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Mass Deacidification at the Bibliothèque Nationale (Sablé-sur-Sarthe Center): Assessment after Two Years of Operation (late 1992)

by PHILIPPE VALLAS

INTRODUCTION

After the failure of the request for proposals made by the Library of Congress last year, the development of mass deacidification techniques seems to be slowing down at present. Although some companies are doing a lot of advertising, most of the major libraries throughout the world are still cautious and prefer to wait and see: the librarians seem to think that the available systems are not satisfactory, and they are more demanding, probably because of the progress in research (particularly in the strengthening of paper).

However, they should keep in mind that a few plants are already operational, and that these plants have for years perfected, and then used the first mass deacidification facilities. And yet, people who work in them have experience that could be invaluable for other libraries. Consequently, it is useful to assess (from the viewpoint of a librarian) the operation of the plant built by the Bibliothèque Nationale of France in Sablé-sur-Sarthe, which came into regular service in 1989.

HISTORICAL BACKGROUND[1-5]

Sablé is a technical center, created in 1979 with the aim of safeguarding the collections of acid books kept by the Département des Livres Imprimés of the Bibliothèque Nationale, which had decided to establish a mass preservation program. First, the books are listed and their bibliographical notices are checked and simplified; then they are successively microfilmed and deacidified; some of them are later restored. The Center microfilms about 20,000 titles each year. First we used a manual deacidification process, which worked very slowly (we had to discard the books) and we could not treat more than 500 or 600 volumes per year. Then the Bibliothèque Nationale made an agreement with the Centre de Recherche sur la Conservation des Documents Graphiques (CRCDG), a laboratory of the Centre National de la Recherche Scientifique (CNRS). The CRCDG developed a process inspired by the Wei T'o plant of the Public Archives of Canada in Ottawa. In 1984, an order was put in by the Bibliothèque Nationale, and 1985 the Mallet Company began to build the plant. In 1987, the first tests were done. Perfecting the process took a long time; we had to make a lot of modifications. The plant came into operational service in 1989.

Current Operations

The current operations are quite the same as in the Wei T'o plant in Ottawa: the volumes are put (closed and vertical) in wire racks and dehydrated for 48 hours in a warm air dryer (60°C), and in vacuum autoclaves (Fig. 1). Thus, the humidity rate is pulled down to less than 1% of the paper weight. Then 8 racks are put in an autoclave under vacuum, which is afterwards completely

Fig. 1. A pre-deacidification drying chamber

filled (under pressure) with a methoxy-ethoxy methyl magnesium solution produced by Archival Aids (UK). This solution is mixed with Freon 12 (90% Freon, 10% solution). The books are left immersed in this deacidifying solution for 10 min.

Afterwards the solution is pumped from the autoclave to the mixing tank, and books are removed from the autoclave and left for 12 hours to dry in the open air, under an air extractor that evacuates the alcohol fumes emitted by the books. Then the volumes receive a stamp showing the place, date and kind of treatment. Books that are damaged are mentioned on the files drawn up on each round of treating. Afterwards the books are put into cardboard boxes and sent back to the Bibliothèque Nationale in Paris.

Our process is almost a closed circuit: the deacidifying solution is used four times in total; then the solution wastes are eliminated with a distilling column; they are put in barrels and destroyed by a specialized company. The Freon 12 is reprocessed by distilling and compression of the vapor remaining in the autoclave after each round of treatment, and it is used again. We only have to fill the tanks full enough that the quantity of deacidifying solution is enough to immerse all the books completely.

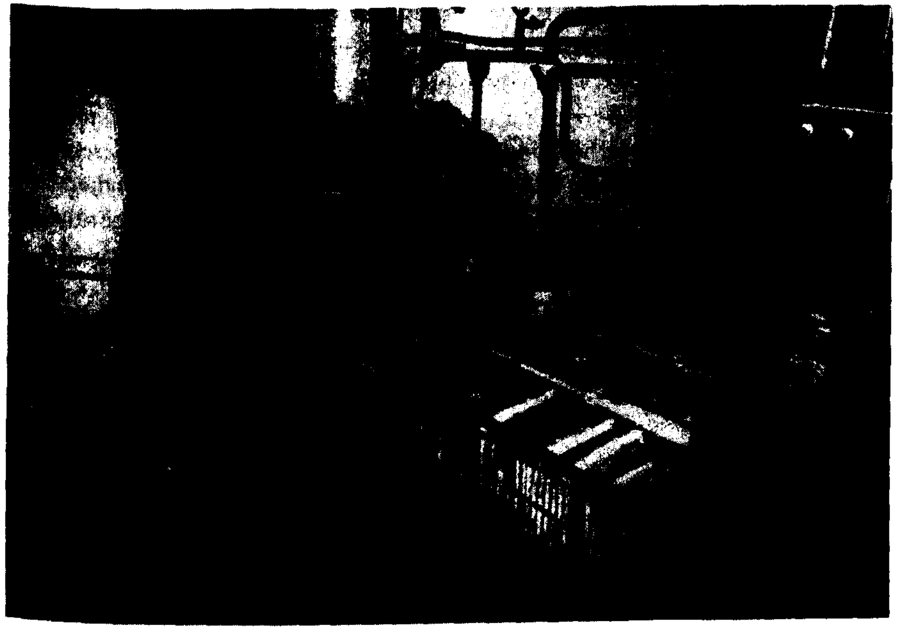

Fig. 2. The deacidification autoclave and racks full of books (some of them are into permanent paper sleeves)

Current Results

From 1987 to 1989, comprehensive tests had been done by the CRCDG about pH (before and after treatment), alkaline reserve, physical consequences of the treatment and behavior of the books towards artificial aging. The results of these tests are well known.[2] I present more recent results to complete them and to express the point of view of the librarians who use the process.

Our process allows real mass deacidification: although only a few thousand books were treated during the test period (1987–1989), the plant deacidified about 18,000 volumes in 1990 and 33,000 in 1991, with only a small staff (2 people to handle the books and draw up the files, 1 chemist to operate the plant); and the deacidification occupies only two thirds of their working time. They only do one deacidification round (from 100 to 200 volumes) each day, four days a week (the fifth day, the chemist distills the old solution and discards the waste). With two more people we could easily do two rounds per day and thus double the output, without any modification of the plant. The only problem would be finding enough volumes for treatment: the books have to be reproduced beforehand, and our microfilming workshop could not work quickly enough.

The plant is reliable (no serious breakdown for two years and limited ordinary maintenance, which is done by the chemist himself) and easy to run.

The volumes we treat belong to the classes considered by the Département des Livres Imprimés to have priority in the Bibliothèque Nationale preservation program. They are mostly French history books and novels, printed in cheap and small (8° and 12°) editions, on poor quality paper (with a high percentage of wood pulp) and published from about 1880 to 1950. Most of them are paperback editions, but a lot of them have got hard covers at the Bibliothèque Nationale.

These books arrive usually in Sablé in very bad condition (a lot of them are chosen because they can't be given to the readers any more): their paper is brown and brittle and it often crumbles in margins; a lot of paperback volumes are already deteriorated and have to be put into sleeves before treatment.

Physical Results

We do not possess the equipment to calculate the mechanical strength of paper. Of course, humidity and pressure variations can damage brittle documents, but we have never found any serious deterioration in books resulting from the treatment.

On the other hand, we have not been able to eliminate a serious drawback of our system: the bending of the hard covers of bound books (the paperback volumes are not modified), which happens when the books are dehydrated before deacidification. But we can partly prevent this problem by laying the volumes quite tightly packed in the racks, standing upright and the spine up. And this drawback usually disappears quite totally after a few months, if the books are tightly packed on shelves, when they get their normal humidity again.

The rings, which were frequent in paper in the past, have completely disappeared since the methanol has been replaced with ethanol in the deacidifying solution.

For the same reason, printing inks and pigments seldom run now. It only occurs for some red or orange edition covers of paperback books; in this case, we insert blotting papers. We have also found that some black-and-white illustrations, on coated paper, show iridescent reflections. The inks of the text almost never run (in only 6 volumes of 15,000 checked in 1991; these 6 volumes are pocket books published after 1925). The oily inks used by the Bibliothèque nationale for stamping are nearly never affected, but some more aqueous inks (for administrative stamping), particularly the blue ones, tend to run slightly.

In some treating rounds, a thin white deposit of magnesium dust forms between some leaves of the books, because of insufficient dehydration; but we can easily remove it by sweeping, and the pH and the alkaline reserve are not modified by this problem.

When the volumes are removed from the autoclave, they emit a strong smell of the ethanol contained in the solution. We therefore have to wait for a few days before putting them in the storage facilities. This smell completely disappears after a few weeks.

Finally, one of the greatest advantages of the Sablé deacidification system is that it hardly requires any selection among the books we receive: only the parchment bindings, and perhaps leather bindings could be damaged by the treating (although we have treated some leather half-bindings without any deterioration); and these kinds of binding are rare among the cheap editions of the nineteenth and twentieth centuries. So we do not have to do much preliminary work: only put into sleeves the books that have fallen apart and protect the few covers that could lose their colors; all things considered, the most time-consuming operations are putting the books into the racks, filling in the files detailing the content of every rack, and calculating some pH as tests (on two volumes per rack).

It is likely that we should have more difficulties with more recent books: a few years ago, we tried to deacidify some pocket books printed in 1960–1970 with the former solution (containing methanol), and we noticed that the ink ran much more frequently and that the thin transparent plastic layer on the covers was often unstuck by methanol. The solution we use now probably could not completely remove these problems, but we think that, for the moment, the real urgency is to deacidify the millions of older documents (produced about from 1870 to 1950), which are now the only ones really in danger.

Chemical Results

We measured the pH, before and after treatment, of 1830 volumes (published between 1900 and 1935) and belonging to 115 treatment rounds made in 1991. They were measured only at the surface of the paper, because we were not allowed to destroy, even partly, books of the national collections.

Although we found considerable variation in pH from volume to volume, the pH is usually very low before treatment: the total average is 4.3 in the center of leaves and 3.5 in the margins. The paper of nearly 20% of the documents has a pH lower than 3 in at least one place. Therefore the overall results after deacidification are considered satisfactory: the total average rises to 8.1 (center) and 7.2 (margins); but the considerable diversity noted before treatment remains. First, diversity from volume to volume: in the 115 deacidification rounds checked, the average pH of the more acid volume of each round was 6.85 in the center of the leaves and 6 in the margins; for the most alkaline volume, it rises to (respectively) 9.3 and 8.6; but we also have noted diversity between different leaves of the same volume, and between different places on the same leaf (in the last case, differences vary between 0.4 and 0.9 pH points).

Are these differences caused by uneven penetration of the deacidifying solution inside the documents? Perhaps this is partly true, but we think that these differences are above all the reproduction of the differences, of about the same scale, that existed before treatment.

In this field too, the results depend on the initial pH of the paper. We noted that, when the initial pH is not higher than 3, the paper remains usually slightly acid after treatment (pH between 6 and 7); the pH after deacidification is always alkaline only if the average initial pH is at least equal to 3.3. And since we treat a lot of very acid books, 25% of them remain slightly acid in at least one place in the margins after treatment, and 5% in the centre (usually between 6 and 7, and very seldom lower than 6). The worst results have been obtained with some kinds of very impermeably coated papers, from good-quality editions: sometimes the pH did not rise higher than 5 after treatment, because of the insufficient penetration of the solution. Fortunately, such books are very few in Sablé, and until now they are all made with at least average-

quality papers (pH ≥ 4 before deacidification). We envisaged treating again the insufficiently deacidified volumes; after some tests, we noted that it was effective, but that it would also oblige us in practice to a very time-consuming selection, and could damage the most brittle papers; so we renounced this idea.

We did not note any difference in the pH (and alkaline reserve) results between the rounds during which the deacidifying solution was used for the first time and the ones during which it was for the third or fourth time.

Do we have to conclude, according to these tests, that the Sablé process is not satisfactory? It is undeniable that its effectiveness is relative in the case of most acid documents. However, these are a little minority, and their pH is still increased by the treatment. We therefore prefer to take an optimistic point of view and to turn the problem around: we conclude that perhaps the best would be, in the future, to deacidify the books before their physical and chemical degradation is too far advanced.

Since we could not destroy documents belonging to the Bibliothèque Nationale, we have calculated the alkaline reserve from leaves used as tests and cut in discarded books donated by other libraries. These leaves were scattered among the volumes in the racks. We have treated some leaves of every book in almost ten rounds, and we calculated the average of the results we obtained. These results (concerning 5 documents) appear in Table 1. Although the pH

Table 1. pH and alkaline reserve of selected volumes

Date of the volume and kind of paper	pH before treatment	pH after treatment	Alkaline reserve
Cheap edition (1949): paper with high percentage of mechanical pulp	4.1	8.2	48 mEq/kg (0.2% alkaline reserve magnesium carbonate)
Cheap edition (1945): paper with a high percentage of mechanical pulp	center: 4.3 margins: 3.3	center: 9 margins: 8.5	62 mEq/kg (0.26% alkaline reserve in magnesium carbonate)
High-quality edition (1857): rag paper	7	10	96 mEq/kg (0.40% alkaline reserve in magnesium carbonate)
Newspaper (May 1991): mechanical pulp paper	6.5	9.5	150 mEq/kg (0.63% alkaline reserve in magnesium carbonate)
Official publication (1991): bleached chemical pulp paper	7.5	9.5	210 mEq/kg (0.88% alkaline reserve in magnesium carbonate)

is greatly increased by the treatment, the alkaline reserve obtained is low when the books were very acid before deacidification.

Can we conclude that the deacidified documents would not be protected for a long time against the return of the acidification? We tried to determine this. We could not carry out accelerated aging tests, because we did not have the necessary equipment, but we began a natural aging test on some volumes kept in our premises (in good and stable environmental conditions). At the moment, the longest passage of time we can use to judge the effectiveness of the deacidifying solution we use now is only 3 years. We built up a sample group of 29 volumes deacidified in 1989, the average pH of which was 3.8 in the centre of the leaves and 4.5 in the margins; after treatment, the average pH increased to (respectively) 8.1 and 8.8, and they remained on the same level in mid-1992. Of course, these tests cannot allow a real assessment of the long-term effectiveness of our process, because too little has passed. We shall have to repeat them regularly for several years on the same books to acquire precise knowledge about that issue.

Conclusion

The mass deacidification plant has operated intensively for more than two years without any serious problem, and we are therefore completely convinced of its reliability. We could also check that it could find its place in a chain of preservation treatments, as a complement of the usual techniques, providing that one also has a big reproduction workshop, able to work at the same rate: after the microfilming, which allows the removal of the original documents from communication to readers, but nevertheless maintains the possibility of consultation, the deacidification slows down the degradation progress and gives an invaluable respite, which allows time for the possible development of a mass restoration or strengthening process.

The technical assessment is positive on the whole: the few undesirable consequences of the treatment (covers bending, smell, magnesium dust) are neither serious nor permanent. If the pH of about 25% of the volumes does not reach neutral pH in all places after treatment, it is because the books we treat are often very acid, and because we have to treat them far too late. The deacidification rate is very satisfactory if one considers that the plant was built to carry out experiments, and we could easily raise it, principally because the preparatory steps (inventory, sorting and protection) are not time-consuming. We could deacidify 50,000 to 60,000 volumes each year, and this could meet the needs of almost any library in the world. The cost is quite low: about FRF

25 to 40 per volume (depending on whether the depreciation – in 5 years – of the plant is taken into account or not).

We shall try to improve our system: a device to proportion more precisely the solution ingredients, another product as substitute for the Freon 12, and a system that allows the books to dry in the autoclave after treatment. We shall also test some paper-strengthening products in addition to the deacidifying solution.

We still have to verify an essential point before we can conclude that the Sablé process is really satisfactory: how long does the paper stay protected by the treatment? Two years ago, the CRCDG carried out some artificial aging tests, and obtained good results[3,4]; but to be certain we shall wait for some years.

In conclusion, we do not assert that the Sablé mass deacidification process is a perfect system. Other libraries tested it and did not choose it for now. Even in France now another process is being developed for the future Bibliothèque de France that would also strengthen the paper. But we are convinced that, throughout the world, librarians will still have to wait for several years before they can use a deacidification system that would be substantially better than the Sablé system. And since libraries keep millions of precious documents that are crumbling very quickly because their paper is acid, we think that, as curators, we should fail in our mission if we do not use as much as possible a well-proven, effective, relatively economical process that, moreover, is not dangerous for documents, people or the environment.

Summaries

Mass Deacidification at the Bibliothèque Nationale (Sablé-sur-Sarthe Center): Assessment after Two Years of Operation (late 1992)

The author assesses, from the viewpoint of a librarian, the mass deacidification plant in Sablé-sur-Sarthe, France, after more than two years of regular operation. Although some drawbacks have not disappeared (pH and alkaline reserve, in particular, sometimes remain quite low after treatment, and it is not known yet for how long the documents are protected), the assessment seems to be very positive. The process is effective, it is not dangerous for books, people or the environment, and the cost is quite low; the plant is reliable, and the volume is high (33,000 volumes treated in 1991). But more improvements to the system will be attempted.

Désacidification de masse à la Bibliothèque Nationale de France (Centre de Sablé-sur-Sarthe). Evaluation après deux années d'utilisation

L'auteur, conservateur à la Bibliothèque nationale, fait le point sur le fonctionnement de l'installation de désacidification de masse de Sablé-sur-Sarthe, après plus de deux ans de service opérationnel. Si

quelques défauts subsistent (le pH et la réserve alcaline, notamment, restent parfois assez faibles après le traitement, et on ignore encore la durée de protection que celui-ci confère), le bilan semble malgré tout très positif: efficace, le procédé ne présente de danger ni pour les livres, ni pour le personnel, ni pour l'environnement, et il est peu coûteux; l'installation est fiable et permet des cadences de traitement soutenues (33,000 volumes de la Bibliothèque nationale ont été traités en 1991). On va tâcher de l'améliorer encore.

Massenneutralisierung an der französischen Nationalbibliothek (Zentrum Sablé): zwei Jahre praktische Erfahrung

Der Autor berichtet aus der Sicht des Bibliothekars über die französische Massenneutralisierungsanlage in Sablé-sur-Sarthe nach zwei Jahren praktischer Arbeit. Obwohl einige Negativa nicht vollständig ausgeräumt werden konnten – pH und insbesondere die alkalische Reserve bleiben manchmal recht niedrig, und insgesamt ist der Zeitraum des durch die Behandlung bewirkten Schutzes unbekannt – ist die Methode insgesamt erfolgreich. Sie bietet keine Gefahr, weder für Bücher noch für das Personal oder die Umwelt. Ihre Kosten sind recht niedrig, die Arbeitsweise zuverlässig, die Leistungszahlen hoch: 1991 wurden 33,000 Bände behandelt. Es sind Bemühungen im Gange, das System zu verbessern.

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Characterization of Low-molecular-weight Polyvinyl Alcohol for Restoration Purposes

by MARINA BICCHIERI, MAURO BORTOLANI & EUGENIO VECA

Introduction

Preservation of paper documents is an urgent problem in archives and libraries. One method of restoring deteriorated documents is to introduce sizes into paper, to enhance its resistance to mechanical stress and penetration by liquids.

The most used sizes in the history of paper are starch, animal glue and rosin. Starch and animal glue do not produce degradation by themselves, but they can be attacked by biological agents. Rosin introduces acidity into paper and causes yellowing and loss of mechanical strength.

For restoration it is better to use synthetic or artificial sizes, to minimize the risk of biological attack. One of the most promising of the synthetic resins for sizing of paper is polyvinyl alcohol (PVA).[1] This material is already used in the paper industry as a pigment coating adhesive.

This study reports the application of PVA for the restoration of paper. The PVA used has 87–89% of hydrolysis degree; its average molecular weight is 14 kDa. It is a white powder soluble in cold water and it has excellent resistance to ultraviolet radiation and to ageing.

We performed a long-term investigation of two complementary aspects: the quality of PVA as a sizing agent and the behaviour over time of papers treated with this product.

Preliminary Investigation

Materials

- aqueous solutions of PVA, 14 kDa (manufacturer: Carlo Erba)
- Whatman paper no. 1 for chromatography; samples 20×20 cm^2.

Table 1. Viscosity of aqueous solutions of PVA, 14 kDa, at 20°C

PVA concentration (% w/v)	Viscosity (cSt)
1	1.53 ± 0.01
3	2.85 ± 0.03
5	6.63 ± 0.07
6	10.02 ± 0.10
8	19.92 ± 0.19
10	29.38 ± 0.29
12	51.40 ± 0.52
15	128.40 ± 1.30
18	257.37 ± 2.58
20	447.82 ± 4.50

Range of concentration

To establish the best concentration of PVA for the sizing of paper, we prepared solutions with concentrations ranging from 1% to 20% (w/v).

It is known that the use of high-viscosity solutions in restoring ancient paper can mechanically damage documents during application. We therefore carried out preliminary viscosity measurements for each solution (Table 1).

Concentrations higher than 15% have been rejected because the viscosity is too high. Other tests on paper, carried out with concentrations of less than 4%, did not give good results for the reinforcement of paper. We therefore restricted our studies, for the preliminary investigation, to concentrations between 5% and 15% (5%, 8%, 10% and 15%).

Table 2. Mechanical measurements on paper treated with PVA, 14 kDa

PVA concentration (% w/v)	Average folding endurance (*n*)	Average tensile strength (kg)
0	17 ± 3	3.80 ± 0.40
1	18 ± 3	3.60 ± 0.20
2	22 ± 4	4.00 ± 0.40
3	32 ± 5	4.40 ± 0.30
5	38 ± 2	4.80 ± 0.10
8	113 ± 10	5.70 ± 0.10
10	171 ± 10	7.80 ± 0.20
15	352 ± 15	9.60 ± 0.30

Table 3. Absorption and reversibility of PVA, 14 kDa. The values are corrected by the moisture content of paper.

PVA concentration (% w/v)	Absorption (g/m^2)	Reversibility (%)
1	2.30 ± 0.01	91.0 ± 1.0
2	4.03 ± 0.01	89.7 ± 1.0
3	4.59 ± 0.01	90.2 ± 1.2
5	8.08 ± 0.01	87.6 ± 2.1
8	11.16 ± 0.01	90.1 ± 1.2
10	13.80 ± 0.01	90.1 ± 1.0
15	22.19 ± 0.01	88.4 ± 1.6

Application on paper

The paper was sized by immersion in solution. Measurements of the absorption of PVA as a function of time showed that the absorption after the first 5 min was negligible. We then used 15 min as the time of immersion.

After drying and conditioning at 23°C and 50% relative humidity (RH),[2] specimens for the mechanical tests were cut from the samples coated with PVA.

Experimental results

Measurements of pH,[3] folding endurance,[4] tensile strength[5] and opacity[6] were carried out in a conditioning room at 23°C and 50% RH on papers coated with PVA and, for comparison, on untreated papers. The amount of PVA absorbed by paper and its reversibility was also evaluated. The results are listed below.

Table 4. Opacity (%) of paper treated with PVA solutions

PVA concentration (% w/v)	Opacity (%)
0	80.10 ± 0.02
1	80.00 ± 0.05
2	79.95 ± 0.05
3	79.15 ± 0.07
5	80.75 ± 0.04
8	79.45 ± 0.02
10	79.40 ± 0.05
15	74.05 ± 0.03

Table 5. Variation field of increments of mechanical properties of paper treated with PVA
increment % = [(treated-untreated)/untreated] × 100

PVA concentration (% w/v)	Double folds increments (%)	Tensile strength increments (%)
1	6	5
2	29	11
3	88	22
5	123	33
8	565	58
10	906	117
15	1970	167

pH

All aqueous solutions of PVA as well as all coated papers have pH = 5.70 ± 0.02.

Folding endurance and tensile strength

After conditioning, for each value of PVA concentration, we performed 20 measurements each for folding endurance and tensile strength. The specimens used for these tests were cut with their edges parallel to the machine direction (preferential direction of the fibres). The results are listed in Table 2.

Absorption and reversibility of sizing agent

The samples, after conditioning, were weighed before and after their immersion in PVA solutions. From the weight difference, corrected by the moisture content of the paper,[7] we evaluated the amount of size absorbed. The same samples were washed twice with 500 ml of distilled water (each bath during 30 min at 30°C) and then weighed, after conditioning, for the evaluation of the size removed by water (reversibility).

The results, corrected by the moisture content of paper, are listed in Table 3.

Optical measurements

Three measurements were carried out for each specimen, and 6 specimens were used for each concentration. The results (Table 4) are the average of 18 measurements.

Table 6. Reversibility (%) of PVA as a function of ageing time and temperature

T °C - RH \ days	0	7	14	21	28	42	56	10 years
95° dry	92.5 ± 0.5	83.5 ± 1.5	79.2 ± 1.1		60.7 ± 1.3	73.5 ± 1.2	50.8 ± 1.6	
85° dry	91.4 ± 0.6	87.9 ± 0.9	85.0 ± 1.3	80.3 ± 0.8				
75° dry	94.1 ± 0.3	93.8 ± 0.4	87.7 ± 0.3	90.3 ± 0.4				
80° 65% RH	92.5 ± 0.4	92.3 ± 0.2						
23° 50% RH	92.3 ± 0.2							89.2 ± 0.3

Table 7a. pH of aqueous extracts (± 0.02) of untreated paper as a function of ageing time and temperature

T °C - RH \ days	0	7	14	21	28	42	56	10 years
95° dry	6.65	6.15	6.10		6.15	6.00	5.70	
85° dry	6.65	6.50	6.75	6.55				
75° dry	6.90	7.00	7.00	6.95				
80° 65% RH	6.70	6.72						
23° 50% RH	6.65							6.68

Table 7b. pH of aqueous extracts (± 0.02) of paper treated with PVA as a function of ageing time and temperature

T °C - RH \ days	0	7	14	21	28	42	56	10 years
95° dry	6.55	6.00	6.05		6.15	6.10	5.65	
85° dry	6.55	6.40	6.25	6.35				
75° dry	6.75	6.75	6.80	6.75				
80° 65% RH	6.75	6.75						
23° 50% RH	6.55							6.48

Table 8a: Intrinsic viscosity [η] and average degree of polymerization (DP) of untreated paper as a function of ageing time and temperature

T °C RH	Days	0	1	5	7	14
95°C dry	[η]	5.234 ± 0.089			4.709 ± 0.153	4.376 ± 0.105
	DP	994 ± 17			859 ± 29	831 ± 20
85°C dry	[η]	5.295 ± 0.058			5.202 ± 0.132	4.987 ± 0.126
	DP	1006 ± 11			988 ± 25	948 ± 24
75°C dry	[η]	5.316 ± 0.053			5.255 ± 0.121	4.979 ± 0.126
	DP	1010 ± 10			999 ± 23	946 ± 24
80°C 60% RH	[η]	5.230 ± 0.079	5.217 ± 0.111	5.054 ± 0.132	4.982 ± 0.132	
	DP	994 ± 15	991 ± 21	960 ± 25	947 ± 25	
23°C 50% RH	[η]	5.221 ± 0.089				
	DP	992 ± 17				

T °C RH	Days	21	28	42	56	10 years
95°C dry	[η]		3.026 ± 0.111	2.809 ± 0.084	2.195 ± 0.058	
	DP		575 ± 21	534 ± 16	417 ± 11	
85°C dry	[η]	4.827 ± 0.121				
	DP	917 ± 23				
75°C dry	[η]	4.889 ± 0.137				
	DP	929 ± 26				
80°C 60% RH	[η]					
	DP					
23°C 50% RH	[η]					4.078 ± 0.111
	DP					775 ± 21

$[\eta] = \lim_{c \to 0} \text{Log}\,[(\eta_{rel} - 1)/c]$, $[c] = [g/dl]$

DP is obtained by multiplying intrinsic viscosity by 190

Discussion of preliminary results

For restoration it is very important to use low-viscosity solutions to obtain a regular application of the sizing agents. The use of PVA solutions at concen-

Table 8b: Intrinsic viscosity [η] and average degree of polymerization (DP) of paper treated with PVA as a function of ageing time and temperature

T °C RH	Days	0	1	5	7	14
95°C dry	[η]	5.789 ± 0.079				3.852 ± 0.105
	DP	1100 ± 15				732 ± 20
85°C dry	[η]	4.579 ± 0.079			4.626 ± 0.126	4.574 ± 0.132
	DP	950 ± 15			879 ± 24	869 ± 25
75°C dry	[η]	4.905 ± 0.089			4.705 ± 0.121	4.474 ± 0.121
	DP	932 ± 17			894 ± 23	850 ± 23
80°C 65% RH	[η]	5.167 ± 0.079	5.137 ± 0.111	4.746 ± 0.137	4.688 ± 0.116	
	DP	980 ± 15	976 ± 21	902 ± 26	891 ± 22	
23°C 50% RH	[η]	5.200 ± 0.089				
	DP	988 ± 17				

T °C RH	Days	21	28	42	56	10 years
95°C dry	[η]		3.560 ± 0.116	3.246 ± 0.116	2.278 ± 0.121	
	DP		676 ± 22	617 ± 21	433 ± 23	
85°C dry	[η]	4.221 ± 0.132				
	DP	802 ± 25				
75°C dry	[η]	4.360 ± 0.121				
	DP	828 ± 23				
80°C 65% RH	[η]					
	DP					
23°C 50% RH	[η]					3.963 ± 0.100
	DP					753 ± 19

$[[\eta] = \lim_{c \to 0} \text{Log}\,[(\eta_{rel} - 1)/c]$, $[c] = [g/dl]$

DP is obtained by multiplying intrinsic viscosity by 190

trations of less than 12% (W/V) does not give problems for application on paper. The 15% solution was used, despite its high viscosity, to estimate the possible application on very damaged documents, which would need stronger reinforcement. The results were unsuccessful because paper treated with PVA at 15% seems to be too stiff and transparent.

Table 9a. Opacity (%) of untreated paper as function of ageing time and temperature

T °C – RH / days	0	1	3	5	7	14	21	28	42	56	10 years
95° dry	85.6 ± 0.1				88.2 ± 0.4	88.9 ± 0.2		89.4 ± 0.4	88.4 ± 0.4	90.4 ± 0.2	
85° dry	85.7 ± 0.1				86.6 ± 0.6	86.9 ± 0.7					
75° dry	85.8 ± 0.5				86.5 ± 0.5	86.5 ± 0.4					
80° 65% RH	88.4 ± 0.5	88.6 ± 0.1	87.2 ± 0.1	85.5 ± 0.3	85.9 ± 0.2						
23° 50% RH	86.5 ± 0.3										86.7 ± 0.2

Table 9b. Opacity (%) of treated paper as a function of ageing time and temperature

T °C – RH	days	0	1	3	5	7	14	21	28	42	56	10 years
	1	85.5 ± 0.2				85.7 ± 0.3	85.3 ± 0.3		82.5 ± 0.2	85.2 ± 0.2	85.7 ± 0.2	
95° dry	2	85.5 ± 0.1				85.9 ± 0.3	85.2 ± 0.1		85.1 ± 0.2	85.2 ± 0.6	85.9 ± 0.2	
	3					89.0 ± 0.6	89.3 ± 0.1		88.9 ± 0.7	88.8 ± 0.8	91.7 ± 0.2	
	1	85.6 ± 0.3				85.7 ± 0.2	85.7 ± 0.1	85.7 ± 0.2				
85° dry	2	85.7 ± 0.2				86.0 ± 0.5	85.7 ± 0.5	86.0 ± 0.6				
	3					87.0 ± 0.5	87.3 ± 0.6	87.9 ± 0.7				
	1	85.8 ± 0.3				85.7 ± 0.2	85.8 ± 0.3	85.8 ± 0.2				
75° dry	2	85.8 ± 0.2				86.2 ± 0.4	86.2 ± 0.3	86.1 ± 0.1				
	3					87.3 ± 0.4	87.3 ± 0.4	86.9 ± 0.2				
	1	88.3 ± 0.3	87.3 ± 0.8	88.0 ± 0.6	87.9 ± 0.2	88.0 ± 0.8						
80° 65% RH	2	88.4 ± 0.8	86.3 ± 0.2	88.1 ± 0.4	88.4 ± 0.5	88.0 ± 0.9						
	3		88.2 ± 0.4	87.9 ± 0.3	87.3 ± 0.3	86.4 ± 0.2						
	1	86.3 ± 0.3										86.3 ± 0.1
23° 50% RH	2	86.6 ± 0.2										86.3 ± 0.2
	3											86.7 ± 0.2

1: before treatment; 2: after coating; 3: after ageing

This preliminary study showed that the presence of the size does not change the optical characteristic of paper if the solution concentration is less than 15%. Further, the PVA increases the mechanical resistance of treated paper by several orders of magnitude (Table 5). The reversibility, a theoretical condition for any means of conservation, is excellent.

ACCELERATED AGEING

A series of accelerated ageing tests was done to confirm the positive results of the preliminary studies. We used three dry tests and one humid one.[8] In addition, we performed a long-term study (10 years) with samples stored at 23°C and 50% RH.

For all accelerated ageing tests, different samples of the same paper were selected at different times of ageing. The conditions of accelerated ageing were:

- 95°C dry: drawing at 0, 7, 14, 28, 56 days
- 85°C dry: drawing at 0, 7, 14, 21 days
- 85°C dry: drawing at 0, 7, 14, 21 days
- 80°C and 65% RH: drawing at 1, 2, 3, 4, 5, 6, 7 days
- 23°C and 50% RH: 10 years.

For the accelerated ageing tests we used a paper manufactured for us by S.I.V.A. (Rome). The composition of this paper is 75% bleached sulfate hardwood cellulose, 25% bleached sulfate softwood cellulose, no size, no coating and basis weight 105 g/m². The PVA sizing was applied by immersion in the 8% solution.

Measurements

On the treated and untreated samples we carried out the following measurements:

- reversibility of sizing agent
- pH of aqueous extracts[3]
- intrinsic viscosity of cellulose and degree of polymerization[9]
- opacity of paper (diffuse reflectance method[6])
- tensile strength[5]
- brightness of paper[10]
- folding endurance.[4]

Table 10a. Tensile strength (kg) of untreated paper as a function of ageing time and temperature

T °C – RH / days	0	1	3	5	7	14	21	28	42	56	10 years
95° dry	6.05 ± 0.42				6.65 ± 0.39	6.13 ± 0.23		6.06 ± 0.39	5.85 ± 0.50	5.82 ± 0.50	
85° dry	6.05 ± 0.40				6.36 ± 0.14	6.58 ± 0.38					
75° dry	6.05 ± 0.40				6.46 ± 0.27	6.36 ± 0.33					
80° 65% RH	5.90 ± 0.28	5.90 ± 0.22	5.90 ± 0.33	5.90 ± 0.28	5.97 ± 0.12						
23° 50% RH	6.00 ± 0.40										6.20 ± 0.40

Table 10b. Tensile strength (kg) of paper treated with PVA as a function of ageing time and temperature

T °C – RH / days	0	1	3	5	7	14	21	28	42	56	10 years
95° dry	8.23 ± 0.47				8.34 ± 0.69	9.11 ± 0.48		7.76 ± 0.36	7.61 ± 0.60	7.50 ± 0.29	
85° dry	7.98 ± 0.45				7.75 ± 0.25	7.90 ± 0.39	7.98 ± 0.33				
75° dry	8.20 ± 0.50				8.14 ± 0.40	7.88 ± 0.68	8.06 ± 0.50				
80° 65% RH	6.88 ± 0.54	7.50 ± 0.46	7.54 ± 0.50	7.85 ± 0.12	7.43 ± 0.08						
23° 50% RH	8.20 ± 0.40										7.60 ± 0.50

Table 11a. Diffuse blue reflectance factor (IRB%) of untreated paper as a function of ageing time and temperature

T °C – RH	days	0	1	3	5	7	14	21	28	42	56	10 years
95° dry	1	87.5 ± 0.2				87.5 ± 0.1	87.5 ± 0.1		88.1 ± 0.1	87.5 ± 0.3	87.4 ± 0.2	
	2					75.3 ± 0.4	78.6 ± 0.8		77.0 ± 0.7	76.5 ± 0.5	70.9 ± 0.1	
85° dry	1	87.2 ± 0.1				87.0 ± 0.5	87.2 ± 0.1	87.1 ± 0.1				
	2					83.9 ± 0.5	83.2 ± 0.2	81.8 ± 0.3				
75° dry	1	88.0 ± 0.1				88.0 ± 0.1	87.8 ± 0.2	87.8 ± 0.1				
	2					86.0 ± 0.1	85.6 ± 0.2	85.7 ± 0.2				
80° 65% RH	1	80.4 ± 0.6	79.2 ± 0.3	80.4 ± 0.3	80.8 ± 0.5	81.0 ± 0.5						
	2		75.1 ± 0.2	74.4 ± 0.2	72.8 ± 0.5	72.0 ± 0.5						
23° 50% RH	1	87.6 ± 0.2										
	2											87.1 ± 0.4

1: before ageing; 2: after ageing

Table 11b. Diffuse blue reflectance factor [IRB%] of paper treated with PVAl as function of ageing time and temperature

T °C – RH	days	0	1	3	5	7	14	21	28	42	56	10 years
95° dry	1	87.5 ± 0.1				87.5 ± 0.2	88.0 ± 0.2		88.1 ± 0.3	87.0 ± 0.3	88.4 ± 0.2	
	2					73.5 ± 0.4	75.0 ± 1.0		74.4 ± 1.0	72.3 ± 0.7	62.2 ± 0.4	
	3	87.5 ± 0.1				84.4 ± 0.2	83.4 ± 0.5		81.7 ± 0.4	79.7 ± 0.4	73.0 ± 0.2	
85° dry	1	87.5 ± 0.1				87.6 ± 0.3	87.4 ± 0.2	87.6 ± 0.2				
	2					84.3 ± 0.5	82.3 ± 0.3	80.0 ± 1.1				
	3	87.6 ± 0.2				87.4 ± 0.4	86.6 ± 0.2	85.8 ± 0.4				
75° dry	1	89.9 ± 0.2				88.1 ± 0.2	87.9 ± 0.1	87.8 ± 0.3				
	2					86.0 ± 0.2	85.3 ± 0.3	85.4 ± 0.5				
	3	90.5 ± 0.1				90.5 ± 0.4	90.8 ± 0.6	87.7 ± 0.2				
80° 65% RH	1	80.0 ± 0.3	80.0 ± 0.4	80.5 ± 0.5	81.3 ± 0.3	80.6 ± 0.5						
	2		75.7 ± 0.6	75.3 ± 0.6	74.6 ± 0.4	72.5 ± 0.5						
	3	80.2 ± 0.1	79.9 ± 0.3	79.5 ± 0.2	79.7 ± 0.2	78.9 ± 0.3						
23° 50% RH	1	88.0 ± 0.2										
	2											87.9 ± 0.4
	3	88.1 ± 0.2										88.0 ± 0.2

1: before ageing; 2: after ageing; 3: after reversibility

Table 12a. Double folds (n) of untreated paper as a function of ageing time and temperature

T °C - RH	days: 0	1	3	5	7	14	21	28	42	56	10 years
95° dry	38 ± 7				27 ± 5	27 ± 5		19 ± 4	13 ± 2	4 ± 1	
85° dry	38 ± 7				39 ± 8	32 ± 7	32 ± 7				
75° dry	40 ± 7				49 ± 9	39 ± 4	39 ± 8				
80° 65% RH	30 ± 5	30 ± 5	29 ± 4	30 ± 6	29 ± 5						
23° 50% RH	38 ± 7										41 ± 7

Table 12b. Double folds of paper (n) treated with PVA as a function of ageing time and temperature

T °C - RH	days	0	1	3	5	7	14	21	28	42	56	10 years
95° dry	1	21 ± 7				4 ± 2	6 ± 1		2 ± 1	2 ± 1	2 ± 1	
	2	40 ± 9				66 ± 11	49 ± 8		52 ± 10	42 ± 1	14 ± 2	
85° dry	1	21 ± 7				16 ± 5	13 ± 3	13 ± 3				
	2	40 ± 9				56 ± 10	50 ± 9	51 ± 9				
75° dry	1	21 ± 7				14 ± 6	17 ± 4	18 ± 7				
	2	39 ± 8				48 ± 8	48 ± 6	52 ± 9				
80° 65% RH	1	28 ± 5	28 ± 2	28 ± 3	27 ± 5	25 ± 3						
	2	40 ± 5	40 ± 5	41 ± 3	40 ± 4	40 ± 2						
23° 50% RH	1	20 ± 5										23 ± 6
	2	40 ± 8										40 ± 7

1: after ageing; 2: after reversibility (after ageing)

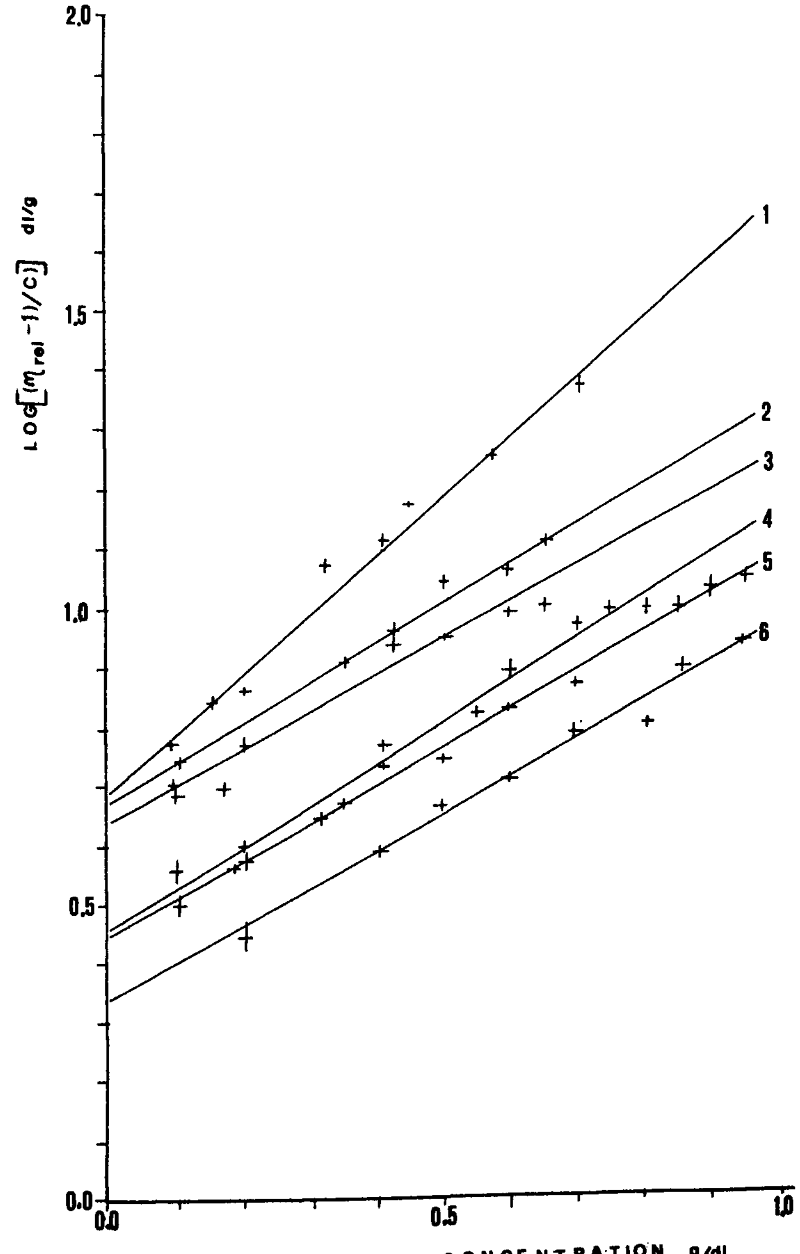

Fig. 1. Determination of intrinsic viscosity of untreated paper aged at 95°C (the bars on each point represent the error related to the measurement). 1. Before ageing. 2. Ageing 7 days. 3. Ageing 14 days. 4. Ageing 28 days. 5. Ageing 42 days. 6. Ageing 56 days.

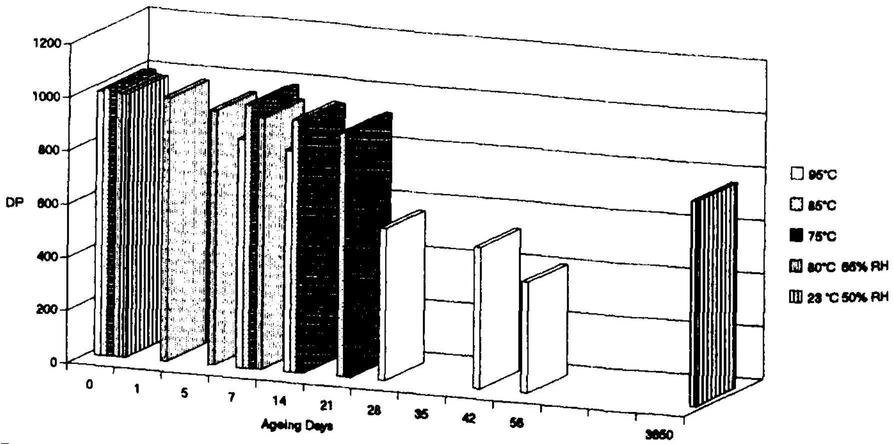

Fig. 2. Average polymerization degree (DP) from intrinsic viscosity of untreated paper as a function of ageing time and temperature

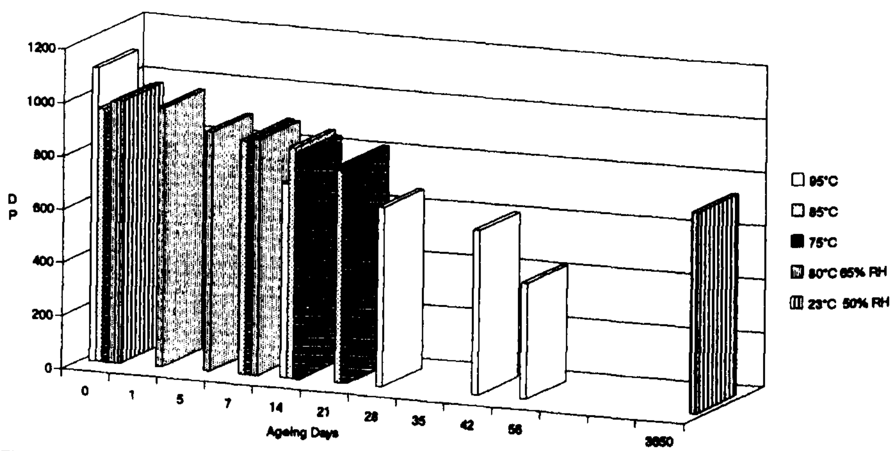

Fig. 3. Average polymerization degree (DP) from intrinsic viscosity of paper treated with PVA as a function of ageing time and temperature

It is well known that applying size increases the rigidity of paper and, consequently, decreases the folding endurance. To find out whether the size could have a protective effect on paper, we did the last two measurements twice: after ageing as described and then also after removing the size, done with the aged samples. The results demonstrate that the paper aged in the presence of PVA has higher folding endurance after the PVA is removed than the untreated aged paper.

The measurements of degree of polymerization were carried out on untreated and on treated papers after the sizing agent was removed.

The behaviour $\log\{(\eta_{rel}-1)/c\}$ as a function of c has been studied for each ageing time, temperature and kind of paper. η_{rel} is the relative viscosity of the solution of paper, that is, the ratio between solution viscosity and solvent viscosity; c is the concentration of the cellulosic solution in g/dl. Measurements show that this behaviour can be represented with very good approximation by a straight line.

The intrinsic viscosity $[\eta]$ has been calculated by extrapolation of the straight line at zero concentration. The straight line parameters have been obtained using a least-square-fit method, taking into account correctly, for each measurement, the proper error.

The results of all physicomechanical measurements are listed in Tables 6-12. An example of the determination of the intrinsic viscosity is given in Fig. 1–3.

Discussion

The sizing agent shows a very good reversibility (Table 6) at every accelerated ageing temperature and also after 10 years of natural ageing. The lowest values for the ageing at 95°C are related to the thermal decomposition of PVA, beginning at temperatures near 95°C.

The comparison of extract pH values for untreated and treated papers (Tables 7a, b) does not show any acidification effect of the PVA. It is more uncertain to evaluate the degree of polymerization, due to the intrinsic heterogeneity of paper. We want to stress that the intrinsic viscosity, for each value of time and ageing temperature, was determined directly from extrapolation at zero concentration of statistically significant samples of data, obtained at different concentrations. The method of treating the data is original and solves the problem of the intrinsic heterogeneity of the paper.

The experimental data do not show appreciable differences between treated and untreated papers. The results obtained with naturally aged paper, in which degradation effects that could be catalysed by the temperature are excluded, confirm the previous conclusions.

The same conclusions can be extended to all the optical properties such as opacity and brightness. Further, the treated papers, after the sizing agent is removed, seem to be less yellowed than the untreated ones. The natural ageing does not causes appreciable optical variation.

The mechanical reinforcement (tensile strength and folding endurance) does not deteriorate with ageing time and temperature (Tables 10, 12). The folding endurance declines only for the ageing at highest temperature, because the sizing agent stiffens, but regains higher values, similar to those of untreated and unaged papers, after the sizing agent is removed.

The PVA then seems to have a protective effect on the cellulosic fibres and, as shown by biological studies,[11,12] confers on the treated paper, in relation to the untreated one, moderate resistance to biological attack. Some papers submitted to accelerated ageing have been treated with an industrial PVA: Unitika Poval UP-050. Chemical, physical and mechanical tests carried out on papers treated with this commercial size give the same results as those obtained for papers treated with the pure product.

The results of restoration trials, executed in collaboration with the CFR (Centro Fotoriproduzione Legatoria e Restauro degli Archivi di Stato – Rome) restoration laboratory,[13] have demonstrated the positive effect of the PVA solutions in practical restoration of paper and have allowed us to choose the best concentration of PVA solutions for each kind of restoring procedure: 6% for reinforcement and lining of paper and 8% for mending tears and suturing cuts.

We emphasize that, as a consequence of our study on the possible application of PVA for restoring ancient and damaged papers, the restorers working for the Italian State Archives are now officially allowed to use this product.[14]

Summaries

Characterization of low-molecular-weight polyvinyl alcohol for restoration purposes

Low-molecular-weight polyvinyl alcohol, used in the paper industry as a pigment coating adhesive, was tested as a re-sizing agent used in paper restoration to strengthen decayed papers. All of the tests (pH, degree of polymerization, folding endurance, tensile strength, opacity, blue reflectance and reversibility) done after accelerated aging in different ambient conditions and for various lengths of time resulted in very good results for the tested type of polyvinyl alcohol for the intended purpose.

Etude d'un alcool de polyvinyle de faible poids moléculaire pour application en restauration

Un alcool de polyvinyle de faible poids moléculaire utilisé dans l'industrie papetière comme liant pour le couchage a été testé comme agent de réencollage en restauration pour renforcer des papiers dégradés. Tous les tests (pH, DP, résistance aux plis, résistance à la traction, opacité, blancheur et réversibilité) réalisés après des vieillissements accélérés de différentes conditions et de différentes durées ont donné de très bons résultats avec le type d'alcool de polyvinyle testé pour cette application.

Niedermolekularer Polyvinylalkohol für die Restaurierung

PVA, der in der Papierindustrie als Bindemittel für den Strich eingesetzt wird, wurde auf seine Eignung zum restauratorischen Nachleimen, d.h. zum Festigen von geschädigten Papier untersucht. Alle Tests (pH, DP, Falzzahl, Zugfestigkeit, Opazität, Weißgrad, Reversibilität), die vor und nach der beschleunigten Alterung bei verschiedenen Bedingungen durchgeführt wurden, zeigen die sehr gute Eignung des getesteten Polymer-Types für den genannten Zweck.

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Hygrometric Half-lives of Museum Cases

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INTRODUCTION

Solander boxes, portfolio boxes, archival document cases and archival music boxes are extensively used for storing photographs, documents, water color paintings, etc. These museum cases are kept in rooms that often have no temperature or relative humidity control. The relative humidity (RH) in the room therefore follows the changes in the outdoor environment.

This situation especially poses a problem on a wet rainy day when the RH is very high or a dry day when the RH is very low and drops below 30% for prolonged periods of time. If the museum case is not able to buffer this change, damage may result to the photographs and paintings stored in it. Hence it is important to know the moisture-buffering capability of these cases.

Moisture-buffering capability varies among the various types of museum cases because of the differences in construction materials and closure characteristics. Four different types of museum cases commonly used in the United States were tested. Within a particular type of case, a number of samples were tested to get statistically sound values. A number of experiments were replicated.

THEORY

Mathematical expression for the relative humidity inside a museum case

Moisture intrusion to or extrusion from a museum case can take place in three ways:

- diffusion of moisture through openings or gaps in the box at a rate proportional to the RH gradient;
- diffusion of moisture through the surfaces of the box at a rate proportional to the RH gradient; and

- adsorption and subsequent desorption through the different layers of a case: base material, lining, fabric and adhesive.[1-3]

A mathematical expression for RH changes inside the museum case is fairly complicated, since the transport mechanism of moisture is a complex combination of these three phenomena. For simplification, we can combine these phenomena under one proportionality constant[4,5]; for isothermal conditions, the expression reduces to

$$\frac{d(RH)}{dt} = k(RH_{env} - RH) \qquad \text{Eq. 1}$$

where

RH = relative humidity inside the box
t = time
RH_{env} = relative humidity of the environment
k = apparent constant of proportionality.

Integrating Eq. 1 between the limits

$$RH = RH_0 \quad \text{at } t = t_0$$
$$RH = RH \quad \text{at } t = t$$

where

t_0 = initial time
RH_0 = initial relative humidity
t = final time
RH = final relative humidity,
we get the expression

$$\text{Ln}\left[\frac{(RH_{env} - RH)}{(RH_{env} - RH_0)}\right] = k(t - t_0) \qquad \text{Eq. 2}$$

By rearranging Eq. 2, we get an equation for k as

$$k = \frac{\text{Ln}\,[(RH_{env} - RH)\,/\,(RH_{env} - RH_0)]}{(t - t_0)} \qquad \text{Eq. 3}$$

The value of k can be evaluated at any time t by knowing the initial RH, elapsed time and relative humidity at time t. Using the k value obtained, the hygrometric half-life of the museum case can be evaluated as

$$t_{1/2} = \frac{\text{Ln}\,[2]}{k} \qquad \text{Eq. 4}$$

The half-life in Eq. 4 is the time required for the RH inside a case, when placed in a higher or lower ambient RH, to change by half the RH difference between the RH inside the museum case and than in the environment. For example, for a museum case initially at 50% RH that is placed in an environment that is 80% RH, the half-life is the time taken to reach 65% RH.

Experimental

Procedure

All experiments were conducted in a humidity-controlled chamber 2 m × 1.3 m × 2 m. Five cases conditioned at 48 ± 2% RH were placed in the chamber at a time. Each case had its base firmly resting on acrylic supports. The temperature of the chamber was maintained constant at 20°C and the RH in the chamber was elevated or reduced. The temperature and relative humidity were recorded digitally by a Campbell Scientific Instruments CR10 datalogger. In the middle of each museum case were a Shinyei Model THT-A resistive bulk polymer type RH sensor and thermistor, both connected to the data logger. Prior to the experiment, the sensors were calibrated at 33% RH and 75% RH using saturated $MgCl_2$ and NaCl solutions and found to have accuracy better than 2%, even with inaccuracy due to hysteresis included. The data were collected each minute, averaged over a 60-min period by the data logger and transferred to a personal computer for analysis. The experimental setup is shown in Fig. 1.

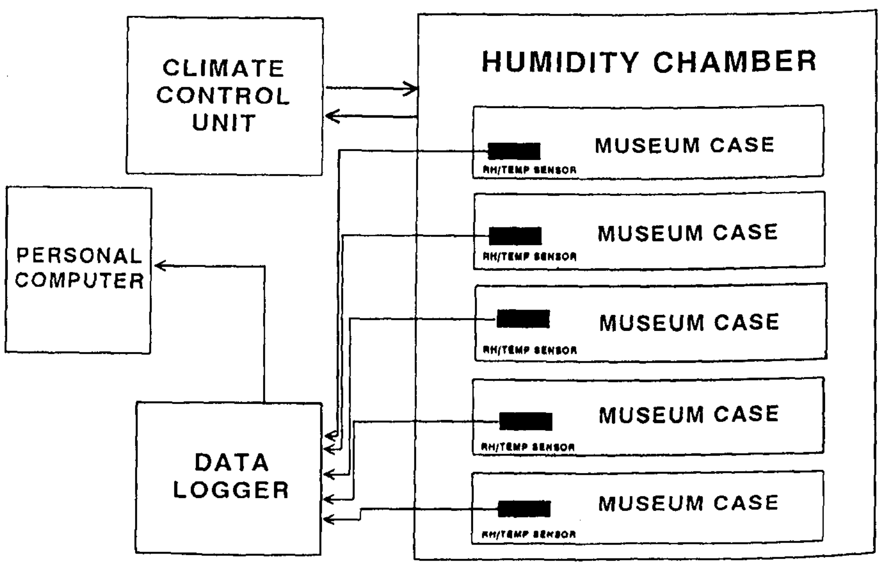

Fig. 1. Schematics of experimental set-up

Experiments were performed for two different environmental conditions:

1) External RH higher than the RH inside the museum case. For condition 1 the ambient RH was maintained at 82 ± 2%.
2) External RH lower than the RH inside the museum case. For condition 2 the ambient RH was maintained at 32 ± 2%.

Description of the evaluated museum cases

Four different types of cases were tested. They differed in construction details and closure characteristics. The section below briefly details the four different cases and mat boards. Further specifications of the cases are in Appendix 1.

Solander box

Made of basswood (an American linden tree, *Tilia americana*, a soft wood) on the sides and binder's board on the top and bottom with Truecore card stock

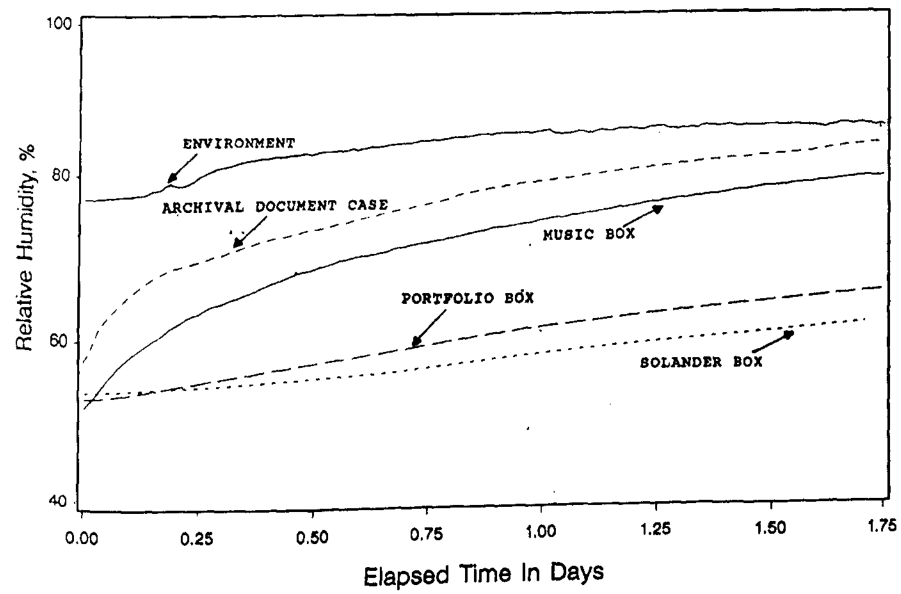

Fig. 2. Behavior of museum cases at high ambient RH

lining (acid-free, lignin-free alpha cellulose purified pulp)[6] and a book cloth fabric. (These materials can absorb and adsorb significant moisture.) The boxes have a lip arrangement for easy opening.

Portfolio boxes

Made of 0.254-cm-thick heavy weight boxboard lined with acid-free Tyvek (a neutral paper made from spun-bonded olefin with a bonded monofilament structure[6]; the outside of the box is covered with black bookcloth. (The closure is better than that of Solander box.)

Archival document cases

Made of 0.152-cm-thick grey board, the box stands vertically and the top fits very loosely over the sides.

Music boxes

Made of 0.152-cm-thick lignin-free paper, they feature a two-piece design with a drop front for easy access.

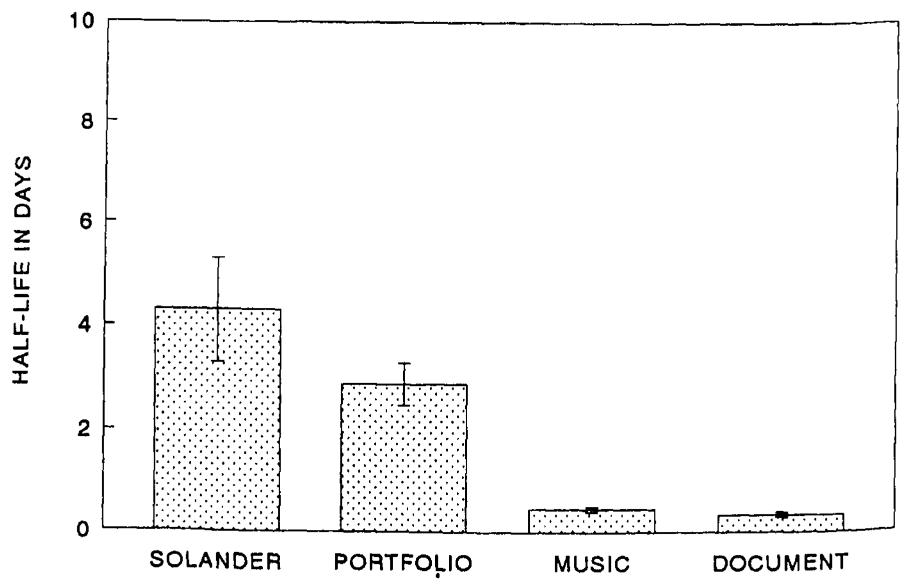

Fig. 3. Hygrometric half-lives of museum cases in high ambient RH

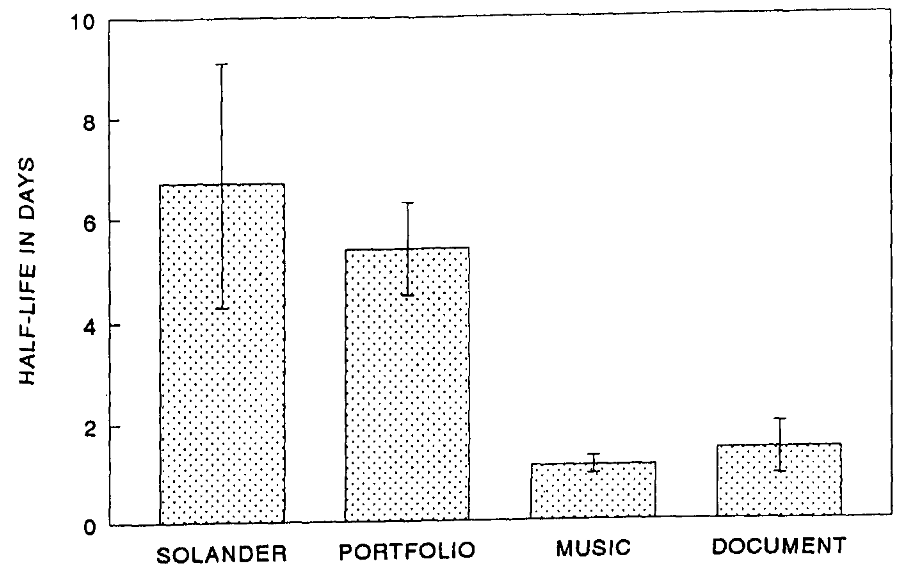

Fig. 4. Hygrometric half-lives of museum cases in low ambient RH

Mat boards

These are 100% cotton rag and 4 ply; the weight at 50% RH is 223 g for a 41 cm × 56 cm board.

Results and Discussion

Five cases of each type were tested and the results are expressed as mean ± one standard deviation (SD). For all four types of cases, the hygrometric half-life at low ambient RH was higher than at high RH; the range of half-lives at low ambient RH was also more than at high ambient RH. The typical response of the four museum cases to high ambient RH is shown in Fig. 2, and the hygrometric half-lives for both high and low ambient RH are shown in Fig. 3 and 4.

Table 1. Hygrometric half-lives of Solander boxes

No.	Ambient RH	Half-life in days mean ± 1SD	Half-life range in days
1	High	4.3 ± 1.0	3.0–6.3
2	Low	6.7 ± 2.4	3.7–10.7

Solander boxes

The moisture-buffering capacity of Solander boxes is listed in Table 1, and is better when the ambient RH was low. This could be attributed to hysteresis: the rate of moisture absorption is faster than the rate of moisture desorption. Overall, the hygroscopicity of the construction materials make Solander boxes good moisture buffers. The variations in hygrometric half-lives are also given in Table 1. The variations in the hygrometric half-life are mainly due to customized manufacturing of each box and their individual closure characteristics being different.

Portfolio boxes

Portfolio boxes had good moisture-buffering capability. Their hygrometric half-lives were slightly less than that of Solander-type boxes, probably because the hygroscopicity of their construction materials was less than those of Solander-type boxes. Portfolio boxes had better closure conditions than Solander boxes.

The variations in half-life for the portfolio boxes (Table 2) were less than those for Solander boxes. This could be attributed to the fact that the closure is more consistent for portfolio boxes since the top face fits more thightly over the bottom.

Table 2. Hygrometric half-lives of portfolio boxes

No.	Ambient RH	Half-life in days mean ± 1SD	Half-life range in days
1	High	2.9 ± 0.4	2.5–3.4
2	Low	5.4 ± 0.9	4.3–6.4

Table 3. Hygrometric half-lives of music boxes

No.	Ambient RH	Half-life in days mean ± 1SD	Half-life range in days
1	High	0.47 ± 0.05	0.40–0.56
2	Low	1.13 ± 0.18	0.83–1.37

Table 4. Hygrometric half-lives of document cases

No.	Ambient RH	Half-life in days mean ± 1 SD	Half-life range in days
1	High	0.35 ± 0.05	0.30–0.44
2	Low	1.46 ± 0.53	0.80–2.13

Music boxes

The hygrometric half-lives and range of half-lives of music boxes are listed in Table 3. Music boxes offer minimal moisture-buffering capability because 1) the thickness of lignin-free type 1 paper is only 0.152 cm and hence moisture can be more easily transferred through the surface, 2) the boxes are constructed as a two-piece design with a drop front for easy access; this is a loose fitting and allows moisture movement through these gaps and 3) the material does not absorb or adsorb much moisture, unlike the materials in Solander or portfolio boxes.

Archival document cases

Archival document cases offer minimal moisture-buffering capability. This probably could be attributed to: 1) the thickness of board is only 0.152 cm and hence moisture can be transferred easily through the surface, 2) the boxes stand vertically and are constructed with a top opening for easy access and one side having a "fold-flat" handle, these features allow sufficient gaps for moisture to leak in and out and 3) the construction materials do not absorb or adsorb much moisture.

The hygrometric half-lives and ranges of half-lives are in Table 4.

Effect of matboards

Solander boxes were tested with and without mat boards. For the experiments with mat boards, four cotton rag mat boards were put inside, and the sensor

Table 5. Hygrometric half-lives of Solander boxes with and without mat boards

No.	Ambient RH	Without mat boards	With mat boards
1	High	4.3 ± 1.0	4.7 ± 0.9
2	Low	6.7 ± 2.4	22.5 ± 13.3

Table 6. Hygrometric half-lives of museum cases

	Solander box	Portfolio box	Archival music box	Archival document box
High ambient humidity ($82 \pm 2\%$)	4.3 ± 1.0	2.9 ± 0.4	0.47 ± 0.05	0.35 ± 0.05
Low ambient humidity ($32 \pm 2\%$)	6.7 ± 2.4	5.4 ± 0.9	1.13 ± 0.18	1.46 ± 0.53

placed between the second and third mat board. Three different experiments were performed, and the results, expressed as mean $\pm$ 1 SD, are compared in Table 5.

Mat boards help in improving the moisture-buffering capacity, more in the case of low ambient RH. Hence, an object placed between the mat boards will have better protection against RH change especially under dry ambient conditions. Another set of experiments was conducted using 30 mat boards conditioned at $48 \pm 2\%$ RH with a sensor placed on top (to illustrate the effect of having a hygroscopic material inside the case, but not directly protecting the photograph or painting). The half-life increased to 9.1 ± 0.7 days in a high-RH environment and to 19.5 ± 9.6 in a low-RH environment. Thus, in addition to the protection mat boards offer to objects placed between them, the presence of mat boards in a Solander box increases the moisture-buffering capability of the Solander box.

Conclusions

The hygrometric half-lives of Solander boxes, portfolio boxes, archival document cases and music boxes for both high and low ambient RH are shown in Table 6.

Portfolio boxes and Solander boxes are good moisture buffers. Archival music boxes and document cases offer minimal protection against ambient RH changes compared with Solander and portfolio boxes. All cases were better moisture buffers against low ambient RH than against high ambient RH. Mat boards help in improving the moisture-buffering capability, with more improvement noted in the case of low ambient RH than in the case of high ambient RH. The greater the number of mat boards, the better the moisture-buffering capability.

Suppliers of Materials

Solander box. Light Impressions, Archival Supplies, 439 Monroe Avenue, Rochester, NY 14607, USA

Portfolio box. University Products, 517 Main Street, P.O. Box 101, Holyoke, MA 01041, USA
Archival document cases and music boxes. Conservation Resources, 8000-H Forbes Place, Springfield, VA 22151, USA

Acknowledgements

We express sincere thanks to Dr. Frank Preusser, Dr. Neville Agnew and Dr. Frank Lambert for guidance and suggestions at various stages in this project. We also express gratitude for the contribution by Loy Fatt Yong in terms of experimental set-up as well as some preliminary results. We wish to express gratitude to Mary Chase, Conservator, Getty Center for the History of Art and the Humanities, for valuable suggestions and for providing most of the cases for testing.

Summaries

Hygrometric Half-lives of Museum Cases

The moisture-buffering capability of four types of museum cases, Solander boxes, portfolio boxes, archival document cases and music boxes, was evaluated. An expression for hygrometric half-life was derived and the half-lives were compared with high, as well as low ambient relative humidity for the four types of cases in terms of their materials of construction and closure characteristics.

Demi-vies hygrométriques de boîtes de conservation

Quatre types de boîtes de conservation (dans la terminologie anglo-américaine: boîte Solander, boîte portfolio, boîtes à archives et boîtes à musique) ont été évaluées du point de vue de leur capacité à réguler l'humidité. Une expression de la demi-vie hygrométrique a été trouvée et les demi-vies ont été comparées avec de hautes et basses humidités relatives environnantes pour les quatre types de boîtes en fonction de leurs matériaux constitutifs et de leur mode de fermeture.

Hygrometrische Halbwertzeiten von Schutzkästen und -kartonagen

Vier Typen von Schutzkästen und -kartonagen (in unübersetzbarer angloamerikanischer Terminologie: Solander-, Portfolio-, Archivalien- und Musikalienkästen) wurden auf ihre Kapazität hin untersucht, Feuchteschwankungen im Umgebungsklima auszugleichen. Es wird der Begriff der hygrometrischen Halbwertzeit geprägt. Die entsprechenden Zeiträume wurden bei Ausgleich gegen höhere und gegen niedrigere Umgebungsfeuchte gemessen. Die sehr unterschiedlichen Werte werden aus Material, Bauweise und Verschlußsystem der vier Kastenformen erklärt.

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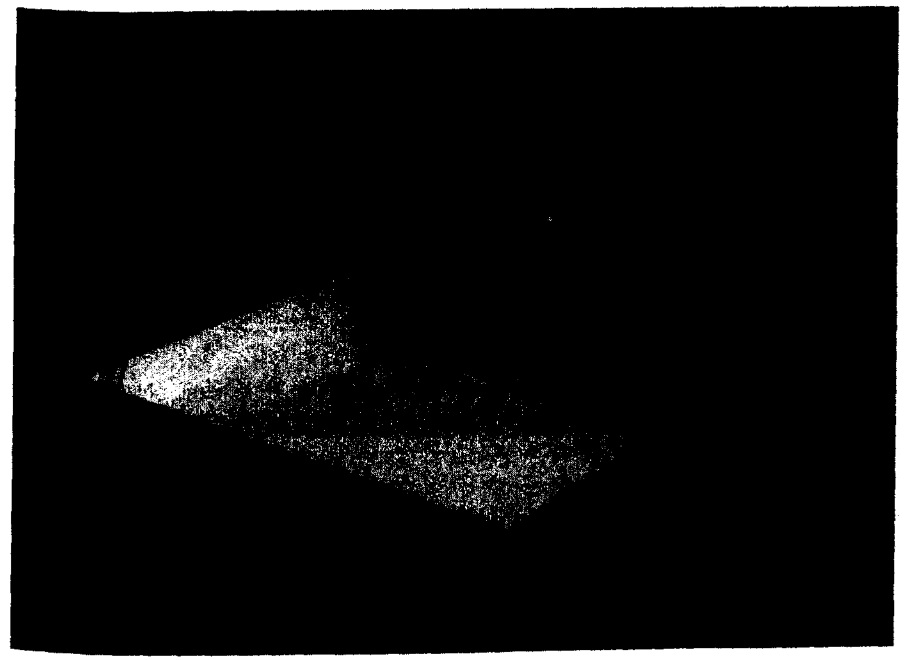
2. Catalog from University Products, Holyoke, Massachusetts, USA.
3. Catalog from Conservation Resources, Springfield, Virginia, USA.
4. Daniel, V. & Maekawa, S.: *The moisture buffering capability of Solander boxes.* Marina del Rey CA: Getty Conservation Institute, 1991 (Internal report).
5. Daniel, V. & Maekawa, S.: *The moisture buffering capability of Solander boxes.* Presented at the WAAC Annual Meeting, Seattle, WA, USA, September 29–October 2, 1991.
6. Personal communication, Niccolo Caldararo, Conservation Technician, Fine Arts Museum of San Francisco.

Appendix 1

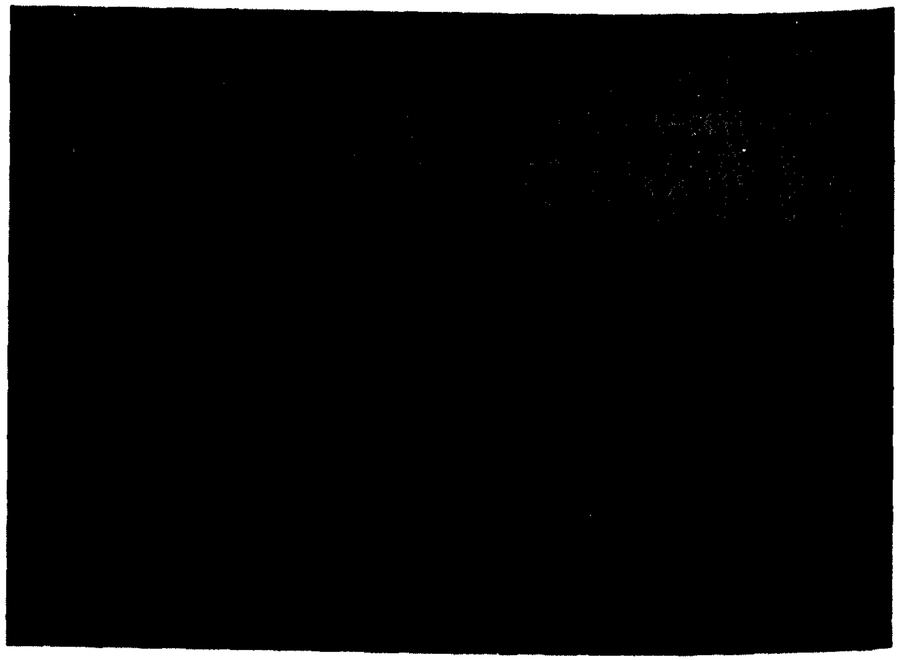
Solander box specifications

Interior dimensions: 42 cm × 57 cm × 6.5 cm
Weight: 2075 g
Base material:
  Top and bottom: 2.5-mm-thick binder's board
  Sides: basswood lined with acid-free board, including spine.
Lining: Truecore 133 Card Stock
Fabric: book cloth, acrylic-impregnated.
Adhesive: anti-tarnish, pH balanced with 0.0008% sulfur content.
Supplier: Light Impressions, Rochester, NY, USA
Modifications made in the Solander box: Most of the Solander boxes used at the Getty Center do not have latches. Hence, we removed the latches in the Solander boxes before conducting experiments.



Portfolio box specifications

Interior dimensions: 36 cm × 46 cm × 5 cm
Weight: 1280 g
Base material: 2.5-mm-thick heavy weight boxboard, lined with uncoated white acid-free Tyvek.
Fabric: moisture- and vermin-resistant black book cloth.
Adhesive: pH balanced.
Supplier: University Products, Holyoke, MA, USA.

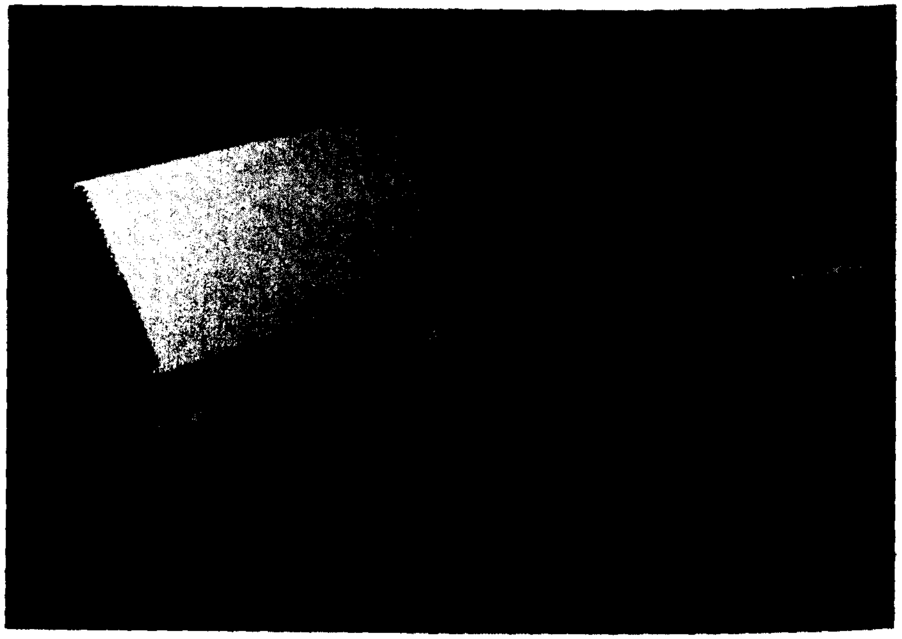


Archival music box specifications

Interior dimensions: 38 cm × 29 cm × 7 cm
Weight: 570 g
Board specification: 1.5-mm-thick, lignin-free type 1 paper.
Supplier: Conservation Resources, Inc., Springfield, VA, USA.

Archival document case specifications

Interior dimensions: 39 cm × 26 cm × 13 cm
Weight: 540 g
Board specifications: 1.5 mm-thick grey board, pH 8.5, acid-free, lignin-free, 3% alkaline buffering.
Edges: metal
Supplier: Conservation Resources, Inc., Springfield, VA, USA.



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Constructing a Mini-vacuum Unit and Using It for Philatelic Materials

by MICHAEL MAGGEN

Introduction

In 1990 I participated in a course in the use of the suction table at the Conservation Analytical Laboratories (CAL) of the Smithsonian Institution, Washington, DC, USA. The main topics of the course were the history of the suction table and the theory and practice of treatment and techniques. This article was written in the spirit of "do it yourself" displayed by some of the course instructors.

Philatelic Material of Besieged Jerusalem 1947

In Jerusalem there is a private philatelic collection (Mr. Rimon J.) that contains rare envelopes dating from 1947, the time of Israel's War for Independence. Jerusalem was under siege at this time, and the postal system was functioning under war conditions. The Jerusalem Mail Service depended on army air transportation, on personal delivery and sometimes even on carrier pigeons. Mr. Levanon, a philatelic researcher and a member of the Israeli Philatelic Organization, recounted in his article "The air mail from besieged Jerusalem 1948"[1] some events concerning the air mail services. During the period when Jerusalem was under siege in the war by March 1948, the main road to Tel Aviv was firmly blocked by Arab fighters. Mr. Rimon J. is the editor of the philatelic review *Holy land postal history*.[1] Here he has published some of his findings on Jerusalem and the air mail services.

The beginning of the postal siege of Jerusalem more or less coincided with the official termination of the British mandate postal services in Jerusalem on April 25, 1948. Consequently, no organized air mail service is known to have operated and only a few letters with some kind of Jerusalem arrival cancellation (army or civilian) are known from this period. However, in the opposite direction, Jerusalem to Tel Aviv, there was an organized and controlled air mail service.

Observation of Paper Objects and the Complexity of Treating Them

The conservation of an envelope initially requires an examination of its folding system and the nature of the adhesive. Most of the envelopes were of poor paper quality; the margins were coated with gum-arabic, which eventually became brown and subject to micro-organism activity. Varied mediums were found on the envelopes, official franks, postal cancellations and personal information that varied from pencils (normal, colour and copy), different inks (water-soluble and water-resistant in different colours) and typewriter characters. This was found on both sides of the envelope.

Fig. 1 and 2 show varied mediums. These paper objects are extremely sensitive to conventional conservation treatments and require a new approach. This was the basis for developing a miniature suction unit. Treatments involved removal of rust stains, mending of tears and flattening by liquid or vapour treatments.

The miniature suction device is a vacuum unit with a modified suction panel allowing for greater control over the introduction of liquid and vapour. The unit has produced excellent results with the cleaning of stains, consolidation of sensitive inks and flattening of deformations.

The Miniature Suction Unit

The cost of constructing a mini-vacuum table can be quite low; the most expensive item is the vacuum pump, which can range between USD 400 and 700. The following elements are required:

- perforated metal sheet (ideally stainless steel), thickness 1.5 mm size 110 mm x 70 mm: a cover of an old radio-transistor receiver can be used;
- light metal brass plate, size 110 mm x 70 mm, thickness 1.5–2 mm;
- aluminium tube, internal diameter 5–6 mm, thickness 1.5–2 mm;
- aluminium profile, U-type, size 5 mm x 5 mm x 5 mm, length 140 mm;
- corrugated metal, size 110 mm x 70 mm (waffle metal sheet);
- epoxy resin; and
- the vacuum pump must be lubricated.

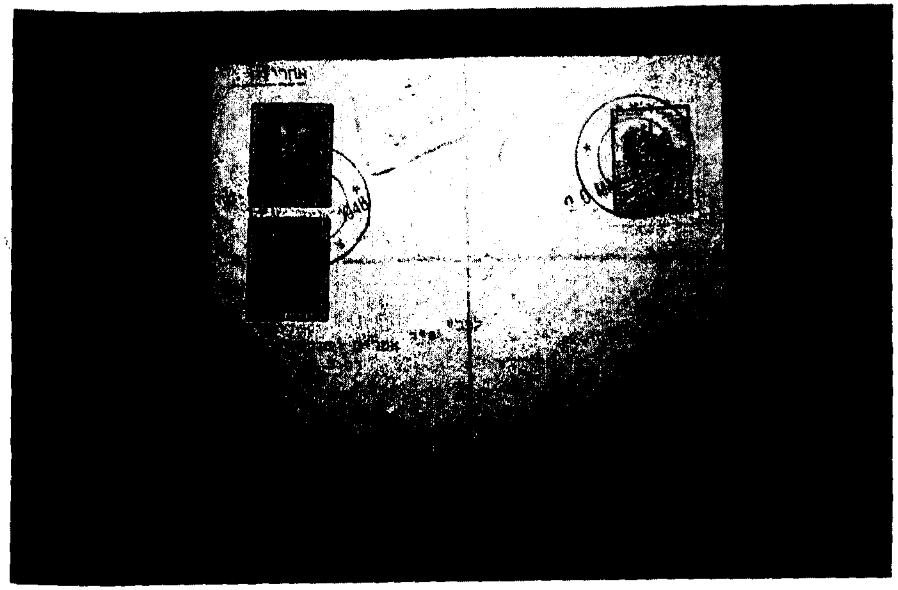


Fig. 1

Fig. 2

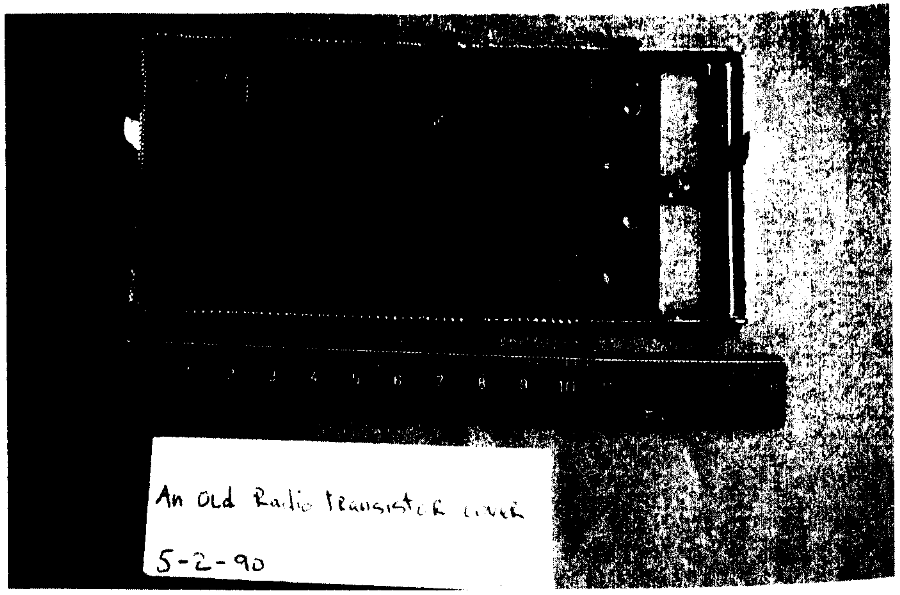


Fig. 3

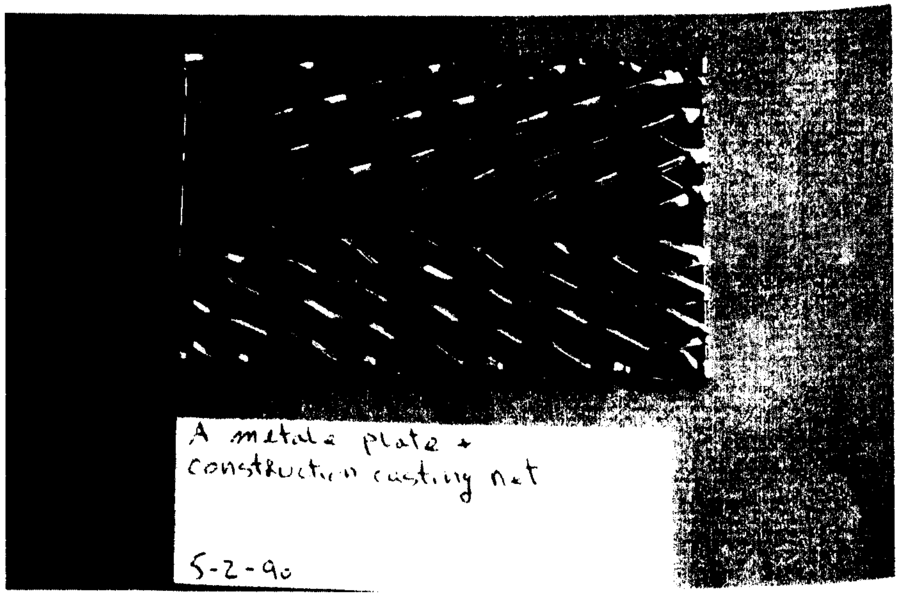
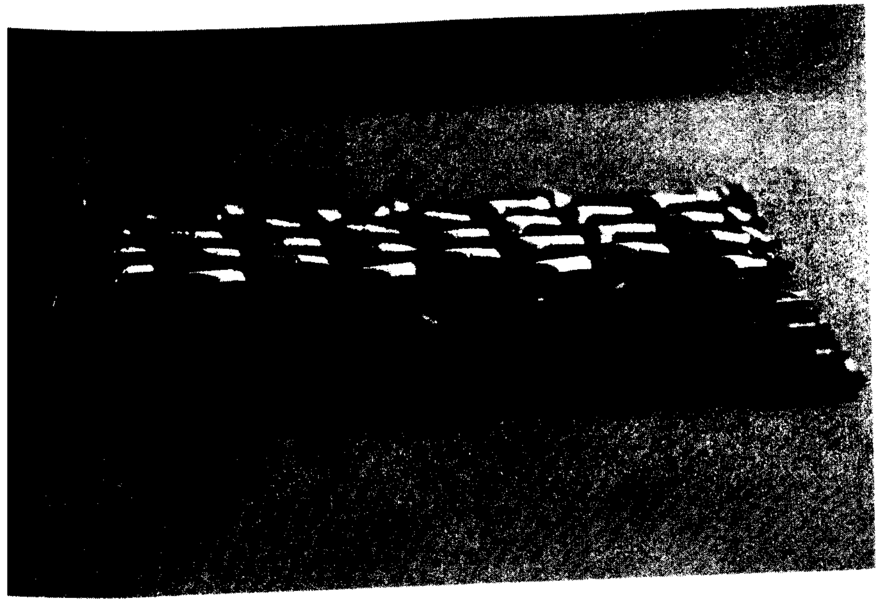


Fig. 4



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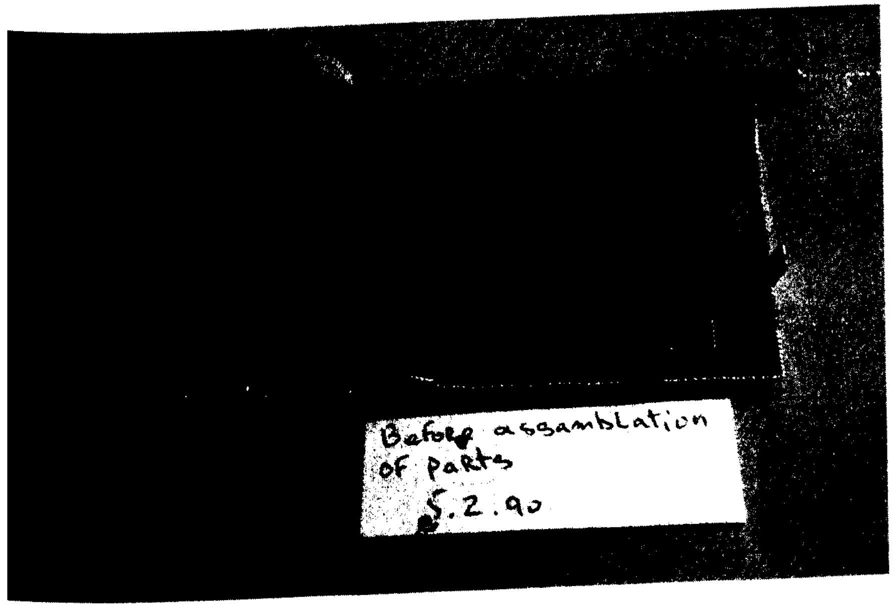

Fig. 6. Before assembling the parts

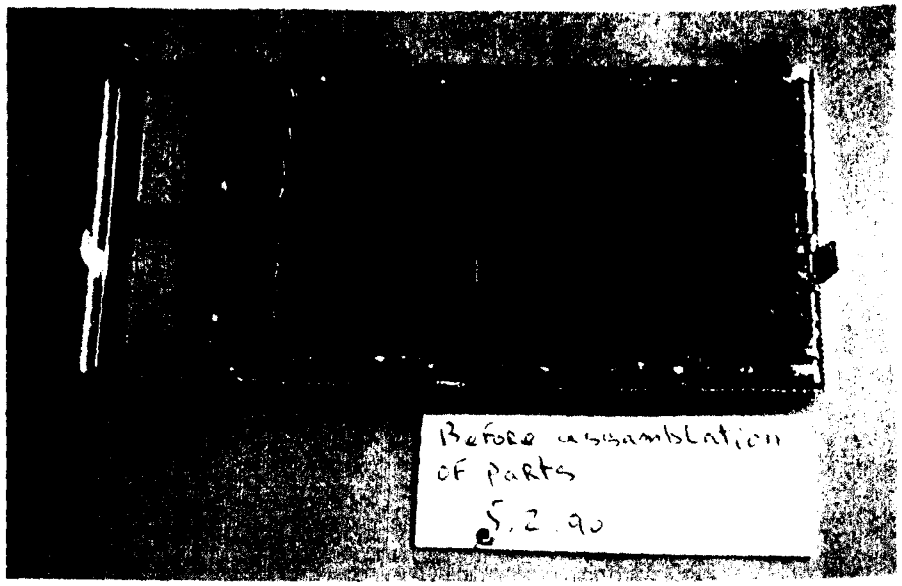

Fig. 7. Before assembling the parts

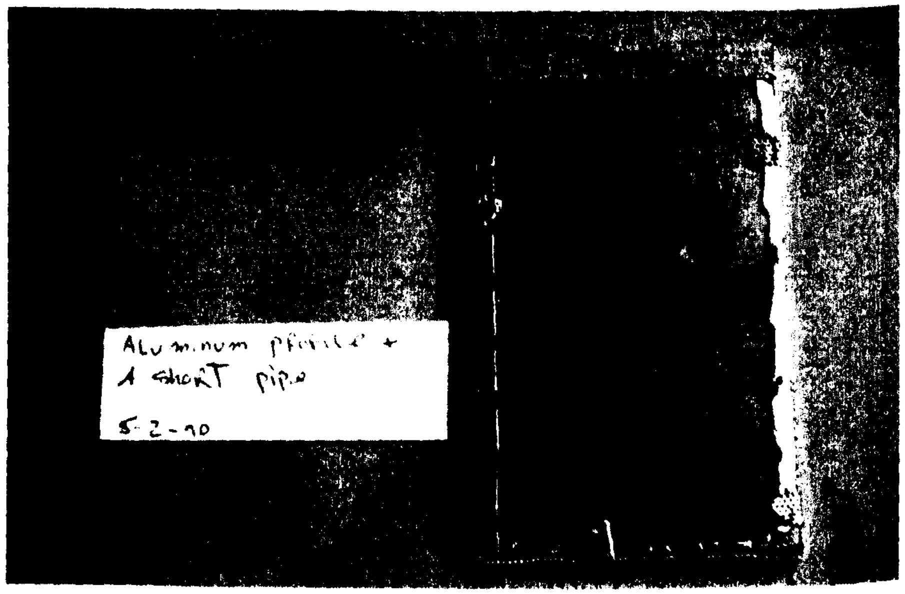

Fig. 8

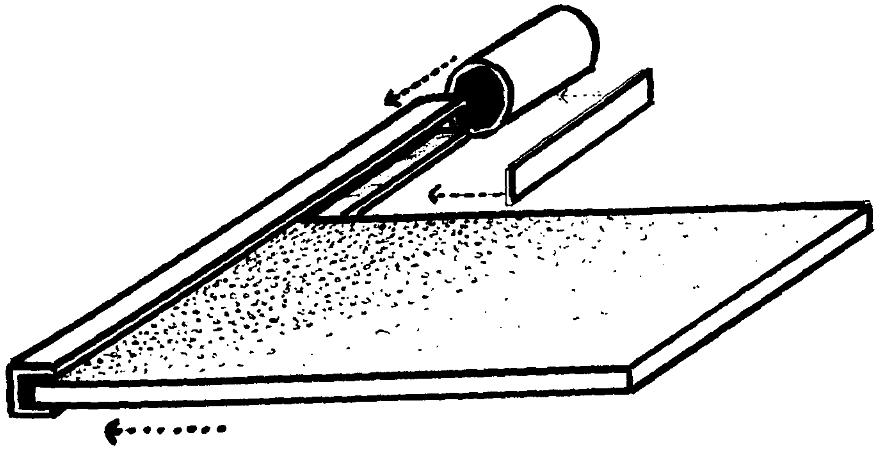

Fig. 9

Fig. 10

The cover of an old radio-transistor receiver is removed from the receiver box (Fig. 3).

The light metal plate and the metal waffle should measure 110 mm × 70 mm. Fig. 4 illustrates the position of the waffle on top of the metal plate; the angle of the ribs was changed slightly, creating the internal space (Fig. 5).

This was placed on top of the perforated metal plate and secured together by bending over the perforated metal edges (Fig. 6, 7).

The new combined element was attached to the aluminium U profile (Fig. 8, 9).

Epoxy resin sealing glue was applied to the bottom cover along the aluminium U profile and on the small aluminium tube, ensuring effective sealing and allowing air to flow down the perforated cover along the aluminium U profile and to the pump without any air leaking. Fig. 10 shows the completed unit.

Some Pre-operation Remarks

The unit was designed as a tool for local treatment. The pump should ideally produce a high vacuum and low air flow. A lubricated vacuum pump produces such vacuum values. This unit was connected to a lubricated vacuum pump,

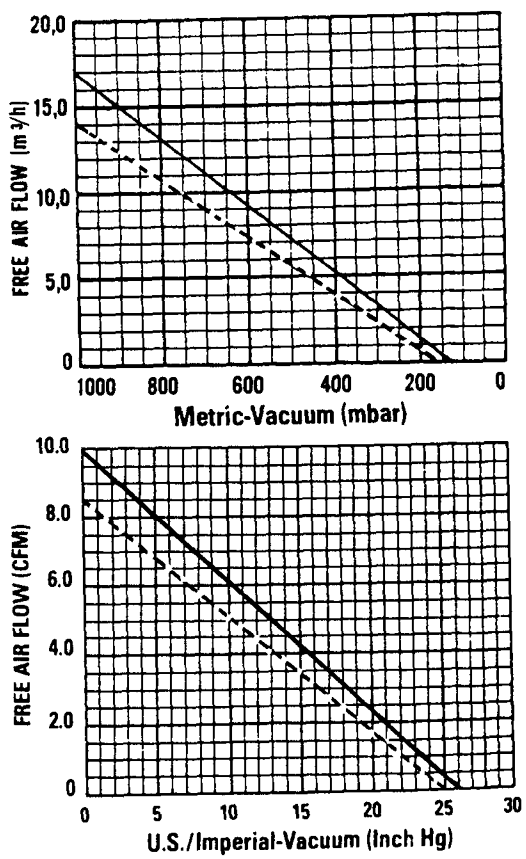

Fig. 11. The solid line is for 60-cycle performance. The dotted line on curve is for 50-cycle performance

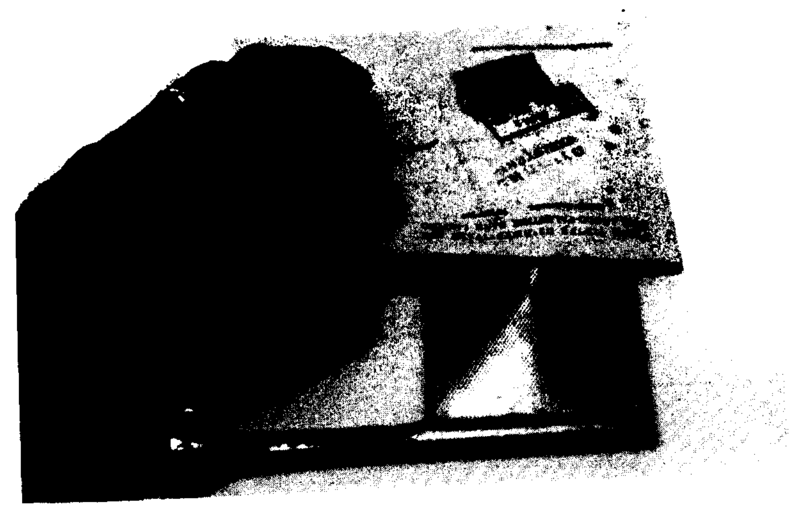

Fig. 12

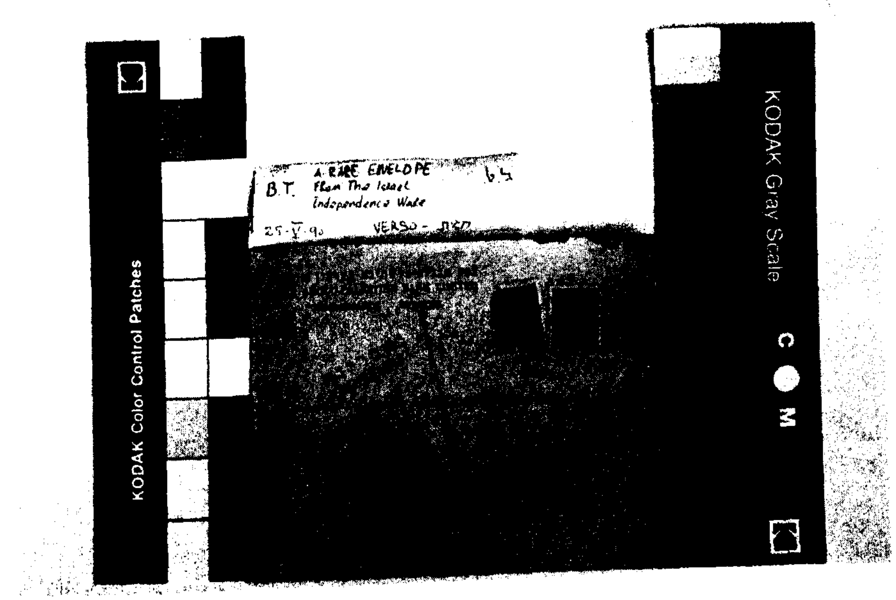

Fig. 13

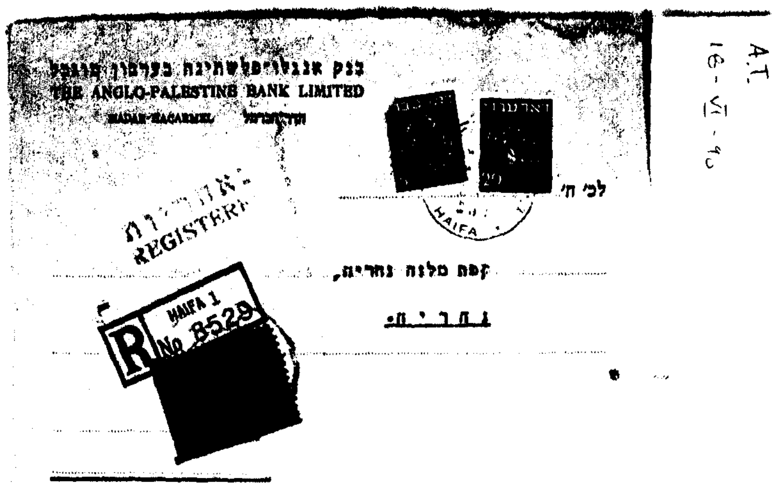

Fig. 14

Fig. 15

such as that made by Gast Company (UK), Model 1022. For vacuum and air flow specifications, see Fig. 11. Such vacuum sources as the centrifugal vacuum table pump or blower are not recommended; they would fail to produce the high vacuum under low-air-flow conditions.

Operational remarks

There are several options to working with the unit inside the envelope side (Fig. 12). It is important to use a blotting paper support to absorb the liquids and the impurities of the dissolved stain and to provide a soft support, preventing alteration of the object surface and texture. Fig. 2 and 13–15 give examples. Fig. 13: foxing; Fig. 2: detailed Fig. 13. The object was treated with an aqueous solution pH 9 (ammonium hydroxide) to eliminate the stains. Fig. 14 and 15 (detail): the object after treatment.

Acknowledgement

I thank Hassia Rimon, Paper Conservator of Tel Aviv Museum for Art, for help in this article.

Summaries

Constructing a Miniature Suction Table and Using it for Philatelic Materials

A miniature suction unit is a type of unit that can be adapted for paper conservation treatment. This article provides a case study of philatelic materials that contain historically significant rare envelopes from 1947 on the airmail services in besieged Jerusalem. The vacuum unit is relatively inexpensive to build. The operation of the system is described. One possible treatment using this unit is removing stains.

Construction d'une table aspirante miniature et utilisation pour des documents philatéliques

Une unité aspirante miniature est une sorte de table aspirante qui peut être adaptée pour restaurer des papiers. Cet article illustre le cas de documents philatéliques que comportaient des enveloppes rares et historiquement importantes de 1947 de la poste aérienne de Jérusalem occupée. L'unité sous vide est peu coûteuse a construire. Son mode opératoire est décrit. Une application possible de cette unité est l'enlèvement de taches.

Der Mini-Vakuumtisch. Einige Bermerkungen zu seiner Konstruktion und zu seinem Gebrauch bei philatelistischen Objekten

Der Mini-Vakuumtisch ist eine Variante der Großform, die für die Papierkonservierung herangezogen werden kann. Der Aufsatz bietet eine Fallstudie für die Ansendung auf philatelistisches Material von historischer Aussage, nämlich einen seltenen Briefumschlag aus dem Jahre 1947: »Luftpostdienst im Belagerten Jerusalem«. Konstruktion und Bau des Mini-Vakuumtisches erfordern verhältnis-

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2. Hon, D. N.-S.: *Yellowing of modern papers.* In: Williams, J. C., ed. *Preservation of paper and textiles of historic and artistic value II.* Advances in Chemistry Series, 193. Washington, DC: American Chemical Society, 1981: 119–42.

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mäßig wenig Aufwand. Es werden einige Hinweise zum Einsatz des System gegeben. Ein denkbarer Bereich ist das Entfernen von Flecken.

Reference

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