevant instruments are well established in conservation research, a CIE L*ab instrument, e.g., and for measuring missing parts in a damaged sheet they can be specially constructed on the base using a light table, a camera, a monitor and again the PC[14].

The first step is traditional leafcasting to fill in missing parts. In the leafcasting program developed in the institute where this report originates there is the option for producing either a one-sided or a both-sided thin strengthening tissue out of the same fibre as used for filling-in, and it is also possible to put in the desired thickness: 0,01, 0,015, 0,02 mm etc., depending on the restorer's opinion, with regard to the state of the object in question. The PC output gives numbers for how many sheets of the object in question can be treated in one process, how big the working area in the leafcasting machine should be with regard to the specific data (size, thickness, missing parts) of the object in question, or, in other words, what masks should be used to reduce the working area; moreover, the output gives numbers on how much fibre of different kinds must be suspended in a known volume of water and how much of this suspension must be used for filling-in the missing parts, for the first and for the second strengthening sheet. In the institute where the system described here has first been developed, i.e. in the Institute for Restoration of Books and Manuscripts in Munich, white cotton, chocolate-brown unbleached cotton linters and sulphate cellulose pre-died in several tints of reddish brown, yellow and blackish blue are used, so that every possible colour that is found in old paper can be imitated.

After leafcasting to fill in missing parts the screen with the sheets (Fig. 1) are put out of the machine, quickly pressed, and the sheets are brushed with thin starch paste or methyl cellulose. Then the first strengthening sheet is made, using the same suspension in the amount given by the computer and using the same masks as before (only inversely positioned, i.e. the mask used to limit the leafcasting area at the left side put now to the right), thus getting a strengthening sheet of

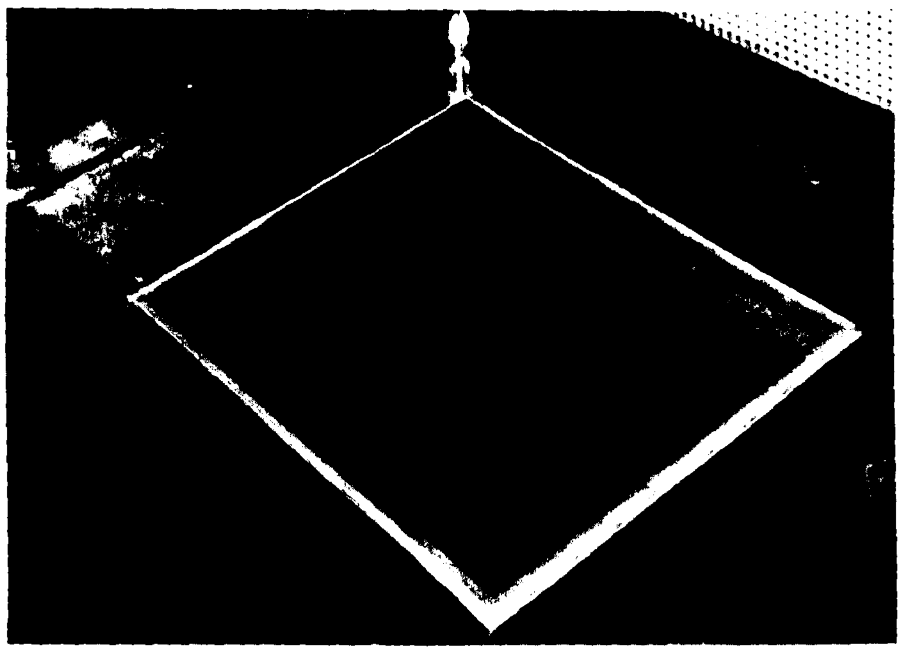


Fig. 1: The screen with leafcast sheets lying in the machine

exactly the size and the colour of the filling-in process and exactly of the aspired thickness. The strengthening sheet made as described is put without pressing, just in the condition as it comes out of the machine, i.e. not yet as a paper but as a thin mud of fibre, wet-in-wet and upside-down onto the leafcast sheet made previously (Fig. 2). Another quick pressing, turning the object upside-down, replacing the sieve used for filling-in by a synthetic non-woven (Hollytex™) and putting the second strengthening sheet, produced in the same way as the first, on the other side of the object in question. The whole process takes some minutes, the number of sheets treated simultaneously is depending on the working area of the leafcasting machine. The newly produced paper at the margins of the sheets treated in this way can be removed when they are still wet; this will be done when the margins are not damaged and when it is desirable to keep their original shape, in the case of deckle edge paper, e.g.. Or they can be cut off after drying, leaving behind on the margin the overlapping fibre that is connecting the new paper to the old and that is drastically increasing the tear resistance of brittle paper. If – nearly invisibly – a small rim of new paper is left all around the old, this increase is even higher.

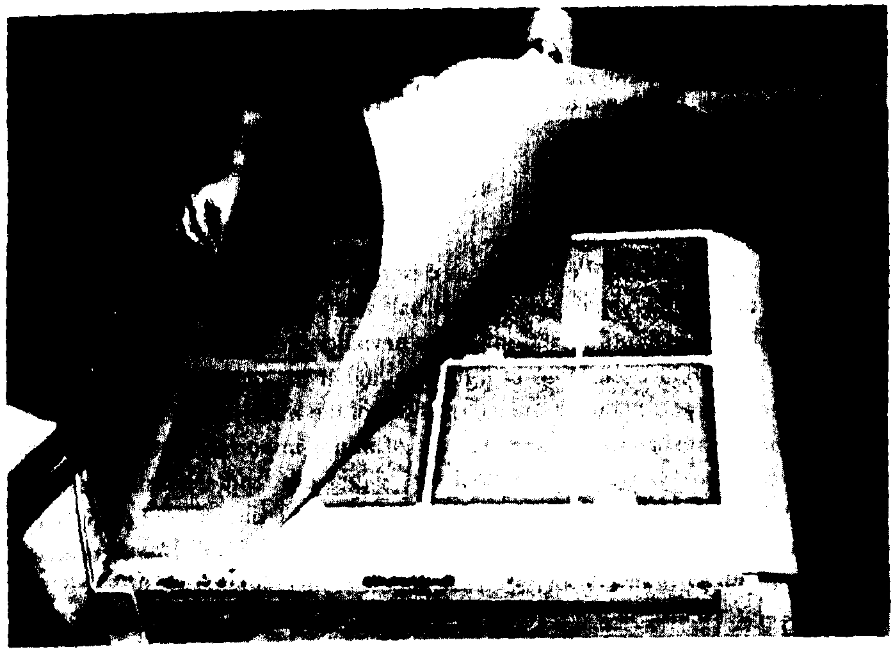


Fig. 2: Putting the second strengthening sheet onto the backside of the leafcast sheets lying on Hollytex

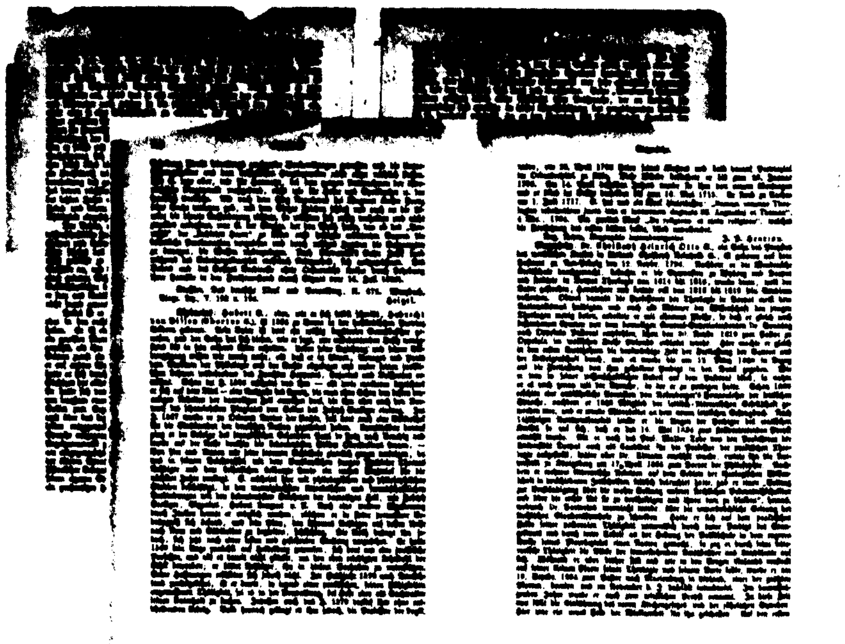


Fig. 3: Brittle paper, before and after strengthening in the leafcasting machine

ACCELERATED AGEING

From all papers treated in the manner as described (splitting, leafcasting, laminating with an acrylic, Parylene coating) one half was submitted to accelerated ageing at 90° 50% for 518 h. The reason for the deviation from accelerated ageing according to ISO 5630 were those of time: the higher the temperature the greater the changes in physical (and chemical) qualities of the material in proof. Altogether, the conditions of accelerated ageing are of minor importance, as relevant results can only be evaluated in comparison within one and the same research project. Accelerated ageing can give only an idea on the direction of the object's behaviour in real ageing, not of its degree. Relevant research must be rerestricted to one single different quality between the papers to be compared:

These papers must be the same with the exception of the very one quality in question[15]. Moreover, the different ageing methods are giving more or less parallel results, as can be seen when same papers are submitted to different ageing methods[16]. The results must be consistent. If they are not, as it is sometimes

Table 2: Tensile post fold N (average)

	control	washed	split paste	split MC	split Acrylic	leaf-cast	lami-nated	Pary-lene
filter MD								
unaged	9,70	9,35	60,98	63,91	24,71	32,78	41,22	34,77
aged	8,21	7,58	43,68	67,49	15,98	36,84	21,57	24,29
filter CD								
unaged	2,69	3,23	29,32	50,99	13,81	19,34	19,37	27,20
aged	3,08	2,38	25,67	56,42	11,13	18,95	13,50	23,26
coated MD								
unaged	64,10	69,15	114,28	128,05	59,24	68,87	89,32	62,90
aged	60,55	60,75	74,68	76,05	57,24	62,66	66,09	57,66
coated CD								
unaged	22,48	22,27	48,94	52,03	30,36	26,70	42,28	23,96
aged	20,36	21,73	40,00	52,99	28,24	27,67	26,32	22,46
groundwood 19th cent. MD								
unaged	14,00	11,73	37,82	52,26	28,97	22,28	40,38	23,13
aged	4,06	8,84	30,70	22,45	20,51	21,48	25,51	2,15
groundwood 19th cent. CD								
unaged	8,89	8,23	32,10	25,28	25,66	15,86	31,05	20,49
aged	2,24	4,31	28,73	20,77	18,15	15,66	20,79	1,45
groundwood 20th cent. MD								
unaged	14,06	21,80	23,29	19,21	21,92	30,55	37,55	10,64
aged	9,05	12,45	16,20	12,79	15,63	21,66	22,45	1,29
groundwood 20th cent. CD								
unaged	6,12	7,36	20,18	23,14	14,87	16,28	37,18	7,93
aged	2,05	3,36	12,07	12,02	11,83	14,65	20,45	0,48
rag 17th century MD								
unaged	10,45	11,36	40,93	53,46	28,67	17,60	43,25	49,95
aged	6,43	8,15	38,29	39,96	21,87	19,34	27,97	39,62
rag 17th century CD								
unaged	8,18	7,35	33,35	34,50	17,88	11,60	23,98	37,09
aged	3,99	4,84	24,67	34,50	16,19	14,68	15,93	25,21
rag 17th century light MD								
unaged	10,33	9,09	47,21	10,81	29,96	34,30	48,66	51,21
aged	18,24	13,08	23,46	56,38	38,30	29,05	32,71	35,31
rag 17th century light CD								
unaged	9,59	6,88	34,81	24,33	27,90	21,50	26,19	35,26
aged	7,59	3,59	27,49	28,76	32,10	23,78	18,08	26,22

Table 3: Relative change (%) of tensile post fold (sqrt(MD*CD) caused by treatment (upper part) or by treatment after ageing

	control	washed	split paste	split MC	split Acrylic	leafcast	lami-nated	Pary-lene
filter								
unaged	100	108	828	1118	362	493	553	602
after ageing	100	84	666	1227	265	525	339	473
coated								
unaged	100	103	197	215	112	113	162	102
after ageing	100	103	156	181	115	119	119	102
groundwood 19th century								
unaged	100	88	312	326	244	168	317	195
after ageing	100	205	985	716	640	608	764	58
groundwood 20th century								
unaged	100	137	234	227	195	240	403	99
after ageing	100	150	325	288	316	414	497	18
rag 17th century								
unaged	100	99	400	465	245	155	348	466
after ageing	100	124	607	733	371	333	417	624
rag 17th century, light								
unaged	100	79	407	163	290	273	359	427
after ageing	100	58	216	342	298	223	207	259
unaged = 100; after ageing:								
filter	98	77	79	108	72	105	60	77
coated	92	93	73	78	95	97	68	93
groundwood 19th c.	27	63	85	59	71	98	65	8
groundwood 20th c.	46	51	65	59	75	80	57	9
rag	55	69	83	86	83	118	66	73
rag light	118	87	63	248	121	97	68	72

the case[17], the ageing method must be examined and a specific reason for the deviation must be explained.

RESULTS

The data of measurements done at the altogether 80 samples (5 papers x 8 states of treatment (6 strengthening treatments plus washing plus control) x 2 states of ageing) or 96 samples (6 papers including "rag light") are given in Table 2, 4 and

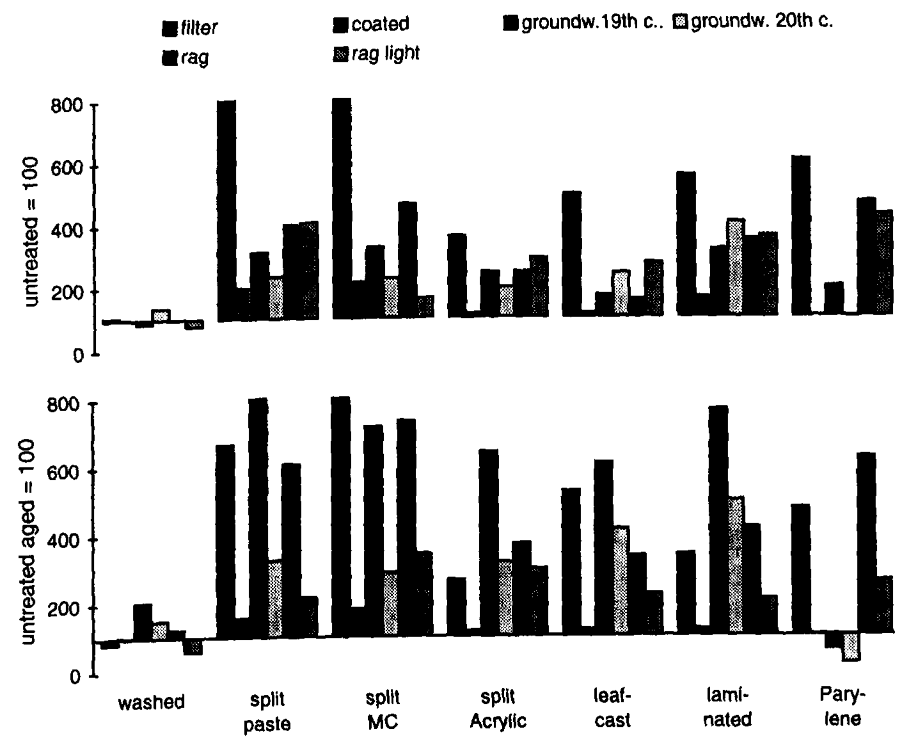


Fig. 4: Relative strengthening effect given as arithmetic middle: sqrt(MD*CD)

5. Table 3 is showing the relative change as percent of the untreated control, before and after ageing. Fig. 4–8 are showing, for clearer presentation, the numbers, either the measured ones or the computed relative changes, in form of diagrams.

EVALUATION OF RESULTS: STRENGTHENING EFFECT

As stated above, only one measurement was chosen to represent the term "strength" or "strengthening effect": tensile strength after one defined fold. From the upper part of Fig. 4 it becomes clear that not all treatments really have a significant strengthening effect on all papers. As none of the treated paper was so weak that it really needed to be strengthened, this issue is of no relevance. Rather, in this actual state, it demonstrates a strong valid principle in any conservation treatment. A good conservation procedure should change as little as possible the original features, while at the same time effectively arrest deterioration of the object being treated. The coated paper, e.g., which is "very strong" (class I) [7] and

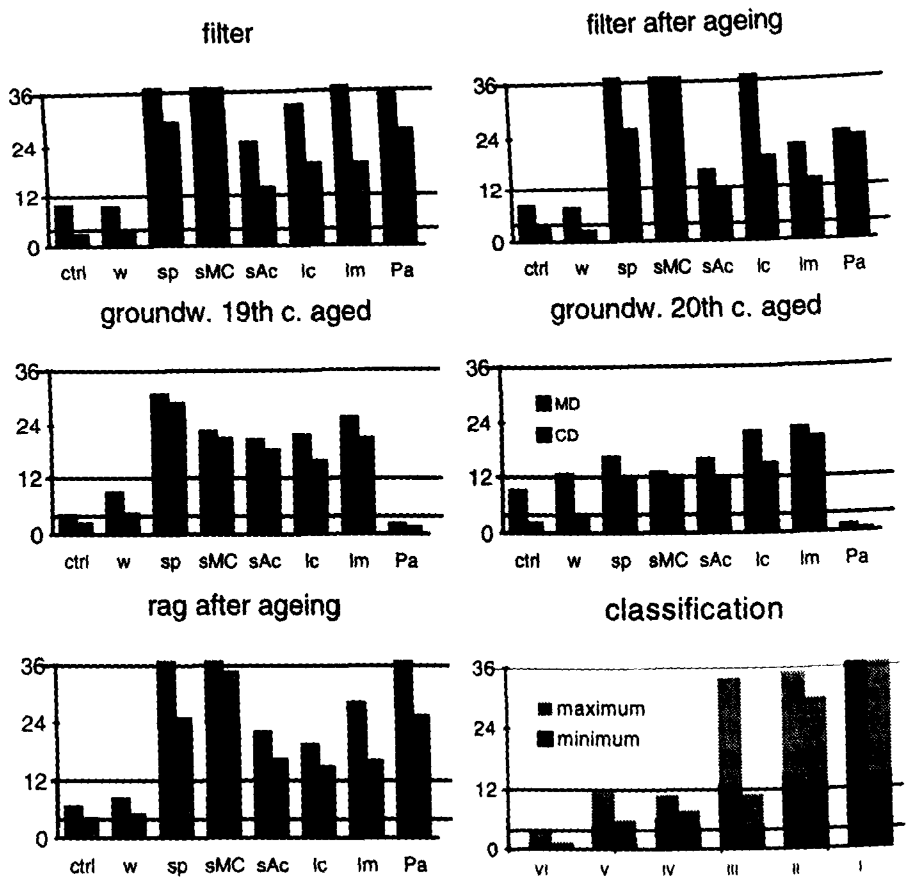


Fig. 5: Increase of Tensile post fold in terms of usability classification[7]

does not need to be strengthened, became even stronger up to the double by splitting using paste or MC as adhesive for the core. By overall strengthening in the leafcasting machine and by coating with Parylene, however, the strength was increased only by a small percentage: nearter to the original. Of some importance may be that the strength of one of the groundwood papers (20th cent.), indeed "usable without restriction" (class III)[7] but fulfilling just the minimal requirements of this class, is nearly not touched by the Parylene treatment. By all other treatments the strength of this paper is at least doubled or nearly doubled (splitting using an acrylic: 195%). The strength of the filter paper, which, due to its production without sizing and its intended use for technical purposes, would be

"to be used with care" (class V)[7] if it were used for printing, is improved at least more than three times by any treatment.

More important is the effect on the papers after ageing. Three papers, namely groundwood 19th, groundwood 20th and rag, are declassified by accelerated ageing from class III[7] "usable without restriction", to class V: "to be used with care". From Fig. 5 it can be seen that any treatment with the exception of Parylene has brought them to class II: "strong".

Fig. 6 is demonstrating that the ageing behaviour of the old papers – with the exception of groundwood coated with Parylene – is significantly improved. On the ageing behaviour of the new papers – filter and coated – the splitting methods and lamination seem to have a slightly negative influence, but the elevant data must not be overestimated. The absolute strength values of the two split papers after ageing are by far higher than that of the untreated control. Very striking, however, is the effect of Parylene coating on the groundwood papers after ageing. Both such papers are in a much worse condition than the control samples. Possibly this has to do with the observation done recently that paper aged in a staple is suffering significantly greater decay than when aged as single sheets[18,19]. The Parylene coating might produce an airtight closure and retain volatile degradation products which provoke further decay, what may also be the reason for the enhanced decay rate in the inner of a staple. The other strengthening treatments seem not to retain these volatile degradation products. Obviously, they can evaporate from the upper layers of the split samples and through the thin strengthening tissue produced in the leafcasting machine; more conspicuous is that this seems to be the case also with the thin acrylic foil or layer of hotmelt used for lamination.

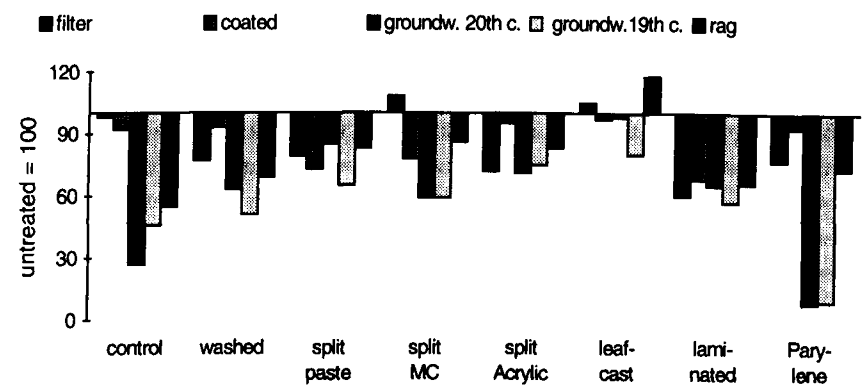


Fig. 6: Relative change of strength caused by ageing

Table 4: Thickness and stiffness

Thickness(µm)	control	washed	split paste	split MC	split Acrylic	leafcast	lami-nated	Pary-lene
filter	136	156	147	116	209	114	178	151
coated	101	110	145	126	234	135	168	104
groundwood 19th century	71	74	128	108	130	95	145	79
groundwood 20th century	72	75	117	92	128	81	130	74
rag	132	129	145	136	256	118	163	134
Stiffness (N)								
filter	0,14	0,15	0,15	0,12	0,22	0,11	0,20	0,16
coated	1,40	1,43	3,05	2,48	4,32	1,54	2,46	1,47
groundwood 19th century	0,13	0,21	0,67	0,72	0,41	0,20	0,54	0,47
groundwood 20th century	0,20	0,18	0,70	0,30	0,31	0,18	1,23	0,25
rag	0,19	0,12	0,62	0,93	0,43	0,31	0,90	0,23

AESTHETICS

As it is very difficult to describe such a delicate matter as "aesthetic quality" of a restoration treatment in terms to be comprehended generally, three qualities have been chosen that, on the one hand, can be measured, and, on the other, are of impact on aesthetics. These qualities are: Thickness (Table 4, Fig. 7 upper part), Stiffness[20] (Table 4, Fig. 7 lower part) and Colour change according to the CIE L*ab system (Table 5, Fig. 8). Additionally fifteen different persons, five restorers, five librarians acquainted with old, rare and valuable books and five persons from outside the world of books and the world of conservation, have been asked to give a ranking what of the six samples, differentiated by the treatment, in each of the five groups of paper they think to have suffered the slightest, second slightest change, or, in other words, are, in their aesthetic appearance, nearest, second nearest etc. to the untreated control. The librarians and even more the outsiders, who were not familiar with restoration treatments, gave their ranking impartially. The restorers, of course, understood, more or less, what strengthening method was used, so that personal preferences could influence their ranking. There was, however, no significant difference between the rankings done by the three groups. Generally, the correlation in terms of mathematics[21] is low: Kendall coefficient between 0,5 and 0,77. The results of this subjective assessment are given in Fig. 9.

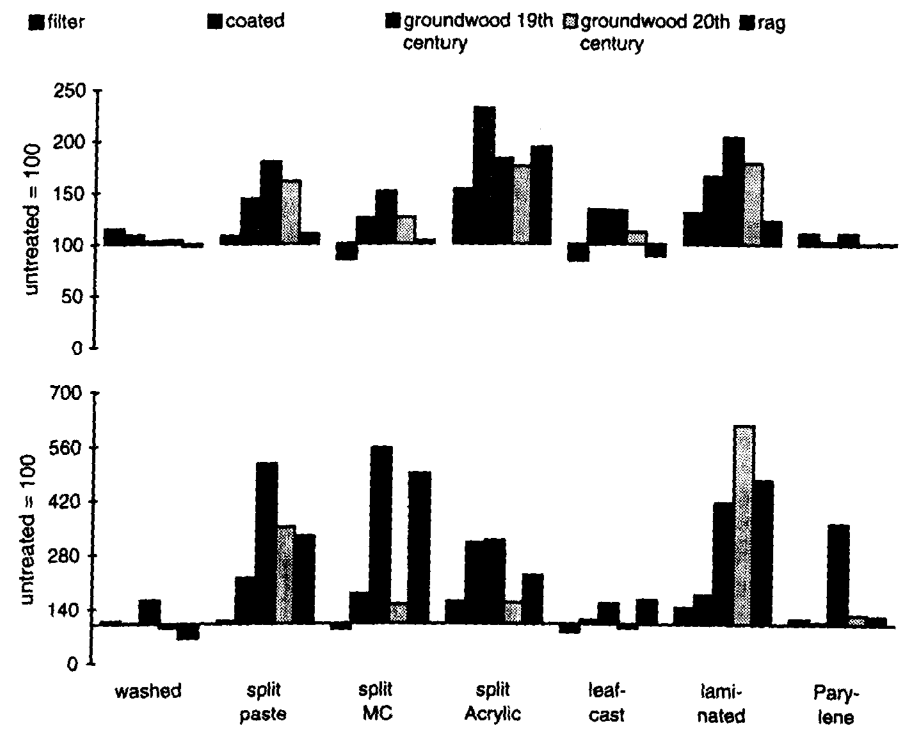


Fig. 7: Relative change of thickness (upper part) and stiffness (lower part)

Thickness and Stiffness

The generally smallest change in thickness is resulted from Parylene coating and overall strengthening in the leafcasting machine. Parylene almost does nearly not affect thickness. Papers which are somewhat fleecy, as filter and old rag, become a little bit thinner by the pressing that is an unavoidable part of the leafcasting process. With the others the thin tissue on the surface is hardly measurable; it seems to be pressed into the surface even of the smooth papers, i.e. the coated one and the 20th century groundwood.

All splitting processes provoke an increased thickness, less if paste or MC is used as adhesive for the core, more with the acrylic. The lower compatibility of synthetics with paper can also be seen from the increased thickness of the laminated papers.

Table 5: Colour change: CIE L*ab

		control	washed	split paste	split MC	split Acrylic	leaf cast	lami-nated	Pary-lene
filter									
L*:	unaged	94,3	93,2	91,9	88,9	94,6	93,7	94,2	94,1
brightness	aged	89,1	87,6	86,9	77,7	88,4	88,1	85,4	88,8
a*	unaged	0,0	0,1	0,3	-0,1	0,0	0,1	0,1	0,2
green-red	aged	1,8	2,1	2,3	3,5	2,1	2,0	2,5	1,8
b*:	unaged	5,2	6,3	6,8	7,0	6,2	5,9	6,9	6,1
blue-yellow	aged	11,5	16,5	18,9	20,0	11,7	13,2	16,6	10,7
coated									
L*:	unaged	94,9	94,0	93,9	93,9	96,1	95,3	94,8	96,0
brightness	aged	92,4	92,4	91,4	91,0	93,8	92,5	86,0	93,2
a*	unaged	0,9	0,6	0,6	0,7	1,6	0,8	1,3	1,6
green-red	aged	0,4	0,4	0,6	0,7	0,5	0,4	1,8	0,0
b*:	unaged	-2,3	-0,3	0,8	0,2	-4,9	-0,9	-3,7	-4,9
blue-yellow	aged	10,3	10,2	10,8	12,1	6,4	9,1	23,3	6,4
groundwood 19th century									
L*:	unaged	85,7	85,6	84,7	82,9	82,59	84,7	85,3	82,1
brightness	aged	79,6	80,8	80,5	78,8	75,21	80	75,2	70,9
a*	unaged	2,3	2,32	2,19	2,71	3,02	2,3	2,57	4,35
green-red	aged	5,51	4,66	4,64	5,24	7,54	4,66	6,97	9
b*:	unaged	19,4	18,7	21,7	22,5	20,79	20,4	19,1	23,8
blue-yellow	aged	22,9	22,9	26	26,1	28,87	23,7	28,5	26,8
groundwood 20th century									
L*:	unaged	79,5	78,5	75,2	73,4	72	75	79,2	79,6
brightness	aged	75,4	72,7	72,6	72,3	68,38	73,4	69,9	66,2
a*	unaged	5,63	3,68	3,61	4,15	5,13	4,04	4,3	4,98
green-red	aged	7,63	5,86	5,62	6,29	7,64	6,75	7,71	9,18
b*:	umaged	23,1	18,7	20,7	21,8	22,93	21,1	19,4	21,3
blue-yellow	aged	25,5	22,9	24,6	25,4	26,25	26,3	25,9	24
rag light									
L*:	unaged	78,9	82,9	77,9	83,9	84,1	81,6	83,3	80,0
brightness	aged	78,7	76,9	72,2	71,9	76,5	74,2	76,9	69,0
a*	unaged	2,9	2,3	2,2	2,0	2,5	2,9	2,4	3,1
green-red	aged	3,5	3,9	5,1	4,1	3,9	3,4	3,7	5,3
b*:	unaged	12,8	14,8	12,6	13,1	14,2	15,1	14,2	15,5
blue-yellow	aged	15,9	17,6	20,5	19,5	16,5	15,5	16,8	18,0
rag dark									
L*:	unaged	73,1	73,7	76,2	79,7	74,2	80,6	82,3	74,5
brightness	aged	57,0	71,2	65,6	64,2	67,5	55,9	62,2	
a*	unaged	3,0	4,0	4,3	3,1	4,7	4,0	2,3	4,7
green-red	aged	5,0	5,3	5,9	5,6	4,8	3,9	4,6	
b*:	unaged	13,7	15,6	17,8	14,9	16,7	17,6	12,5	18,6
blue-yellow	aged	13,9	19,4	19,2	19,4	16,0	11,1	14,0	

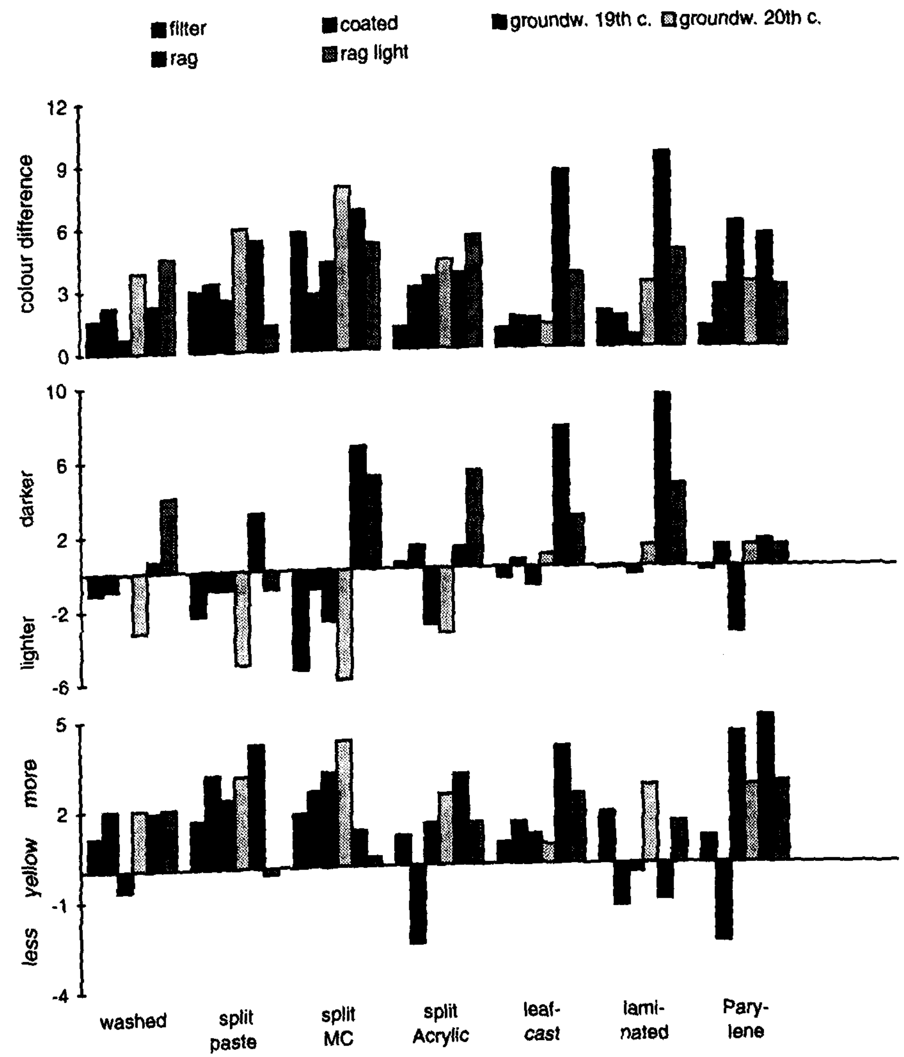
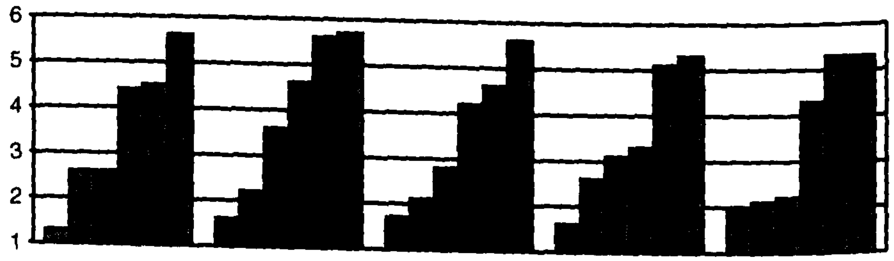


Fig. 8: Colour change

Regarding the change of stiffness, there is a clear superiority of the leafcasting process; likewise the Parylene treatment is resulting in nearly no increased stiffness. The exception (groundwood 20th century) may again be the result of uneven application. The papers have been Parylene treated as book blocks slightly fanned, as it is the normal condition of this treatment. This method results in half-



filter	coated	gr.19th c.	gr.20th c.	rag
leafcast	Parylene	leafcast	Parylene	leafcast
split paste	laminated	Parylene	leafcast	Parylene
Parylene	split MC	split paste	split MC	split paste
laminated	split paste	split MC	split paste	split MC
split MC	split Acrylic	split Acrylic	split Acrylic	laminated
split Acrylic	leafcast	laminated	laminated	split Acrylic

Fig. 9: Personal assessment

moon-shaped parts where less coating is achieved, down to none, while the outside parts of a sheet get a more intensive coating.

Splitting and lamination methods result in an increase in thickness up to more than five times. The measured numbers are in a wide range: obviously the result of unevenly applied adhesive

Colour Change

Any treatment changed the colour of the samples, and it is difficult to see a regularity. Possibly the old rag paper must be excluded from observation, because it is too irregular in itself. A colour measurement may only give reasonable results if exactly the same spot is examned before and after a treatment instead of different samples of the same kind, as it was done for this project.

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Restricted to the more uniform, i.e. the machine made papers, overall strengthening in the leafcasting machine has obviously effected the smallest colour

change: the samples have become a little bit more yellow. Any splitting method had the same result, but in a remarkably higher degree. Splitting, mostly if done with starch or MC as adhesive for the core, slightly increases the brightness of the paper, as explained by the removal of coloured products of paper decay in the enzyme bath which is used to remove the support paper. Note that: the colour of these decay products which constitute yellowing is not yellow in the chronometric meaning; it is "dark". The "yellow" tint of the papers has been slightly increased by the splitting process. All these colour changes are beyond visibility.

Subjective Assessment

As just mentioned, the ranking done by fifteen persons consulted for their opinion which of the six treatments have changed the five papers the least, more and the most, is far from being uniform. Regarding filter paper, the older, and in the context of aesthetics more important, the more fleecy groundwood and historic rag, leafcasting is nearest to the principle that conservation treatment should not change the aesthetic appearance of an object. For smooth papers, i.e. for coated and calandered ones, as is the newer groundwood, Parylene is the winner. Possibly Parylene is the method of the future for coated papers, when graphs of artistic value and therefore, if damaged, to be restored in the original format, will come into the restoration workshop.

CONCLUSION

As a general result it can be stated, that splitting, overall strengthening in the leafcasting machine and laminating give good strength to paper endangered by brittleness and have a good ageing stability. From the aesthetic point of view leafcasting turns out to be superior to the other methods. If really brittle papers are concerned, as they participated in this project only in their state after ageing, this statement might need to be limited: Overall strengthening by leafcasting means that the strengthening fibre is put onto the surface of the object, while for splitting it is put into the interior. Possibly for brittle paper the tissue must be made thicker: so thick that the aesthetic appearance is affected. For splitting of re ally brittle paper a thicker core might be necessary, again with negative influence on aesthetics, i.e. on thickness and stiffness. Any synthetic adhesive, it might be used for the core in splitting or as hotmelt for laminating was found to have a negative influence on the papers as compared to starch and methyl cellulose. Parylene, on the other hand, again a synthetic, gave surprisingly positive results: very satisfactory for modern smooth papers, best apt for the coated. Highly alarming, however, is the negative influence of this treatment on the ageing behaviour of groundwood paper. Its mechanism and the relevance of the results of accelerated ageing to the real ageing behaviour must be further studied.

SUMMARIES

The Effect of Different Strengthening Methods on Different Kinds of Paper

Five different papers, three old ones, as they might be the object of a strengthening treatment in the restoration workshop, have been strengthened according to four different relevant treatments (or six, as one of them was used in three variants), submitted to accelerated ageing and checked for the strengthening effect, its stability and for change in aesthetic appearance. All methods, namely splitting using different adhesives for the core, overall strengthening in the leafcasting machine, lamination using a heatset acrylic and Parylene coating, gave sufficient strength to the papers, Parylene coating with the alarming exception that it provokes enhanced decay during accelerated ageing of groundwood paper. The impact of the different strengthening methods is depending on the kind of paper. Leafcasting seems to be best apt for old, Parylene coating for modern supercalandered and coated paper. As one of the methods, i.e. overall strengthening in the leafcasting machine is not very well known in the conservation community, a more detailed description is given to explain the procedure.

L'effet des différentes méthodes de consolidation des différentes sortes de papier

Cinq différentes sortes de papier, dont trois anciennes, dans l'état où elles se trouvaient lorsqu'elles sont arrivées dans l'atelier de restauration afin d'y être consolidées, ont été traitées selon quatre méthodes différentes (ou selon six, car une des méthodes a été appliquée en trois variantes), puis soumises à un vieillissement accéléré et testées sur l'effet de consolidation obtenu ainsi que sur leur résistance au vieillissement et sur le changement de leur apparence esthétique. Toutes les méthodes, c'est-à-dire l'exfoliation du papier en utilisant différentes colles pour le noyau, le renforcement de la surface avec une couche de fibre à l'aide d'une machine, le laminage avec une résine acrylique et l'enduction de parylène, donnent une solidité suffisante aux papiers avec l'exception alarmante que le parylène provoque lors du vieillissement accéléré une dégradation nettement plus rapide du papier de pâte mécanique. L'influence des différentes méthodes de consolidation sur l'apparence esthétique du papier varie selon les différentes sortes de papier. Le renforcement mécanique de la surface avec une couche de fibre semble être la méthode la mieux adaptée pour les papiers anciens alors que le procédé au parylène convient aux papiers modernes hypercalandrés et aux papiers couchés. La méthode du renforcement de la surface en utilisant un laminoir n'est pas très connue dans le monde de la restauration, on donnera une description plus détaillée pour expliquer la procédure.

Die Wirkung verschiedener Festigungsmethoden auf verschiedene Papierarten

Fünf verschiedene Papierarten, davon drei alte, wie sie zur Festigung in die Restaurierwerkstatt kommen mögen, wurden nach vier verschiedenen Methoden entsprechend behandelt (oder nach sechs, da eine in drei Varianten angewandt wurde), dann beschleunigt gealtert und auf die erzielte Festigungswirkung, deren Alterungsbeständigkeit und auf die Veränderung des ästhetischen Erscheinungsbildes untersucht. Alle Methoden, d.h. Papierspalten unter Verwendung verschiedener Klebstoffe für den Kern, Übervliesen im Anfasergerät, Laminieren mit einem Acrylat-Schmelzkleber und Beschichten mit Parylene geben hinreichend Festigkeit, Parylene freilich mit der alarmierenden Ausnahme, daß es beim beschleunigten Altern den Abbau von Holzschliffpapier deutlich befördert. Der Einfluß der verschiedenen Festigungsmethoden auf das ästhetische Erscheinungsbild unterscheidet sich nach den Papierarten. Für alte Papiere erscheint Anfasern als am besten geeignet, für moderne kalandrierte und gestrichene das Parylene-Verfahren.

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Influence of Paper Raw Materials and Technological Conditions of Paper Manufacture on Paper Ageing

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INTRODUCTION

Paper continues to be one of the major transmitters and carriers of written heritage of our time. But also paper does not endure forever, and is subject to ageing in the same way as all organic substances. Paper ageing has developed into a major problem of our time and is studied by restorers and conservators in archives, libraries, museums and galleries. In a wider context it is high time also for the parties involved in paper manufacture, printing, sale and publishing to join the research of the problems relating to paper ageing, supported as necessary by relevant institutions, so that by the adoption of appropriate recommendations and standards the types and manner of use of paper most suitable for particular applications would be determined, and the criteria for evaluation and storage of written cultural heritage would be established.

The mechanism of paper ageing is influenced by numerous interactions between paper components and the substances of environmental origin, with its impact shown in particular in deteriorated mechanical strength, chemical stability and optical characteristics of paper.

The terms *durability* and permanence describe longevity of paper. While the permanence of paper depends on chemical resistance of its components and the influence of external factors, paper durability depends mainly on physical and mechanical characteristics of principal raw materials (fibres, fillers, sizing agents), additives and on contamination of these by ions from the environment, the action of light, heat, humidity and microorganisms. The term "paper ageing" refers primarily to deteriorated mechanical strength, chemical stability and optical characteristics of paper.

Paper ageing can basically be attributed to three *principal parameters*, both endogenous and exogenous (Figure 1):

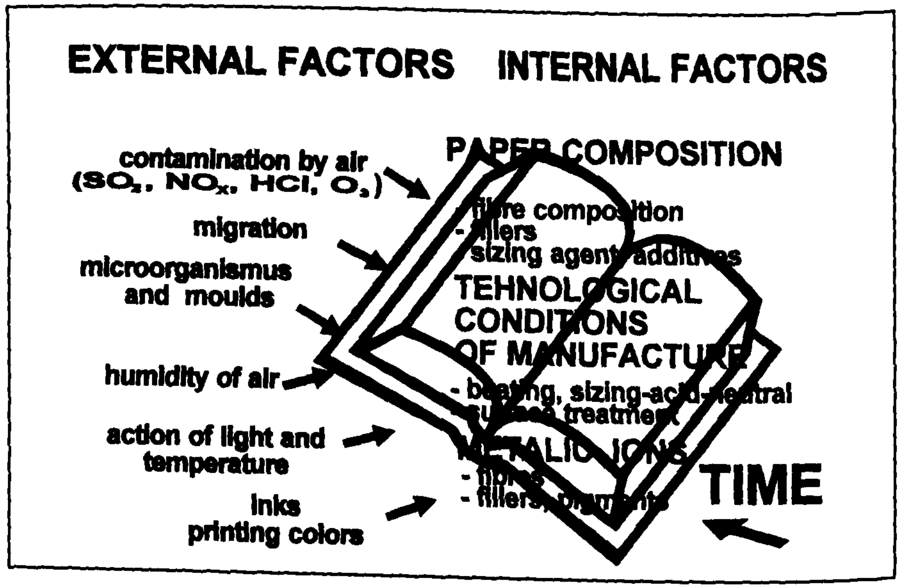

Fig. 1: The influence of internal and external factors on paper ageing.

- causes resulting from inadequate composition of pulp fibres and the rest of raw materials, and from technological conditions of paper manufacture,
- the influence brought about by processes of writing (inks), printing (printing colours) and paper processing and use in general,
- contamination by air (SO_2, NO_x,O_3), action of light, increased temperature and humidity of the atmosphere, neither should we disregard the action of microorganisms and moulds.

The difference in quality of individual types of paper lies in their overall composition with regard to raw materials. The properties of modern types of paper may appear very similar to a non-professional. Only by comparing their chemical, physical, mechanical and optical characteristics, and by natural and artificial ageing, can qualitative differences between individual types of paper be identified, in particular those relating to their use today as well as several hundred years from now.

Study of Permanence and Durability of Paper

In the framework of the "Study of Mechanism of Paper Ageing" research was mainly focused on the influence of internal factors: composition of cellulose fibres

and the rest of the raw materials included in each of the selected types of natural and surface-treated paper on permanence and durability under extreme conditions of artificial ageing – increased temperature and relative humidity, action of light excluded.

Selection of Paper and Methods of Testing

During the research more than 20 specimens of paper were examined, and from those 8 specimens of natural paper and 6 specimens of pigmented and coated paper were chosen as research results (Tables 1 and 2).

Table 1: Natural paper grades with respect to composition of raw materials and technology of manufacture

Paper grade I	Origin	Fibre composition	Filler	Sizing agent	Optical whitener	Sizing	Grammage g/m²
1. Permanent	Semi-industrial	50% cotton 50% hemp	$CaCO_3$	AKD	no	neutral	80
2. Permanent	Semi-industrial	20% cotton 40% softwood pulp 40% hardwood pulp	$CaCO_3$	AKD	no	neutral	70
3. Woodfree	Semi-industrial	50% softwood pulp 50% hardwood pulp	$CaCO_3$	AKD	no	neutral	60
4. Wood containing	Semi-industrial	50% CTMP 50% pulp	$CaCO_3$	AKD	no	neutral	60
5. Recycled	Industrial	30% deinking 30% woodfree w.p. 30% SGW	$CaCO_3$	AKD	no	neutral	70
6. Recycled	Industrial	60% deinking 35% woodfree w.p. 5% waste paper	$CaCO_3$	AKD	yes	neutral	70
7. Woodfree	Industrial	40% softwood pulp 60% hardwood pulp with Cl	Clay	rosine size	yes	acid	80
8. Woodfree ("Bio")	Industrial	60% softwood 40% hardwood Cl free	Clay	rosine size	no	acid	80

Specimens of natural paper (1.–8., Table 1) were classified according to the composition of pulp fibres into woodfree, woodcontaining and recycled paper, manufactured (in neutral or acidic system by using $CaCO_3$ or clay as filler) by a semi-industrial plant or available in the market in the form of industrial product. Woodfree papers from the ICP semi-industrial production machine were made in a neutral system, by using AKD sizing agent, from annual plants and cotton; cotton and quality pulp of coniferous and deciduous trees (group of permanent papers); and a mixture of pulp fibres. Industrial specimens of woodfree paper were made in an acidic system of sizing, and they differed in the composition of their pulp fibres, with one containing chlorine-bleached pulp and the other containing the pulp bleached without using chlorine. Wood-containing papers contained 50% of CTMP. The two specimens of industrially produced recycled paper differed in the proportion of deinking fibres, groundwood, waste paper and fresh pulp fibres in recycled pulp.

The group of surface-treated papers (1.A.–3.A., Table 2) was defined by the composition of pulp fibres in base paper and the type of coating (thickness of coating, type of pigment used clay or calcium carbonate). Woodfree base paper deriving from industrial production was coated in laboratory by clay and $CaCO_3$.

Table 2: Surface treated paper grades with respect to base paper and type of surface treatment

Paper grade II	Origin	Base paper	Coaating g/m_2	Pigment	Binder	Co-binder	Optical whitener
1.A. Woodfree coated paper	Laboratory coated paper	Industrial woodfree base paper	15	Clay	SB latex 1	no	yes
1.B. Woodfree coated paper	Laboratory coated paper	Industrial woodfree base paper	15	$CaCO_3$	SB latex 1	no	yes
2.A. Recycled pigmented paper	Industrial product	95% deinking, 5% Sa pulp	5–6	Clay	SB latex 2	starch	no
2.B. Recycled pigmented paper	Industrial experiment	95% deinking, 5% Sa pulp	5–6	$CaCO_3$ 35% Clay 65%	SB latex 2	starch	no
3.A. Coated recycled paper	Semiindustrial experiment (Dixon)	Base paper grade I. / 5.	15	Clay	SB latex 3	CMC	no
3.B. Coated recycled paper	Semiindustrial experiment (Dixon)	Base paper grade I. / 5.	15	$CaCO_3$	SB latex 3	CMC	no

Industrial paper from recycled base paper was pigmented by clay and, in semi-industrial production, also by a mixture of clay and $CaCO_3$. In the specimen of the third group, neutral recycled industrial paper of the first group (group I./5.) was used as the basis and was coated by using the ICP semi-industrial coater under identical conditions by clay and $CaCO_3$ pigment.

The selected specimens of natural and surface-treated papers were exposed to conditions of artificial ageing in accordance with ISO 9706 at 80±1°C and 65±2% relative humidity of air, excluding the action of light, over periods of 6, 12 and 24 days.

For all conditioned paper specimens, permanence and durability were determined prior and subsequent to artificial ageing by the international standard method used for each particular characteristic:

- basic characteristics (grammage, bulkiness, moisture content, ash or filler content),
- chemical stability: pH, lignin content (Kappa number), Degree of polymerisation (limit viscosity), Degree of oxidation (Cu number),
- mechanical strength: tensile breaking strength, elongation, bursting and tearing resistance, folding endurance, stiffness,
- optical stability: whiteness, brightness, yellowing, opacity, scattering and absorption coefficient of light,
- surface characteristics: porosity, surface wettability-angle of contact.

RESULTS AND COMMENTARY

The results of measurements of basic characteristics, chemical stability, mechanical strength and surface characteristics performed prior and subsequent to artificial ageing on natural and surface-treated specimens of paper are shown in corresponding figures.

BASIC CHARACTERISTICS

On the basis of monitoring the influence of artificial ageing on each of the selected specimens of natural (permanent, wood-containing, recycled) and surface-finished (pigmented, recycled and coated woodfree) papers, no great changes were observed in the obtained values for grammage, bulkiness, moisture, ash and filler content of most natural papers. A smaller decrease in grammage and bulkiness was observed in the case of wood-containing and coated papers. With pigmented papers, bulkiness slightly increased, grammage decreased a little, and ash content remained unchanged. In general it may be said that such very slight changes are due to non-uniformity and non-homogeneity of the specimens.

CHEMICAL STABILITY

Particular reactions relating to the decomposition of cellulose molecules were studied by means of standard chemical methods. Chemical stability of selected papers prior and subsequent to paper ageing was studied by measuring pH of the extract and Kappa number, and by determining limit viscosity, Cu number and α-cellulose. In the case of CTMP fibre papers, attempts at determining Kappa number were unsuccessful because of extremely low values. Because of inconstant dissolving of individual specimens of paper, the determination of α-cellulose also failed to yield repeatable results. In general, it may be said that, for measurements of viscosity and Cu number to be carried out as appropriate, adequate preparation of the paper specimen and complete dissolving are of great importance.

pH

The process of hydrolysis and oxidation relating to the decomposition of the cellulose molecule leads to the formation of carboxyl groups, which means that acidity of paper rises, while pH drops.

Hydrolysis and oxidation of the cellulose molecule are due to the action of acidic environmental factors or to increased acidity of acidic papers, with the presence of aluminium sulphate leading to the development of free acid i.e. H_2SO_4, which accelerates hydrolytic as well as oxidative decomposition of the cellulose molecule.

As most of paper specimens were made in neutral and alkaline medium, pH values ranged between 8.5 and 9.5, and pH did not undergo any major changes. In the case of natural papers made in acidic medium, also, pH was between 4.6 and 5.1, and acidity did not change substantially.

Viscosity

Determined on the basis of changes and decrease in viscosity in the process of artificial ageing were hydrolytic and oxidative decomposition of cellulose molecule,

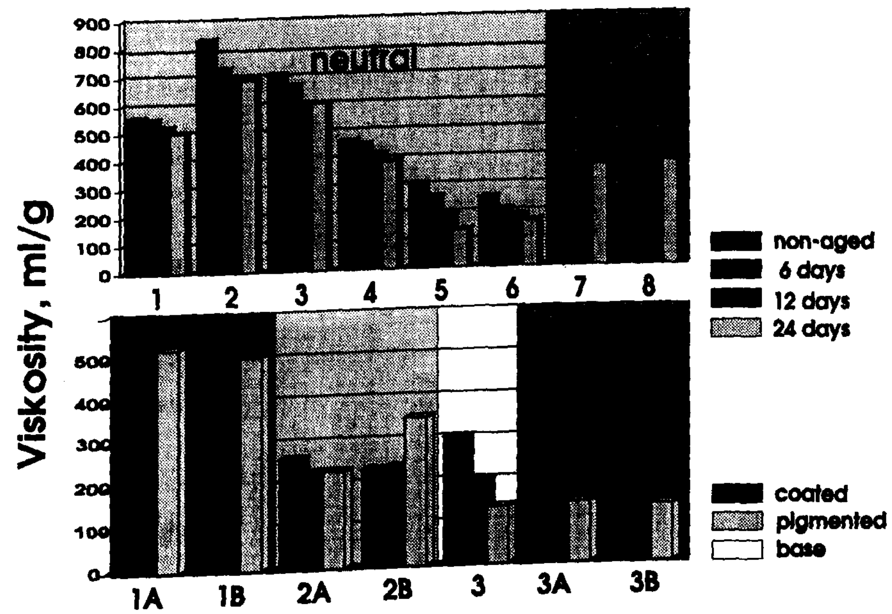

Fig. 2: Decomposition of cellulose molecule chain: limit viscosity (Ewnn method).

microbiological contamination, and chemical-mechanical decomposition relating to depolymerization of the molecule, which is evaluated on the basis of the decrease in average molar mass or degree of polymerization.

Figure 2 shows depolymerization of the cellulose molecule with all papers of limit viscosity according to the Ewnn method. Decrease in viscosity is most marked in acidic natural papers, where degradation in comparison with initial state is the greatest. The values relating to recycled paper are extremely low also, and their degradation develops with time. Thus it may be said that the recycled fibres having been used, were already very much decomposed and damaged. It is interesting that the degree of decomposition in the case of using CTMP fibres is considerable, but it does not deteriorate essentially with time and is much more favourable than in the case of recycled fibres. This could be explained by the fact that in the process of making CTMP fibres (heat, pressure, chemicals) long-chain molecules are not obtained. However, as the fibres are insignificantly damaged from chemical viewpoint, they exhibit considerable resistance to hydrolytic and oxidative decomposition, if paper manufacture is carried out in neutral medium and if there is no oxidizing action of external origin. Regardless of pigmentation, coating and pigment type, surface treatment has favourable effect on chemical stability of the cellulose chain, since initial values are retained to a considerable degree in comparison with natural papers.

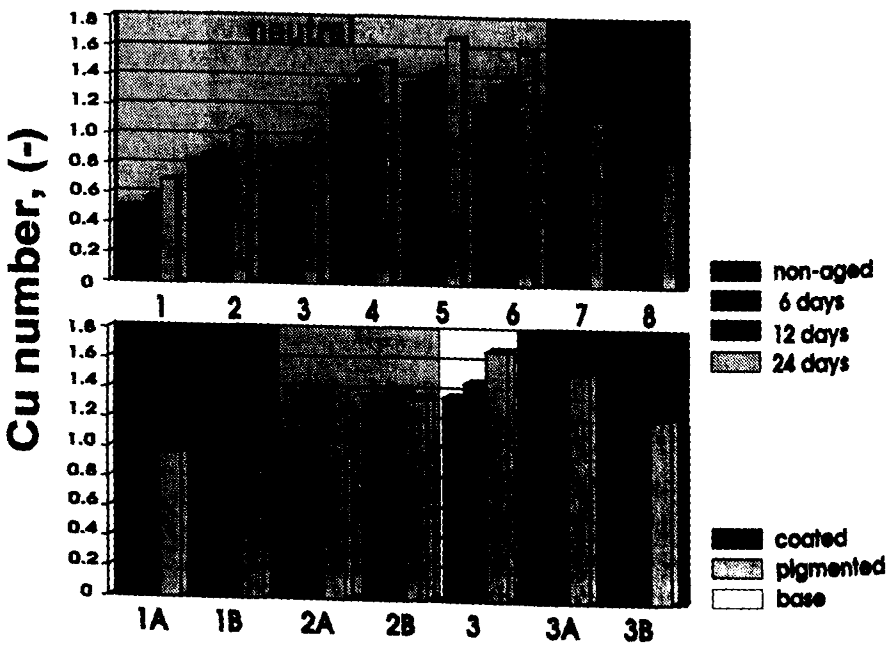

Fig. 3: Oxidative decomposition of cellulose molecule: Cu number

Cu number

Conditions relating to ageing increase the number of reductive groups from cellulose and hemicellulose, which are transformed in the process of oxidation from hydroxyl into aldehyde groups. Cu number increases with the increase in the degree of oxidation – but by such determination the quantitative level of reaction with respect to keto groups and subsequent carboxyl groups cannot be established.

The results of measurement of Cu number are shown in Figure 3 and reveal an increase in oxidative decomposition for all specimens of paper. Increased decomposition with respect to initial condition is by far the greatest in acidic natural papers. It is favourable that this value is lower in papers made from cellulose bleached without using chlorine. Very high values were obtained in the case of wood-containing and recycled papers, but increased oxidative decomposition due to ageing was not so marked as in the case of acidic papers, if aluminium sulphate was present.

Surface treatment of paper by pigmentation and coating will reduce oxidative decomposition in particular in the case of using recycled paper as the base. More favourable results were also obtained in the case of using $CaCO_3$ coating.

MECHANICAL STRENGTH

Mechanical strength of paper in the process of ageing is influenced by reactions between fibres in paper (fibre-to-fibre bond) and by reactions inside the cell walls of fibres. Changes – decrease in mechanical strength – are influenced by chemical reactions of hydrolytic and oxidative decomposition and lead to weaker interfibre bonding.

Due to the process of internal and external interfibre bonding (crosslinking) stabilization of individual forms of resistance and slight increase in mechanical strength are also possible.

The testing methods used included determination of tensile breaking strength, length, elongation, tearing and bursting resistance, folding endurance and stiffness.

Tensile breaking strength and elongation

In the process of depolymerization (hydrolysis, oxidation) stability of individual fibres is reduced, reflecting in decreased tensile strength and elongation. What increases, however, is the binding capacity between individual decomposed cellulose chains in the process of crosslinking – through the formation of covalent bond between hydrogen bridges of a particular molecule, which may in the process of ageing lead to stabilization of individual fibres. This may also increase static strength and crystallinity – the number of free, unreacted positions decreases, and this considerably reduces proneness to mechanical defects.

The results of decrease in tensile strength is minimum (slightly but not substantially higher than in acidic papers). Measurements. Figure 4, for all specimens of natural neutral papers confirm this. With some specimens, however, slight increase in fibre-to-fibre bonding was observed.

Tearing resistance

In general, tearing resistance of paper decreases with ageing. The results of measurements which are shown in Figure 4 reveal considerable decrease in tear resistance of natural acidic papers. With other papers, no substantial decrease was observed, which can be explained by increased fibre-to-fibre bonding and crosslinking, as could be easily seen in recycled paper in which no substantial changes were observed in spite of very low initial values. This outcome confirmed the previously obtained results of measurement of chemical characteristics. In the case of surface-treated papers with neutral base, also, this characteristic was found not to decrease substantially.

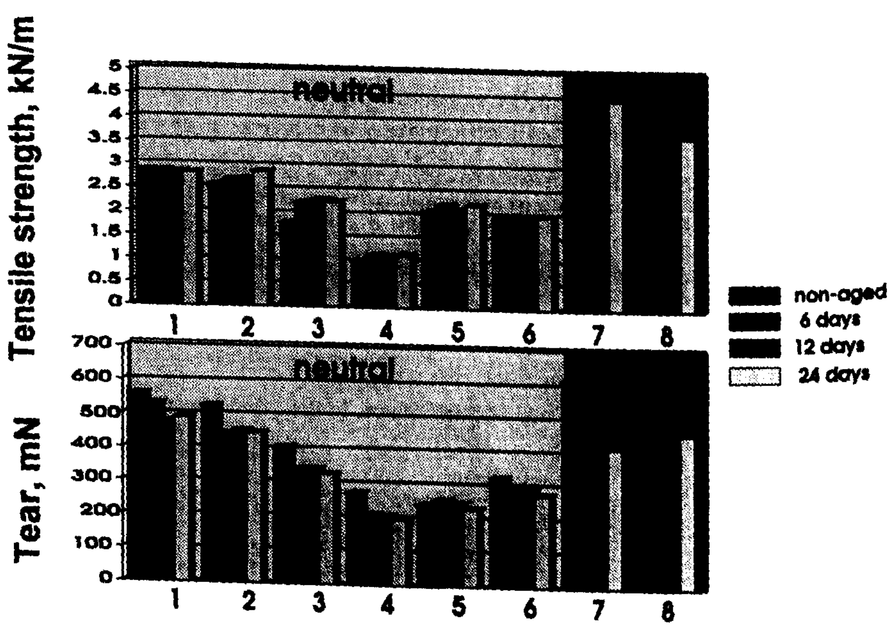

Fig. 4: Ageing effect of natural paper grades on mechanical properties: tearing and tensile breaking strength resistance.

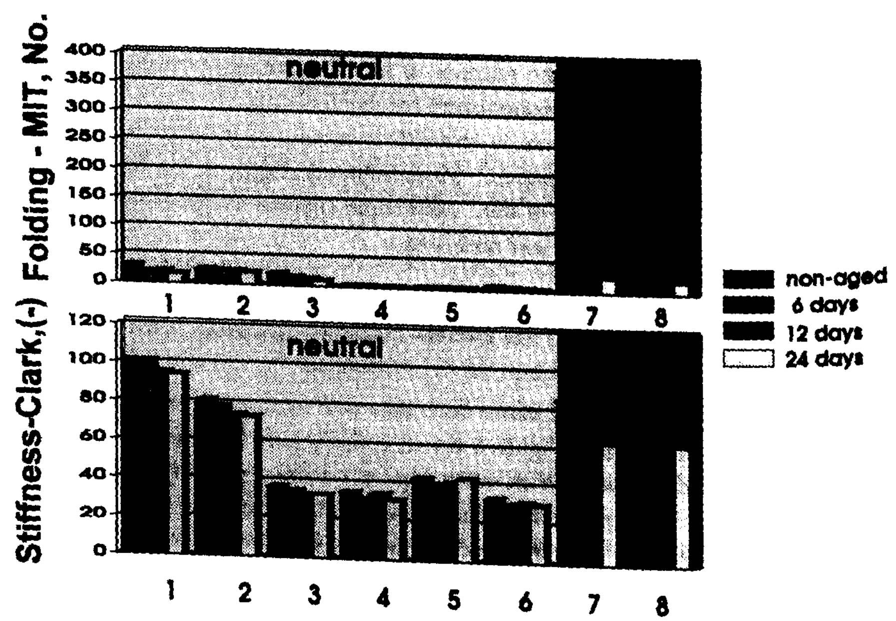

Fig. 5: Effect of ageing natural paper grades on mechanical properties: stiffness and folding endurance (MIT; 1000 g).

Folding endurance and stiffness

Crosslinking between cellulose chains and increased crystallinity have great impact on changes in folding endurance and stiffness of paper because of increasing fibre-to-fibre bonding (cf. Figure 5).

The decrease was most marked in the case of acidic papers, where no difference was observed between cellulose bleached by Cl and without it. With other natural papers, the values do not deteriorate substantially. Great stability was observed particularly in wood-containing and recycled papers, but initial values were also extremely low. Also in the case of pigmented and coated papers no major decrease was observed.

OPTICAL STABILITY

The effect of accelerated artificial ageing of selected specimens of paper on changes in optical characteristics was studied: whiteness, brightness, yellowing, and opacity, scattering coefficient and absorption of light by Kubelka-Munk method.

Whiteness, brightness, yellowing

With all of the selected specimens of natural as well as of surface-treated papers, considerable deterioration of optical characteristics of whiteness, brightness and yellowing was observed. This deterioration was the least marked in the case of natural permanent paper, and most marked in acidic paper filled with clay, regardless of the method of bleaching pulp fibres, and the same was also true of wood-containing and recycled papers.

In using calcium carbonate as pigment for pigmenting and coating purposes, when compared with clay, whiteness and brightness deteriorated, while yellowing was less marked (cf. Figure 6, 7).

In the case of oxidative decomposition of the low-molecular part of carbohydrates in particular, carbonyl groups develop, which have considerable influence on changes in and deterioration of whiteness, brightness and on increased yellowing. Carboxyl groups, in general, have a less marked impact on deterioration of the said characteristics, but may additionally enhance the influence of carbonyl groups, thus leading to further deterioration of optical stability. In the case of using high-yield pulp and wood-pulp, functional groups within lignin and extracts cause major changes in whiteness, brightness and yellowing. Yellowing, de-

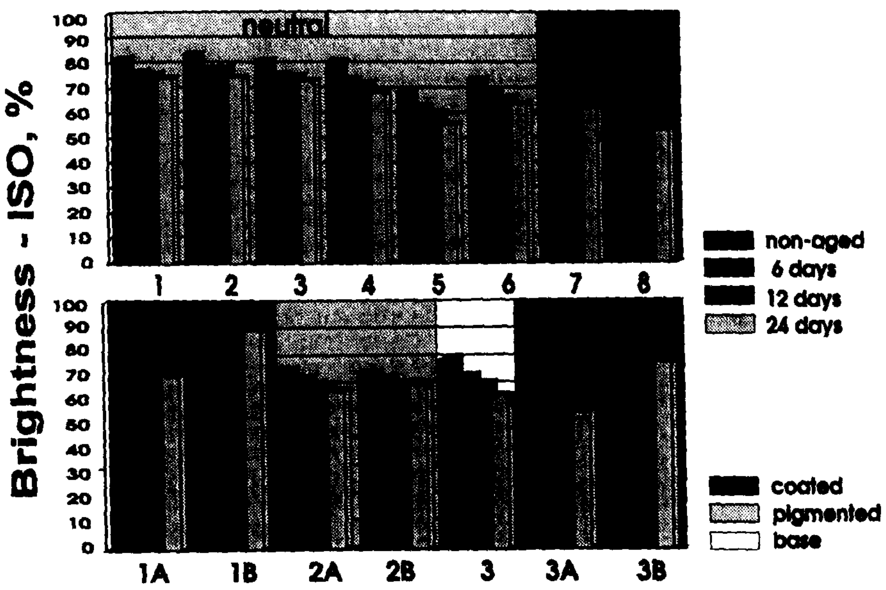

Fig. 6: Optical stability: brightness decrease.

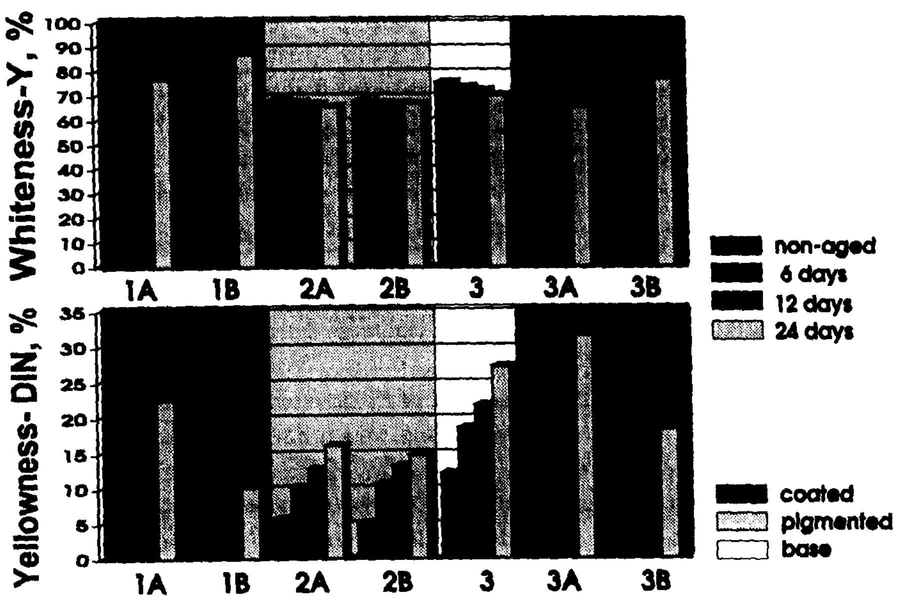

Fig. 7: Optical characteristics of surface treated papers: increase of yellowing.

creased whiteness or brightness may result from exposure to light, or may in the absence of light occur as the result of increased temperature or relative humidity of the atmosphere (as in the case of artificial ageing). In this way, new products of oxidation are obtained, and under favourable conditions these further accelerate decomposition and deteriorate optical characteristics. Metallic ions, such as Cu, Mn, Fe, cause accelerated yellowing and deteriorated whiteness and brightness both in the case of bleached and unbleached pulp fibres. These metallic ions are photocatalytic and are subject to considerable absorption in UV range, and are reduced thereby. They cause accelerated photo-induced decomposition of carbohydrates. Metallic oxides and hydroxides catalyze hydrolysis of the cellulose molecule even in the absence of acidic substances. Such reactions are always irreversible-unidirectional, and are even accelerated by increased temperature.

Opacity, scattering and absorption coefficient of light

With all natural and surface-finished papers, opacity will in conditions of artificial ageing increase (cf. Figures 8, 9), not because of light scattering but primarily due to very great increase in light absorption. With acidic and recycled papers, this is assumed to be due to increased crystallinity of cellulose fibres. Also in the case of surface-treated papers, opacity was found to increase considerably, primarily when clay was used as pigment, but mainly due to considerable increase in absorption coefficient. This effect, however, renders these papers not recommendable for further use, because in this way their resistance to external influences is reduced even more.

Surface Characteristics

Selected specimens of paper were also used to examine the influence of ageing on possible changes in surface porosity: Gurley method and surface wettability-angle of contact with water-surface hydrophilicity or hydrophobicity.

The results of measurements reveal that ageing does not cause any major changes in porosity, the exception being recycled papers, both those without surface treatment and the pigmented ones, where a slight increase in paper porosity was observed, which may not have favourable effect on durability if taking into consideration the action of factors of external origin.

The results of measurement of wetting (angle of contact) indicate that no major changes occurred on the surface of all neutral papers with the surface remaining more or less hydrophobic. With wood-containing papers, and in part also with

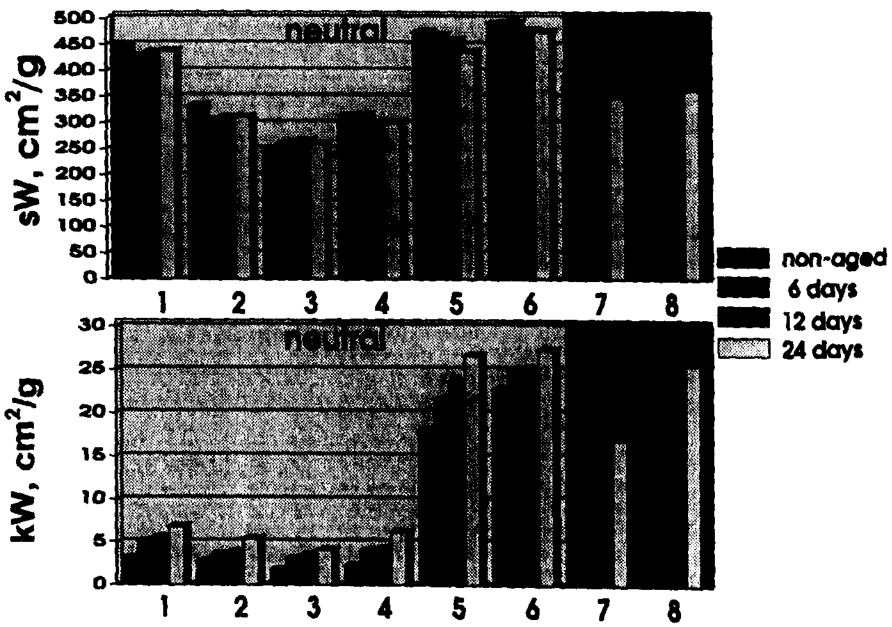

Fig. 8: Optical stability: effect of light scattering and absorption on the opacity of natural paper grades.

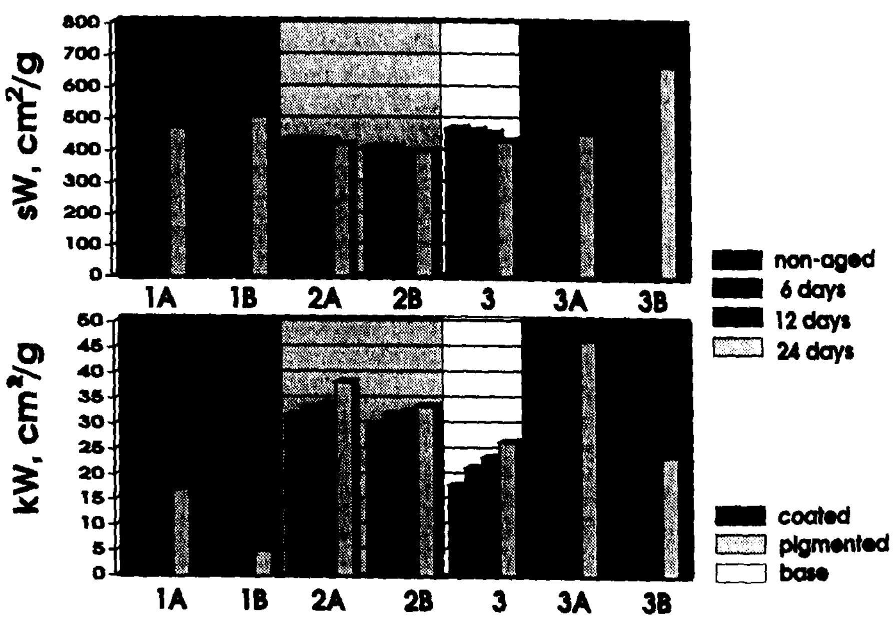

Fig. 9: Optical stability: effect of light scattering and absorption on the opacity of natural paper grades.

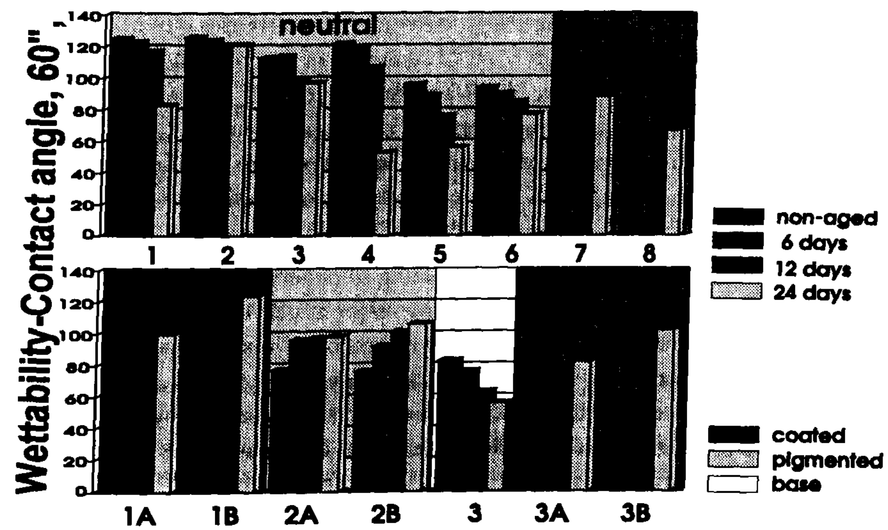

Fig. 10: Surface characteristics: changes in surface wettability, hydrophilicity or hydrophobicity measured with contact angle.

recycled natural paper, wetting contact angle decreases – surface hydrophilicity increases and reducing the durability if taking into consideration the action of factors of external origin.

It is noteworthy that, as shown in Figure 10, pigmenting and coating increase surface hydrophobicity of paper, with the effect being more marked in the case of $CaCO_3$ than clay, which is also favourable for decreasing the possibility of action on paper of such external factors as could lead to hydrolytic decomposition and oxidation of the cellulose molecule.

The results reveal that surface treatment of paper (surface sizing, pigmentation and coating) increases surface hydrophobicity of paper, with the effect more pronounced in the case of using $CaCO_3$ than pigment. The reason for this may be in greater crosslinking (interfibre bonding) on the surface resulting from the addition of polymeric bonds in connection with surface finishing.

CONCLUSION

The results of determination of chemical stability, mechanical strength, optical stability and surface characteristics of each of the selected types of natural and surface-treated paper in the process of artificial ageing have revealed the following:

- Use of recycled pulp fibres and high-yield mechanical fibres (CTMP, up to 50%) ensures considerably high level of retention of mechanical strength and chemical stability, but leads to significant deterioration of optical characteristics. In this connection, however, it needs to be pointed out that, with respect to initial condition existing prior to ageing, basic fibres are already very much decomposed, with the values of each particular form of resistance being much lower than is the case of quality pulp fibres of woodfree papers.
- Surface treatment by pigmenting and coating of papers made from alternative and recycled pulp fibres does not have any major impact on changes in chemical stability and mechanical strength. Deterioration of optical characteristics is slightly less marked when using calcium carbonate than pigment. This also has favourable effect on decrease in porosity and increase in surface hydrophobicity of all types of papers. This condition poses great advantage because it reduces the possibility of the action of external factors on paper surface.
- Use of quality primary pulp fibres ensures fairly good chemical, mechanical and optical stability regardless of the type of process used to obtain basic pulp fibres. The basic prerequisite for this, however, is that paper be made in a neutral medium, for it is well known, and our testing confirms this, that in long-time perspective the influence of acidic system of paper manufacture on final characteristics of paper is disastrous.

In conclusion let us say that the use of recycled fibres of undefined origin and of mechanical pulp fibres is adequate and recommendable for printing papers whose intended period of use does not exceed a few decades to a century. In the case of printed and written materials of permanent value, on the other hand, high quality primary pulp fibres must be used in a neutral medium in the absence of optical bleaching agents and with calcium carbonate as alkaline buffer reserve.

SUMMARIES

Influence of paper raw materials and technological conditions of paper manufacture on paper ageing

Quality difference between particular paper grades is to be found in their total raw material composition. The properties of modern paper grades can seem to be, for a non-expert, very similar. Only chemical, physical, mechanical and optical properties of particular paper grades as well as the test of natural and artificial ageing can show the difference in their quality. The applicability in present time and after several hundreds of years have to be considered above all.

The results of our research work confirmed the well known recognition of world wide investigations, that the use of high yield fibres, groundwood fibres, and recycled fibres of more or less

undefined source, is acceptable but recommended only for all those graphic papers and papers for general use in which permanence is intended to be no more than a few decades. For the printed and written material that represents permanent value, it is important to use quality primary pulp fibres during the manufacture in neutral or weak-alkaline medium, without optical brightening agents and using calcium carbonate as alkaline reserve, as defined by the ISO 9706 standard.

Influence de la matière première utilisée et des conditions de fabrication sur le vieillissement du papier

La différence de qualité entre les diverses sortes de papier repose sur la composition tout à fait différente de leur matière première. Aux yeux des profanes les propriétés des différentes sortes modernes de papier semblent être très similaires. Seules les propriétés chimiques, physiques, mécaniques et optiques des différentes sortes de papier ainsi que l'examen de leur vieillissement naturel ou artificiel peuvent mettre en évidence la différence de leur qualité. Il faut considérer en premier lieu leur applicabilité à des fins actuelles ainsi qu'après plusieurs centaines d'années.

Les résultats de nos travaux de recherche ont confirmé la conclusion bien établie par les investigations faites dans le monde entier, selon lesquelles l'utilisation de fibres à haut rendement, de fibres de pâte mécanique et de fibres recyclées d'origine plus ou moins indéterminée ne devrait intervenir que dans la fabrication de papiers graphiques ou de papiers à usage courant dont la résistance au vieillissement n'a pas besoin d'excéder quelques décennies. Pour les documents imprimés ou les écrits qui représentent une valeur à long terme il est important d'utiliser des fibres primaires et il faut que la fabrication se réalise en milieu neutre ou légèrement alcalin sans produit de blanchiment optique et avec du carbonate de calcium comme réserve alcaline, tel que c'est défini dans ISO 9706.

Der Einfluß des Rohstoffes und der Herstellungsbedingungen auf die Alterung von Papier

Der Qualitätsunterschied zwischen bestimmten Papierarten wird durch ihren Rohstoff bestimmt. Die Eigenschaften moderner Papierarten können in den Augen von Laien als sehr ähnlich erscheinen. Nur chemische, physikalische, mechanische und optische Eigenschaften bestimmter Papiere wie auch Untersuchungen zur wirklichen und beschleunigten Alterung können in solch einem Fall Qualitätsunterschiede aufzeigen. Die zweckentsprechende Benutzbarkeit soll an erster Stelle betrachtet werden in der Gegenwart und nach mehreren hundert Jahren

Die referierten Forschungsergebnisse bestätigen die wohlbekannte, auf weltweiter Forschung beruhende Erkenntnis, daß Hochausbeute-Fasern, von Holzschliff und Recycling-Fasern mehr oder weniger undefinierbarer Herkunft nur für solche graphischen und allgemein gebrauchten Papiere eingesetzt werden sollen, deren Alterungsbeständigkeit nur einige Jahrzehnte betragen muß. Für gedruckte und geschriebene Dokumente von langandauerndem Wert ist es wichtig, Primärfasern einzusetzen und im neutralen oder schwach alkalischen Bereich zu produzieren, ohne optische Aufheller und mit Calciumcarbonat als alkalische Reserve, wie in ISO 9706 definiert.

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The Conservation of the Dead Sea Scrolls in the Laboratories of the Israel Antiquities Authority in Jerusalem

by ESTHER BOYD-ALKALAY & LENA LIBMAN

INTRODUCTION

The Dead Sea Scrolls are possibly the most important archaeological findings of the last half century. After the first discovery in 1947, systematic archaeological searches were carried out in the Qumran area north of the Dead Sea, which was Jordania territory until the Six Day War of 1967. In the period until 1956 eleven caves were investigated in the area of Qumran on cliffs extending over a distance of 8 km.

Some of the scrolls were found wrapped in linen cloths in jars, others in niches in the walls of caves or on the floor buried in dust and partially disintegrated by the action of water, insects and moulds. After two thousand years in the caves the scrolls were stored under drastically different climatic conditions in the premises of the Rockefeller Museum, then Jordanian Jerusalem.

The majority of the scrolls are written on hides, some on papyrus. The languages are mainly Hebrew and Aramaic but a few are written in Greek. Most of the scrolls range in date between the second century BCE and about 70 CE. The scrolls include Biblical and Apocryphal texts as well as texts related to the Essenes, a sectarian community whose existence came to an end in 68 CE with the Roman invasion of the area.

SKIN MATERIAL

The skin of the Dead Sea Scrolls is of sheep and goats but it is neither leather nor parchment, as we understand these terms to-day. The skins were prepared differently – probably in compliance with rabbinical rules. As confirmed by analysis, the writing material is a kind of parchment lacking the lime which confers durability. The rules for preparing skins as writing material during talmudic times

specify three main steps: first, removal of the hair in an enzymatic dehairing bath containing some or all of the following: plants, animal fats, eggs, milk, wine, vinegar, urine, dung and salt. Second, treatment with flour in order to soften the hide and smoothen it, and third – unique for the Jews in Palestine – sprinkling it with a solution containing various vegetables and cracked gall nuts, which tanned the hides lightly on the surface. Cedar oil was applied to some of the skins as well. These treatments improved their durability and facilitated their use as writing material, which was usually carried out on the grain side. This sequence of treatments was corroborated in 1972 by chemical and histological examination of skins from Qumran by Dr. E. Reed of the Department of Leather Manufacture in the University of Leeds.

The resultant skin, called "gvil" in Hebrew, needed to be flattened out so that it could be written on but neither were the external layers pared off nor was it subjected to any other thinning process. Talmudic rules for preparing the hides enabled the artisans later to split the skins into two layers, the grain or thinner side, called "Klaf" (Hebrew for "peeling"), and the heavier flesh side, called "duksustos" (Greek for "thicker, inseparable"). The various empirical rules for treating hides over a period of 300 years and the many additives used in these times, such as oil, alums and other minerals, and tanning with various vegetables concentrations provided skins of different thicknesses and of colours varying from pale yellow to dark brown, also depending on the nature of the skin and the damage it suffered over the years.

THE INK

All the ink is carbon ink. Analyses of these inks by William S. Ginell of the Paul Getty Institute of Conservation (1993) revealed in them only trace amount of iron, copper, zinc, titanium and manganese. Identification of the inks as carbon or lampblack based inks is consistent with the results of analyses of residues found in ink pots discovered at the site in Qumran. There are, however, scrolls, such as the Genesis Apocryphon in the Shrine of the Book, Jerusalem, as well as fragments in the Israel Antiquities Authority's collection, which are written with an ink which appears to be quite different from that used for the other scrolls. The damage caused by this type of ink seems similar to the familiar darkened and disintegrated lines of writing caused by iron gallotannin ink. Ginell supports the conclusion that the ink used was nevertheless not iron ink He points out that the Genesis Apocryphon is the only major scroll written in Aramaic and he suggests that the texts came from an area where the ink ingredients or the techniques employed caused this rare type of degradation, which is indeed unusual for carbon inks.

Primary Storage and Conservation Treatment

By the end of 1959 most of the fragments that had been found and those that had been bought from Bedouins searching the area were arranged in the so-called "Scrollery" in the Rockefeller Museum in Jordanian East Jerusalem. The scrollery was a large room with some twenty trestle tables where fragments of the scrolls were placed between sheets of glass. Photographs dating from the fifties seem to show a lack of present-day awareness of environmental control. According to Reed[1], "the fragmentary condition of many of the scrolls was clearly due to indiscriminate handling on the part of the original finders. Much later sorting of masses of fragments could have been avoided if all attempts to flatten, unroll or flex the objects in any way had been resisted until laboratory conditioning was possible."

In these first years irreversible damage was caused by using cellotape™ for joining fragments and covering cracks. The scrolls were moistened and loosely flattened between plates of window glass without framing the edges. Harold Plenderleith, at this time Keeper of the Research Laboratories, British Museum, and Director of the International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome, was approached. He described[2] how he attempted to separate and analyze fragments contained in three boxes which had been sent to London. "Exposure overnight at 75 % relative humidity caused insufficient relaxation of the parchment. A further 6 hours at 80 % relative humidity made the membrane limp and various strata could be separated by careful manipulation with and ivory paper knife. A complication presented itself in the form of black bituminous substances which permeated the tissue and prevented the membrane from being separated. This substance was the ultimate decomposition product of the animal membrane. It seems likely that this gelatinization and later congealation had been caused by the prolonged action of water. The method eventually adopted was to expose the scroll fragments at 100 % relative humidity for a few minutes and then to transfer them to a refrigerator for an equivalent time. The degree of freezing was sufficient to congeal the surface of the black material while leaving the membrane sufficiently limp."

Penderleith visited Jordanian Jerusalem in March 1962. He attempted to unroll a rigid scroll. The method described above having failed, he carried out a dissection with appropriate tools using a support the thinnest white silk, spread thinly with polyvinyl acetate and brought into intimate contact with the cleaned flat surface of the scroll. He recommended that the leather be sterilized to eliminate fungi and bacteria. We do not know whether his recommendations were adopted.

In 1963, Valerie H. Foulkes visited Jerusalem, Jordan, in order to prepare the scrolls for an exhibition in the British Museum (what Plenderleith had unsuccessfully tried to prevent for conservation reasons). Miss Foulkes reported[3]: "It was a

shock to discover the extent of the contamination caused by Scotch Tape. The majority of the fragments I found had not only been joined but also backed with this material, in places with several layers of it. In addition, red gummed paper and black passe-partout tape had been employed. The sellotape was removed with a scalpel and, as recommended by Mr. Plenderleith, with trichloroethylene. Gummed silk strips or gold beater skin was used in order to join the fragments, with PVA as adhesive. Special leather dressing was applied to the verse. Surface consolidation and increased legibility were achieved without surface gloss by thinning the dressing with benzene before application. The document was placed in 75 % relative humidity for 3 hours so that it could be pressed flat safely and then framed for exhibition."

The scrolls having passed through many hands in different places, were exposed to drastic environmental changes and were treated in various ways. This is the self-evident cause for their poor condition to-day, which had been noticed already in 1962 by Francis Frank, Principal Librarian of the British Library. In a letter to Father De Vaux, the President of the Board of Trustees of the Ecole Biblique, Jerusalem, he wrote: "The fragments must first be freed of the cellulose acetate tape which was used to hold them together." John Allegro of the University of Manchester, a member of De Vaux's team, wrote in a letter to the Editor of the Observer on 11.12.1966 :"...On a recent visit to the museum, I saw for myself just how perilous is the situation. Fragile fragments, which have been out of their desert habitat now for more than 14 years, are still lying between the glass plates where we left them many years ago, mostly unsecured, and in some cases, as I was horrified to see, subjected to intolerable pressure by the plates lying on top of one another in a large cabinet ..."

After the Six-Day War in 1967 the scrolls passed into Israeli hands. In the seventies a team of conservators from the Israel Museum initiated work on the scrolls. Some of the glass plates were replaced by acid cardboard, of the kind available in Israel at the time, and the fragments were treated with thymol. The cellotape and some of the stains were removed with trichloroethylene. The fragments were reinforced with lens tissue; polyvinyl acetate or an acetone solution of Perspex™, ie. of an organic glass of PMMA, were used as adhesive. As a result, the parchment glitters like glass and becomes rigid and fragile. The process was very lengthy and a much more rapid pace of treatment was called for.

Recent Treatment

In 1991 a laboratory for the conservation of the scrolls was established by the Antiquities Authority in its store in the Rockefeller Building in Jerusalem. Ini-

Fig. 1: Scheme of the position of the fragments on the glass plates and indicating the cellotape

Fig. 2: Damage caused by cellotape

tially, a team of two conservators was appointed, with Esther Boyd-Alkalay acting as organizer and consultant.

As mentioned, almost all the fragments in the glass plates were "reinforced" with cellotape, some in two layers, a treatment very common in the fifties. We were shocked, just as Valerie H. Foulkes had been thirty years earlier, to see the extent to which the fragments had been penetrated by the adhesive and/or the lubricants of the cellotape. The aging of the oils and the pressure of the glass had caused darkening to the extent that some of the texts were no longer legible and, worst of all, the edges had already gelatinized. In addition, faulty treatment in the fifties, sixties and seventies – excessive humidity, leather dressing, PVA and Perspex solution – added to the damage. The cellotape had to be removed without delay but this proved to be an unbelievably lengthy process, which required a larger team of conservators. Additionally two more persons were appointed. A stereomicroscope and a vacuum disk were acquired; a Leister blower unit proved to be very useful for the safe removal of the tape. Invaluable help was provided by specialists of the Paul Getty Institute for Conservation.

Experiments with blank samples of parchment led to the exclusion of the use of parchment glue and adhesives based on organic solvents, because of difficult reversibility and, in some cases, creation of a rigid surface. It was found that water-based adhesives such as methylcellulose could be used. This was placed on Japanese tissue in a thin layer, left to dry to form a film and then applied in narrow strips with little moisture. According to Reed[1], light application of water-based adhesives relaxes the skin and activates the linking of the proteins in them; however, gelatinized areas present almost insurmountable problems.

Everyone experiencing the removal of sticky stains from porous materials knows how lengthy this procedure is and how much more laborious when the material is skin! It was thus realized that the immediate removal of the cellotape and the stains by our team of four workers would divert our attention from the most urgent tasks. Therefore a "first-aid treatment" was formulated: it implied the removal of the fragments from the acid boards and glass plates and placing them between acid-free cardboard. A work record was established, fully documenting the condition of the fragments. It provides a description of the damage suffered by the skin and the text, it details our intervention or that known to have been carried out previously and it includes a scheme showing the position of the fragments and where cellotape had been applied. The fragments were attached to Japanese paper with hinges prepared from the same paper, arranged in the order shown on the original photographs. If the cellotape had covered the fragment completely and hinges could not be used, the fragment was inserted in a sleeve made of Japanese paper, which was then attached to a sheet of lens tissue. These were enclosed in acid-free boards in passe-partout form. The upper board carries the shelf number and a colour code indicating the condition of the fragment.

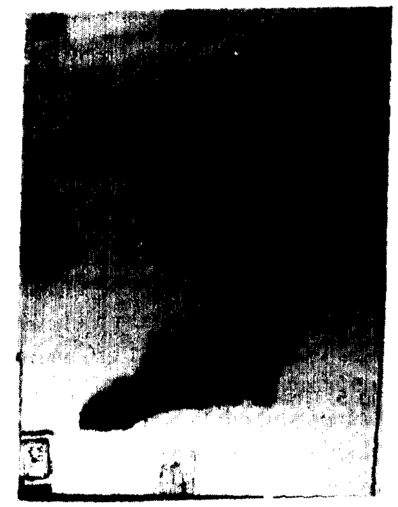

Fig. 3: Fragments with cellotape

Fig. 4: The same, reverse side

When attempting to remove the cellotape, minute crumb-like fragments were often found. The well-established method of protecting the recto side temporarily with Japanese tissue, which had previously been coated with methylcellulose, and was applied with a little surface moisture and light pressure with sand bags, was used in these cases. The removal of the cellotape cannot be standardized because the extent of adherence of the tape and the degree of oxidation of the substance that penetrated into the support varies. Since the

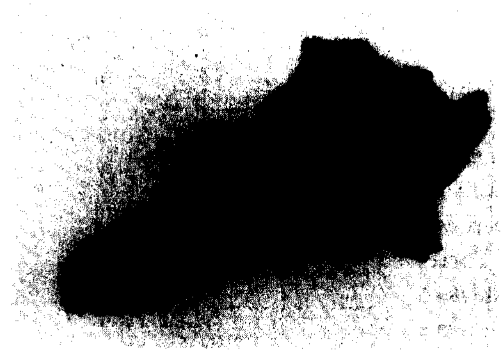

Fig. 5: The same, after treatment

Fig. 6: Sewing between stabile tex

solvents will not only remove the adhesive, but may also dry the skins and extract the lipids of the hides, the treatment with solvents is carried out only for the purpose of reducing the dark and sticky residues which render the text illegible. After removing the cellotape bit by bit which the aid of the Leister air gun blower unit, very good results were obtained in clearing the text, which had been completely obscured by stains, by applying vapours of organic solvents to the surface or by the use of an earth poultice with drops of solvents. These treatments are very time-consuming and need to be repeated often until the greasy glue softens and can be removed mechanically by hand with a tiny rubber eraser if possible.

STORAGE

High humidity and temperature accelerate degradation by activating chemical and biological processes. On the other hand, low humidity causes parchment to become brittle and contraction may cause peeling of the ink. Michael Schilling and William S. Ginell[4] (1993) suggested that a reasonable compromise had to be made by keeping the relative humidity between 35 and 40 %. They concluded that more study was required to understand the relationship between stress and dimensional response.

The storage room at the Rockefeller building is kept under constant temperature and humidity control. We are trying to ensure good buffering surroundings by housing the acid-free boards containing the fragments in drawers, which will be replaced by acid-free boxes – one of our present enterprises.

Unfortunately, we cannot keep the scrolls permanently in this mounting. We must comply with the demands of the readers who often need a direct view of both sides of the fragments. Until recently access was allowed to fragments attached to the acid-free boards; these were inserted between two custom-made Perspex plates. This procedure was not considered satisfactory and a solution came to us while we were preparing the scrolls for exhibition with Ms Doris Hamburg of the Library of Congress.

The fragments are now presented to the reader sewn between two layers of stabile tex stretched in an acid-free passe-partout, which is enclosed in a frame made of two clear Perspex plates in a way that does not allow the Perspex to come into contact with the fragments. The frames can be turned over without damaging the fragments. The stabile tex consists of a very thin transparent polyester net, available in various shades chosen to match that of the fragment so as to give the reader the clearest view of the text. Many frames have been made in order to increase the accessibility of the scrolls, to insure their safety and to satisfy the demands of the readers. The fragments sewn in the polyester are subsequently stored between acid-free boards.

The first-aid treatment is now completed. This, together with the documentation and colour code on each board indicating the damage and its extent and showing the priority for removing the cellotape and the stains and for reattaching the delamination skins and peeling inks, is considered to be the prerequisite for the completion of the work.

OUTLOOK

The Dead Sea Scrolls constitute an almost virgin field for conservation research. Fortunately, since 1992 investigations are being carried out in collaboration with the Paul Getty Institute for Conservation, which aim at determining the character of the damage and the changes which may occur and answering questions related to the climate in the caves, the origin of the minerals found in the scrolls and the causes of the physical, chemical and biological damage.

We are dealing with skins produced some 2000 years ago over a period of 300 years; some are split, some are tanned only at the surface and some more deeply. The damage varies from deep dark fragile areas to transparent gelatinized membranes. Some skins are delaminating and some inks are spreading, peeling and corroding. In addition, there is the major damage of the cellotape. Samples of damaged blank skins analyzed in the laboratories of the Paul Getty Institute before and after treatment showed that there was no loss of natural oils of the skins. The use of the stabile tex proved to be appropriate.

Unfortunately, the process of ageing cannot be halted – we shall be pleased to slow the pace. We are eager to accomplish this with as little intervention as possible and by employing reversible methods. We hope that our work will contribute to the preservation of these two-thousand year old treasures for future generations.

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SUMMARIES

The conservation of the Dead Sea scrolls in the laboratories of the Israel Antiquities Authority in Jerusalem.

The origin and nature of the Dead Sea Scrolls are briefly described. The condition of the scrolls and the damage they suffered after their discovery by inappropriate treatment, particularly the use of cellotape, are reported. The scrolls were subjected to first-aid treatment by the present team and are now being freed from the cellotape, stains removed and the fragments housed in passe-partouts and stabile tex.

La conservation des rouleaux de parchemin de la Mer Morte dans les laboratoires de l'Office de Protection des Monuments Antiques d'Israel à Jérusalem

On décrira sommairement l'origine et la nature des rouleaux de parchemin de la Mer Morte, et ensuite l'état dans lequel ils se trouvent ainsi que les dégradations qu'ils ont subies après leur découverte en raison des traitements mal adaptés qu'on leur a infligés, en particulier par les bandes adhésives. Ces rouleaux de parchemin ont fait l'objet d'un premier traitement d'urgence au cours duquel on les a délivrés des bandes adhésives. On a également éliminé les taches dont ils étaient souillés et à l'heure actuelle ils sont conservés dans des passe-partout entre des couches solides de tissu en polyester.

Die Konservierung der Rollen vom Toten Meer in den Laboratorien des Israelischen Denkmalamtes in Jerusalem.

Es werden kurz die Herkunft und die Art der Rollen vom Toten Meer beschrieben, und dann ihr Zustand sowie die Beschädigungen, die sie nach ihrer Entdeckung durch unangemessene Behandlung, insbesondere durch Selbstklebestreifen, erlitten haben. Die Stücke wurden einer Erste-Hilfe-Behandlung unterworfen und weisen jetzt keine Selbstklebestreifen mehr auf. Flecken wurden entfernt, und jetzt sind die Stücke in Passepartouts zwischen festem Polyester-Netzgewebe aufbewahrt.

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