Journal of Thermal Analysis, Vol. 40 (1993) 285-302

THERMAL ANALYSIS AND THE SCIENTIFIC CONSERVATION OF CULTURAL MATERIALS

A study of the effects of conservation treatment on the Fanshawe archive

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Prior to treatment, letters dating from 1665–66 were characterised using SEM, FTIR, ESCA or XPS, TG, TMA and DLTMA. All three papers were similar in composition and were basically cellulosic materials. Two which had been sent from Lisbon contained trace amounts of Fe and Cu; these impurities were also present in a letter sent from Dublin. All three letters had been written with iron gall ink. The letter from Dublin had an additional feature in the ink in the form of small bright specks of mica. The papers were examined after conservation treatment using the above same techniques in an attempt both to determine and quantify any changes which had occurred during the treatment process. Scanning electron micrographs showed that pronounced changes had occurred to the surfaces of the treated papers. With XPS it was possible to measure the change in the surface composition of the papers which occurred on treatment. It was also found that the treatment reduced the thermal stability of the papers in all three cases.

Keywords: conservation of cultural materials

Introduction

Valence House Museum (Dagenham, England) has, since 1963, housed not only a large collection of Fanshawe family portraits but also a very rich family archive which comprises estate and private papers from the sixteenth to the twentieth centuries of at least two branches of the family. Of national and international interest are the papers of Sir Richard Fanshawe (1608–66) relating to his three embassies to the Iberian Peninsula in the 1660s. It is from within this collection that three documents were selected for conservation and treated using both aqueous and non-aqueous methods of deacidification. Since the three documents

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were basically of a similar composition and of the same age it presented a unique opportunity to observe and measure the effect of various methods of deacidification treatment on seventeenth century paper.

The paper samples

For the conservation treatment, three letters of the period mid-1665 to early 1666 were chosen, mainly for the following reasons: obvious signs of damage, such as tears, partial water damage, and microbial attack; range of provenance (they contained three different watermarks); their substantial area of blank paper (for sampling); and their lack of any great intrinsic importance. The aim was to test the effect of three different types of deacidification treatments (one non-aqueous and two aqueous) with a view to using the optimum method for the documents of greatest importance. Similarly in terms of characterisation, the aim was to optimise measuring procedures for the smallest possible sample size and also to explore new techniques for testing papers where there is no sampling requirement.

Sample 1 was treated by a non-aqueous method of deacidification, using a preparation containing methyl magnesium carbonate. Initially the letter was washed in deionised water for one hour. This resulted in partial fading of the stain due to microbial damage. The paper was reinforced with lens tissue on the inside and over the stained area where the paper was noticeably weaker.

Sample 2 was treated with saturated calcium hydroxide solution (2 g/litre) and reinforced with lens tissue and archival paste. The paper was then cold pressed between felts.

Sample 3 was treated with light magnesium carbonate solution (4.5 g/l) into which some CO_2 had been introduced.

Results and discussion

Scanning electron microscopy (SEM)

The upper surfaces of the paper were examined using a Jeol Superprobe 733 before and after conservation treatment. Samples were mounted on double-sided tape and gold coated for about two minutes using a Nanotech sputter-coating unit. Secondary electron images were recorded using Ilford 120 film.

All three samples before treatment showed the presence of loose fibres at low magnification (Fig. 1). Figure 2 shows Whatman filter paper no. 1 at the same magnification where there is a high degree of inter-fibre connections. At higher magnification (×1000) it was possible to see the presence of many small particles of irregular shape adhering to the fibres (Fig. 3). Fibres seemed to be flattened compared to the Whatman paper at the same magnification (Fig. 4). The latter shows clearly the concave part of the cellulosic fibre which has been described as the most accessible and reactive zone in the fibre cross-section [1]. (Whatman filter paper no. 1 was used throughout the study as a standard cellulose reference sample.)

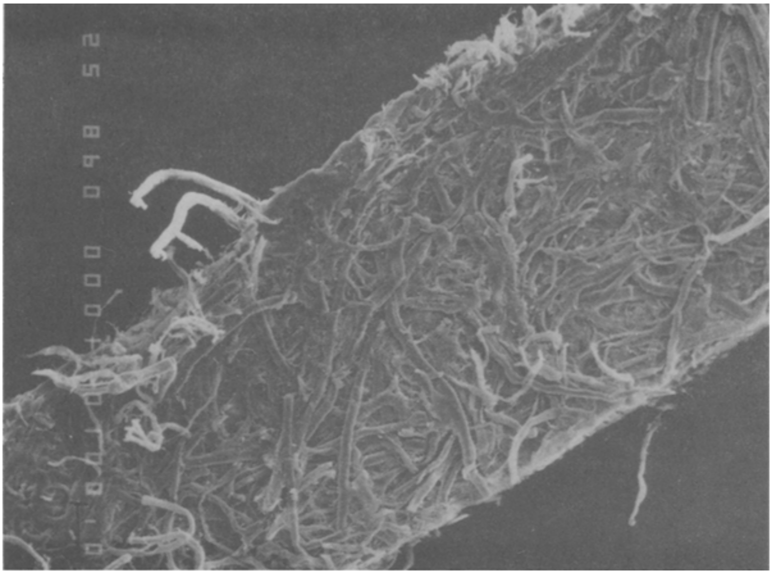

Fig. 1 Sample 1 before treatment (×86, bar=100 μm)

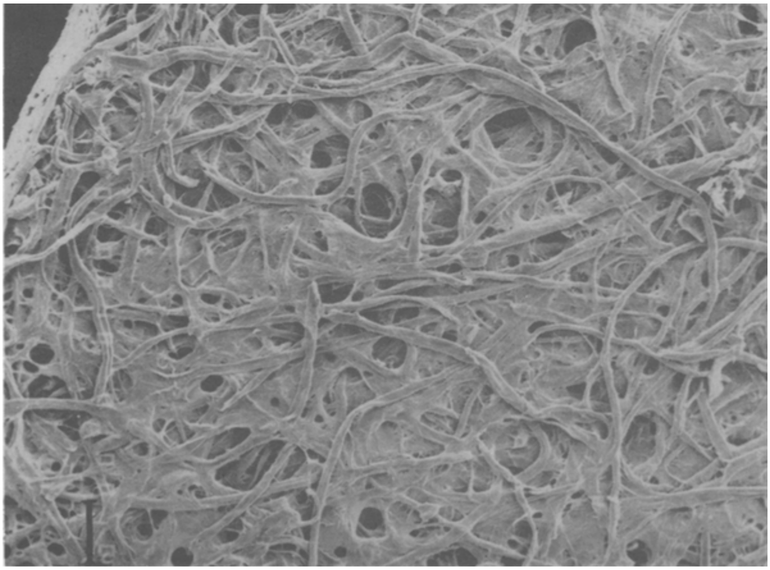

Fig. 2 Whatman filter paper no. 1 (×86, bar=100 μm)

After examation at low magnification (×86) it was possible to see that in all three samples all forms of treatment had created a more open structure (Figs 5, 6).

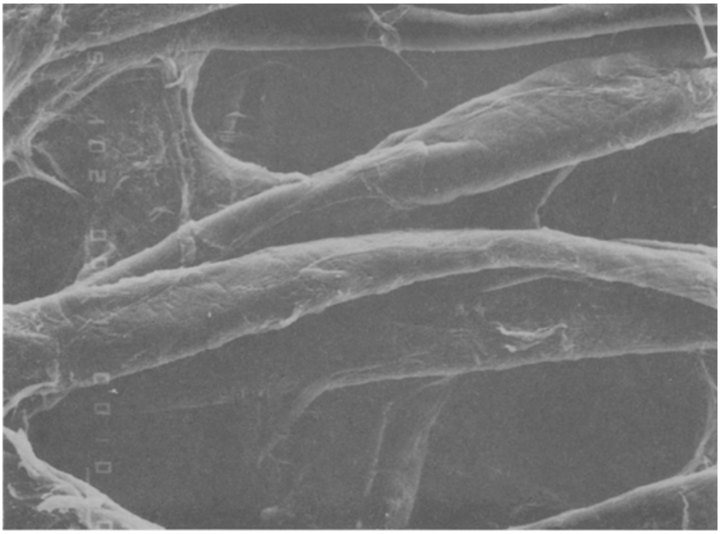

Fig. 3 Sample 1 before treatment: fibres appear to be flattened and small irregular particles appear to be adhering to them (×1000, bar=10 µm)

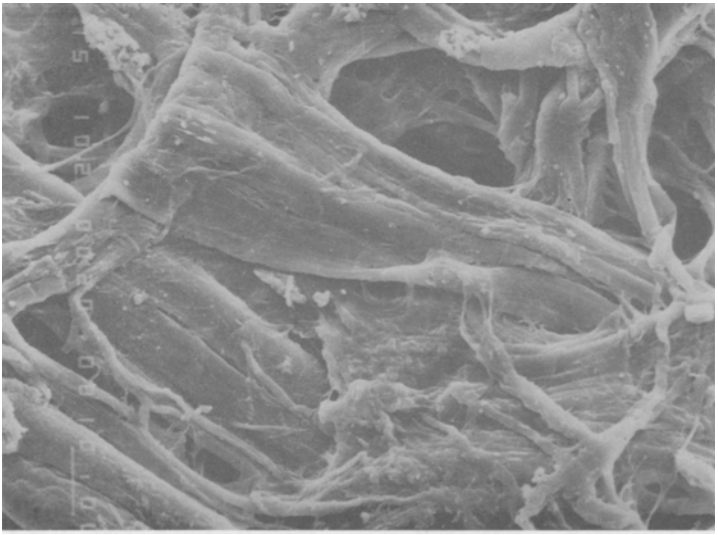

Fig. 4 Concave part of the cellulosic fibre (Whatman filter paper ×1000, bar=10 µm)

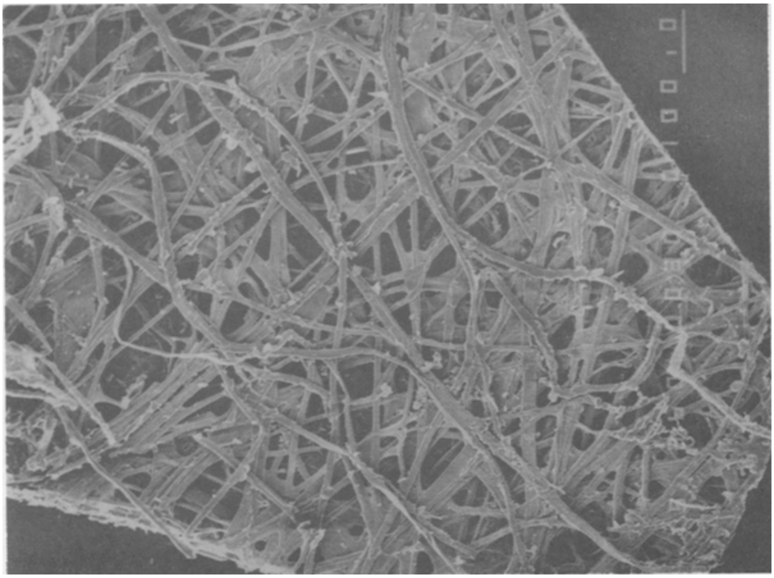

Fig. 5 Sample 1 after non-aqueous de-acidification (×86, bar=100 μm)

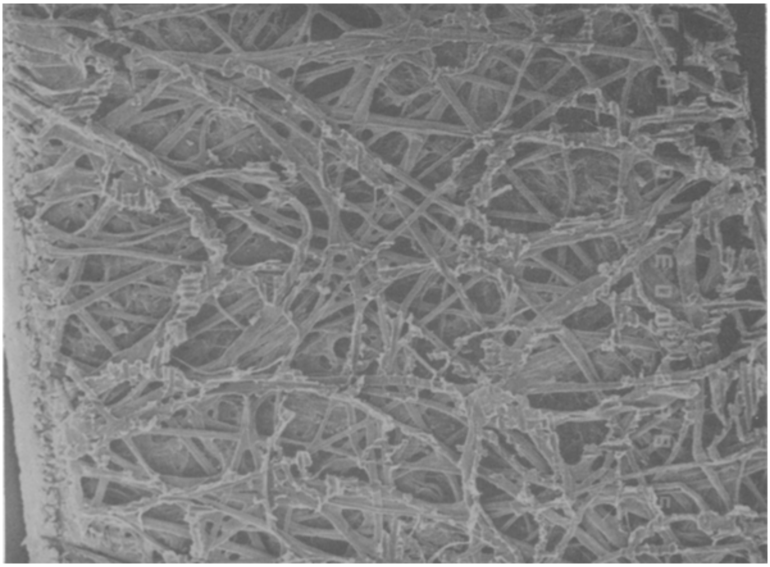

Fig. 6 Sample 3 after aqueous de-acidification (×86, bar=100 μm)

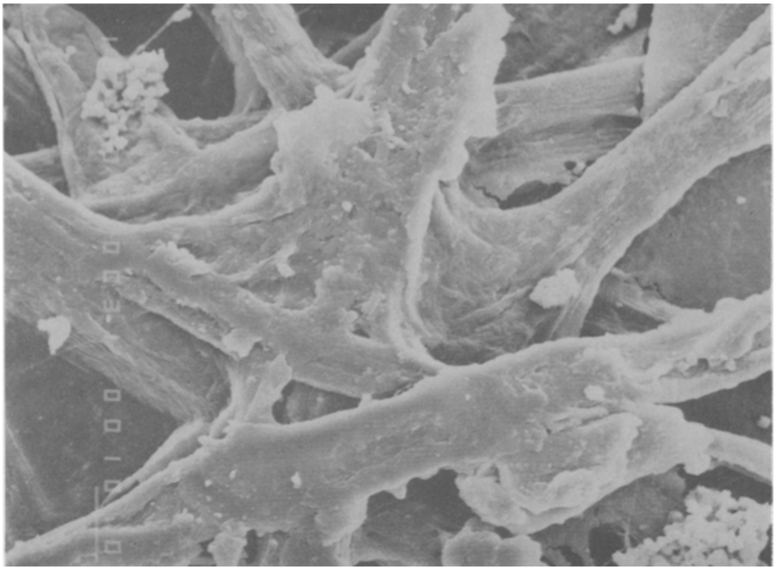

Fig. 7 Sample 1 after treatment: fibres show a smoother and more regularly coated surface (×1000, bar=10 µm)

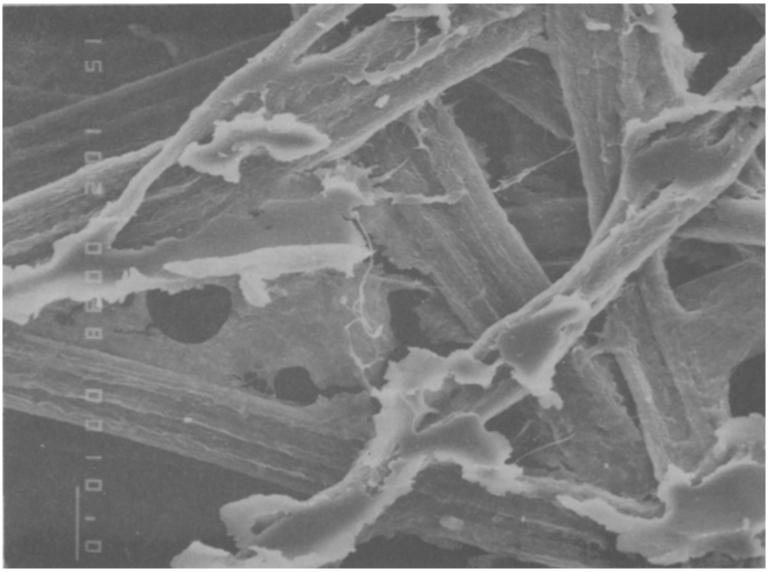

Fig. 8 Sample 3 after treatment: a slight convolution of one of the central and more heavily coated fibres seems to have occurred (×1000, bar=10 µm)

There were no loose fibres, the random distribution of surface deposits had been removed, and the fibre surfaces appeared to be smoother and to be more regularly coated. Where the aqueous method of treatment was used, the appearance of one of the central and more heavily coated fibres in Figs 7 and 8 suggests that a convolution of the fibre may have occurred. This change has been previously attributed to the effect of distilled water on cellulose fibres which can lead to fibre cleavage [1]. No such effect was observed for the non-aqueous treatment.

Energy dispersive X-ray analysis (EDX)

Elemental composition of paper samples before and after conservation treatment was determined with the Jeol 733 Superprobe using a LINK AN 10000/55S Energy Dispersive System (EDS). Results are shown in Table 1*a*. The three papers are of similar elemental composition with small variations in Mg and Al content. Most striking are the changes which occur after conservation treatment. In the case of sample 1 there is a significant increase in the Mg content; this also occurs to a smaller extent in sample 3. For sample 2 there is noticeable increase in Na content. In all three samples conservation treatment appears to have reduced trace levels of Cu and Fe.

Table 1a Elemental composition (EDX) of paper samples before and after conservation treatment

Sample	Elemental composition									
	Ca	S	Si	Cl	Mg	K	Al	Na	Cu	Fe
1 Before	+++	+	+	+	+	+	–	–	–	–
1 After	+	+	+	–	+++	–	–	+	abs	abs
2 Before	+++	+++	+++	+++	+	+++	+	abs	–	–
2 After	+++	+++	+++	+	abs	+	abs	+++	abs	abs
3 Before	+++	+++	+++	–	+	+	+	+	–	–
3 After	+	+++	+	+	+	+	–	+++	abs	abs

Table 1b (i) Elemental composition of 'bright speck' from sample 2

Si	Al	Mg	K	Ti	Fe
+++	+++	+++	+	+	+

Notes:

1. Number of '+ ' indicates the relative level of the elements detected in a given sample.
2. '–' indicates that the elements found are at trace level.
3. 'abs' indicates not detected.

Table 1b (ii) Percentage semi-quantitative analysis (EDX) of bright speck on sample 2

SiO_2	TiO_2	$Al2O_3$	FeO	MnO	NiO	Cr_2O_3	MgO	CaO	K_2O	Na_2O
40.3	7.2	16.6	11.0	0.1	0.08	0.2	16.1	0.5	7.3	0.4

Sample 2 also contained small bright specks on the surface of the ink. Several of these specks were removed and analysed. Table 1*b* (i) shows the elemental composition of such a speck and Table 1*b* (ii) gives its semi-quantitative analysis. Analysis was carried out at a beam voltage of 15 Kv using the ZAF 4 programme in the LINK software. Values obtained were compared with data in [2], which showed that the material could be characterised as a sheet-silicate belonging to the mica group.

XPS analysis

X-ray photoelectron spectroscopy (XPS or ESCA) provides the unique combination of surface chemical state and quantitative compositional information for all elements from lithium to uranium. The sample is irradiated with a beam of low-energy monochromatic X-rays. These X-ray photons interact with the sample atoms to generate photoelectrons whose energies are related to the atom and orbitals from which they originated. As only those photoelectrons generated from the top 1–3 nm of the sample surface are detected, the photoelectron spectrum is therefore surface specific.

Table 2 Surface composition (XPS) of paper samples before and after treatment

Sample	%C	%N	%O	%Ca	%S	%Si	%Fe	%Mg	%Na
1 Before	72.0	5.1	20.2	1.0	0.6	0.7	0.3	–	–
1 After	61.0	1.6	30.1	–	0.7	1.1	–	5.5	–
2 Before	66.2	8.8	20.9	1.3	1.4	0.7	0.7	–	–
2 After	79.6	1.5	16.9	0.6	–	0.8	–	–	0.5
3 Before	70.0	7.2	21.5	0.6	0.8	–	–	–	–
3 After	64.8	2.5	26.6	1.0	0.6	3.6	–	–	0.9
Whatman	65.0	–	33.9	–	–	1.1	–	–	–

All XPS experiments were performed in an M Probe XPS instrument (Surface Science Instruments Inc.) operating with a base pressure of the order of 10^{-9} mbar. This instrument uses monochromatic AlK_α as the source radiation which can be focused into pre-selected spot sizes from 1000×400 mm (eliptical) down to 150 mm^2 (circular) at constant flux.

Previous work has demonstrated the effectiveness of XPS in determining the presence of carboxyl groups in paper samples [3]. In the present study it was thought that it could also act as a sensitive probe for determining the changes which occur during treatment, such as confirming the presence of carbonate deposited on the fibres of the papers.

Results are shown in Table 2. The surface compositions (calculated as atomic percentages) reveal that there is a closer similarity between samples 1 and 3 than with sample 2. This is not surprising since both letters (1 and 3) were written in Lisbon. Both also contain a small amount of iron. Apparently after the invention of the 'Hollander beater' in the late 1600 s, metallic impurities (copper and iron) were introduced into the paper pulp by contact with the metal rotary grinders [4]. The presence of these metallic impurities at trace levels was also observed by X-ray analysis (Table 1*a*).

The HCMC treatment used for sample 1 caused an increase in the magnesium concentration on the surface of the paper of 5.5% compared to the untreated paper. The $Ca(OH)_2$ treatment used for sample 2 caused an increase in the calcium concentration of 0.4% (an increase in calcium concentration has previously been reported for filter paper treated with $Ca(OH)_2$ [5]. The light magnesium carbonate solution together with CO_2 caused a small decrease in the calcium content of 0.5%. In all cases there was a dramatic decrease in nitrogen content (Table 2), this indicating that the size, a gelatin glue, had been removed during treatment.

Figure 9 (1) shows information on the chemical states of carbon for the surface of Whatman filter paper. The XPS spectrum has been resolved into three components; the principal peak (C2) at 287.0 eV was assigned to C–O type bonds, and the remaining two, the higher energy shoulder at 288.2 eV (C3) and the low-energy shoulder at 285.0 eV (C1), to C=O (or O–C–O) and C–C and C–H type bonds, respectively [3].

Results for the three untreated samples showed that in comparison to Whatman filter paper the level of C–O type bonding was considerably reduced. The XPS spectrum of untreated sample 1 (Fig. 9 (2)) shows that the main peak occurred at 285.0 eV (C1) indicating a higher proportion of C–C and C–H bond type and a considerably lower proportion of C–O than in the filter paper; the C=O in sample 1 at 288.2 eV (C3) was assigned to C=O bonding (some contribution from the C=O of the amide group present in size). Sample 3 showed a similar XPS spectrum to sample 1; sample 2 (Fig. 10 (1)), however, showed an additional peak, a shoulder at 288.8 eV (C4), which was assigned to carboxyl group. The increase in proportion of C–H or C–C bonds in the untreated samples compared to the filter paper may be due to ageing effects (C=C bonds are formed during the ageing of cellulose [6]) and to the presence of size.

The chemical states of carbon at the surfaces of the treated papers were also recorded. With the non-aqueous de-acidification procedure there was a significant increase in C–O and O–C–O type bonding (Fig. 9 (3)); an indication that the treatment had increased the cellulosic nature of sample 1. With the aqueous forms of deacidification, samples 2 and 3 showed a negligible increase in this type of bonding (Fig. 10 (2)). They showed instead a significant increase in C–C and C–H type bonding; in sample 1, on the other hand, there was a substantial decrease. It was also observed that for treated sample 2 the carboxyl groups

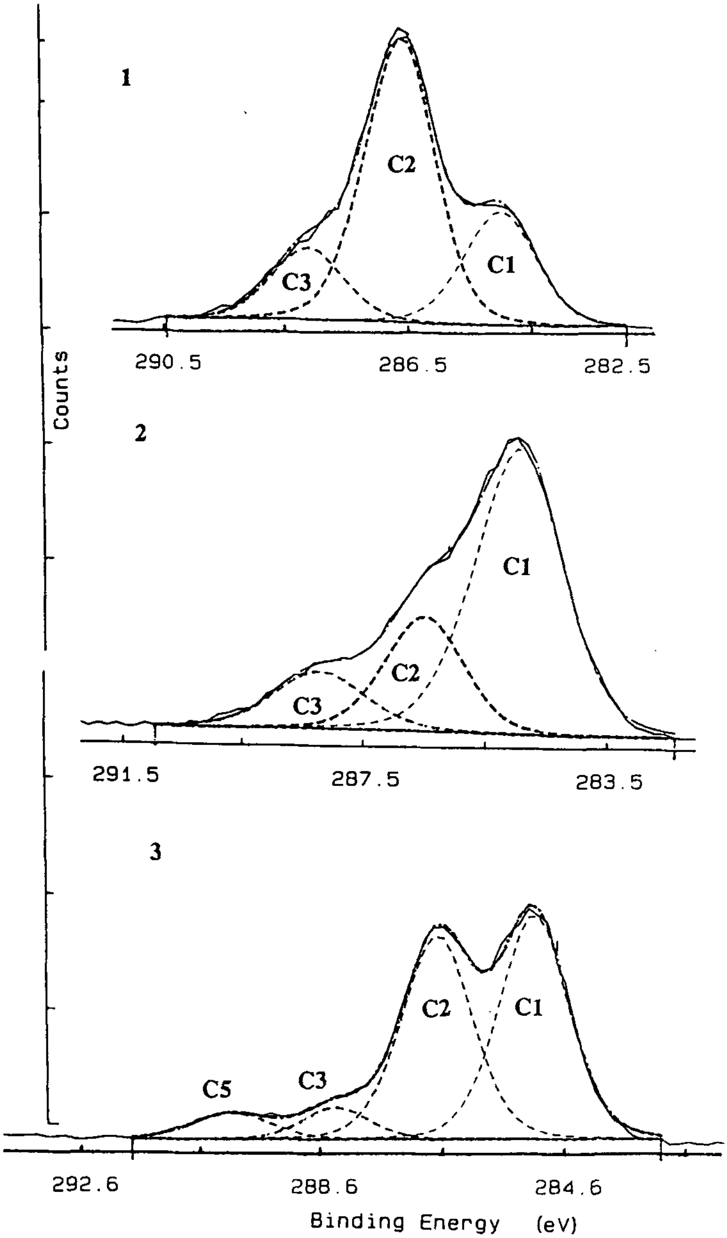

Fig. 9 XPS spectra of (1) Whatman filter paper, (2) sample 1 before treatment, (3) sample 1 after treatment

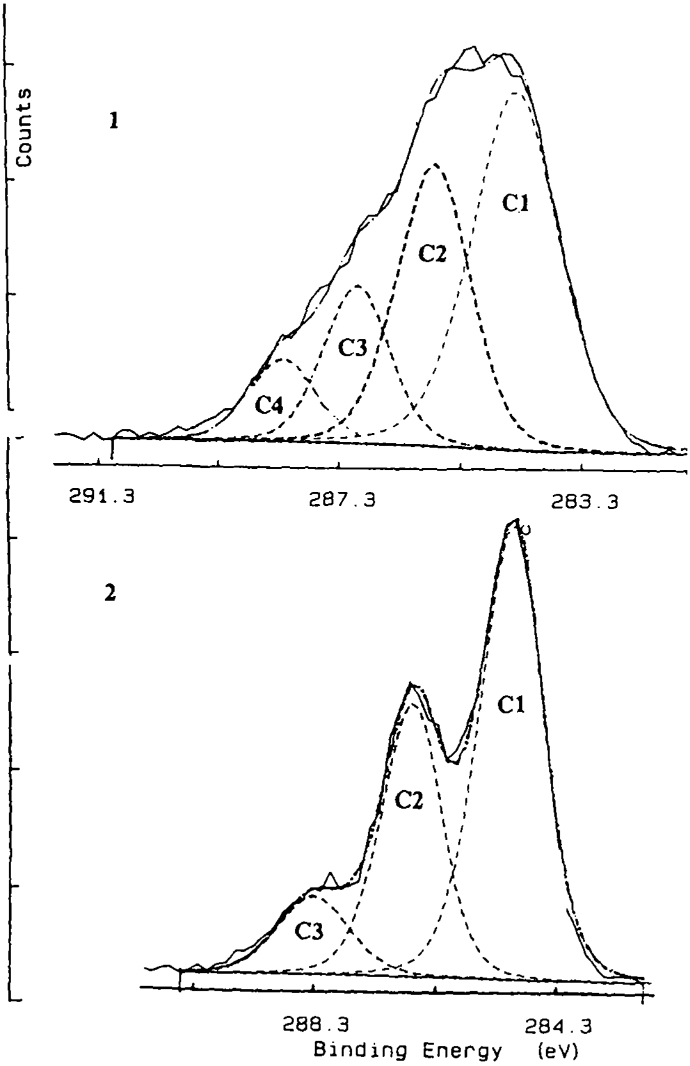

Fig. 10 XPS spectra of (1) sample 2 before treatment, (2) sample 2 after treatment

which were present initially, had been completely removed (Fig. 10 (2)). Treated sample 1 showed an additional feature, a peak at 290.1 eV (C5) which was assigned to carbonate group and was not observed in the other two samples. Preliminary measurements on sample 1 using Dielectric Thermal Analysis (DETA) [7] indicated that there was an increase in capacitance of the treated sample compared to the untreated and that the increase was in the direction of the value recorded for Whatman filter paper. This implies that there is a larger amount of charged groups present on the surface, i.e. the carbonate as observed by XPS. It must be emphasised at this stage that the XPS data represent only preliminary measurements; further work in progress will be reported elsewhere.

Thermomechanical analysis (TMA)

TMA with constant load was performed on a Stanton Redcroft TMA 691 instrument. Measurements were made at room temperature using a load of 0.2 mN. Samples (4 mm^2) were placed under a flat probe (5 mm diameter) and the thickness measured. They were then immersed in water and the degree of swelling over a period of two hours was recorded. This approach has been used previously in studies of fresh and aged papyrus [6], where it was found that if fresh papyrus was used as a reference (100%), the ancient papyrus (578 A.D.) showed swelling of the order of 5–6%. In this study Whatman filter paper was used as the reference (100%). Sample 1 before treatment showed swelling of the order of 50–55%, but after treatment swelling increased to 75% (Fig. 11). It must be emphasised that, while these results require confirmation, the increase in swelling of this order of magnitude for treated sample 1 is obviously a disadvantage, as this implies that the treated sample would also be more sensitive to elevated levels of relative humidity.

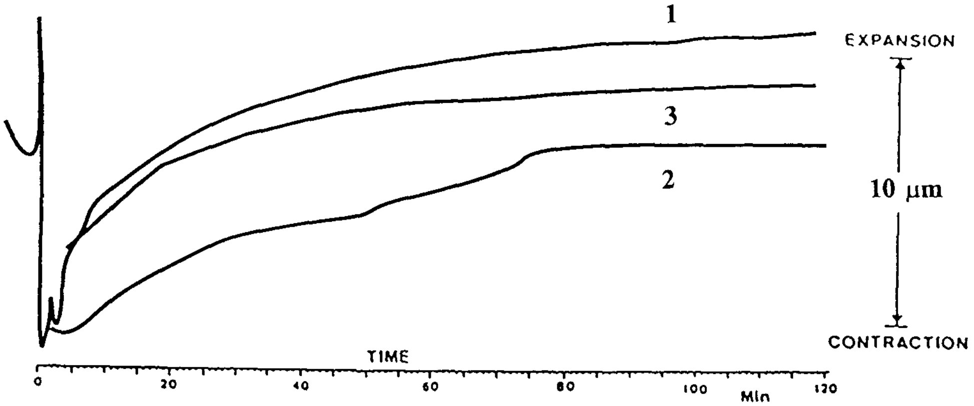

Fig. 11 TMA curves of (1) Whatman filter paper, (2) untreated sample 1, (2) sample 1 after treatment

Dynamic load thermomechanical analysis (DLTMA)

DLTMA measurements using the Mettler TMA were also carried out on the samples with the fibre extension mode. A tensile-strain measuring device was used to determine the amount of extension or shrinkage which occurred in the samples as they were heated at a linear rate, in this case 20 deg·min^{-1} and under the action of an oscillating load, 0.25 N± 0.2 N. The samples (10 mm × 4 mm) were clamped along their long axis and heated over the temperature range –50° to 300°C. Two effects were observed: shrinkage over the temperature range 40° to

150°C, and at slightly higher temperatures the discolouration and eventual charring. Shrinkage in cellulose has been observed previously over this temperature range with thermomechanical analysis [8], this being caused by loss of sorbed water resulting in shrinking of the fibrils and reduction in pore size [9]. With sample 1, the degree of shrinkage observed (0.18%) was noticeably less for the sample after conservation treatment (0.12%) and was similar to that observed in Whatman filter paper (0.1%). With sample 2, the degree of shrinkage was greater than for sample 1 (0.2%) and increased slightly after conservation treatment (0.23%); sample 3 behaved in a similar manner to sample 2 (Fig. 12).

The temperature at which all the treated samples started to discolour and degrade was lower than the value for the untreated samples and Whatman filter paper. This indicated that there was a decrease in thermal stability of the treated samples, which was confirmed by the observations recorded in the following section.

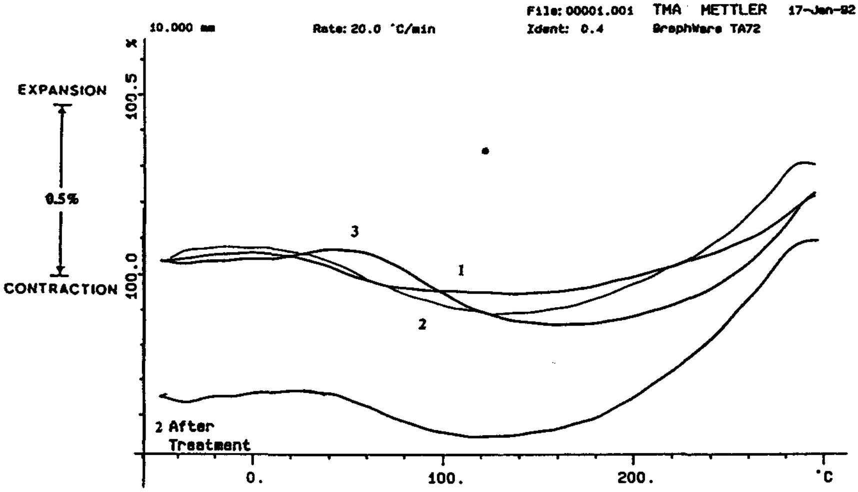

Fig. 12 DLTMA curves of (1) Whatman filter paper, (2) untreated sample 1, (3) untreated sample 2. The single curve in the lower region is that of sample 2 after treatment

Thermogravimetry (TG)

Samples were heated at 2 deg·min^{-1} in platinum crucibles in a thermogravimetric analyser (PE TG7) over the temperature range 30°–950°C. Nitrogen was passed over the sample at a flow rate of 30 cm^3/min. Shapes of the TG curves were similar to those previously observed for cellulose [8], and resulted from preliminary loss of water followed by a combustion loss of about 85%. The aged paper samples were not as thermally stable as the Whatman sample and samples 1 and 3 were similar with respect to thermal stability; the onset of degradation occurred at lower temperatures than Whatman (Whatman,

T_o =329°C; sample 1, T_o =318°C; sample 2, T_o =313°C; sample 3, T_o=317°C). Figure 13 shows the TG curve for sample 2 together with the DTG curve and the calculation of T_o onset (temperature of degradation) from the DTG peak.

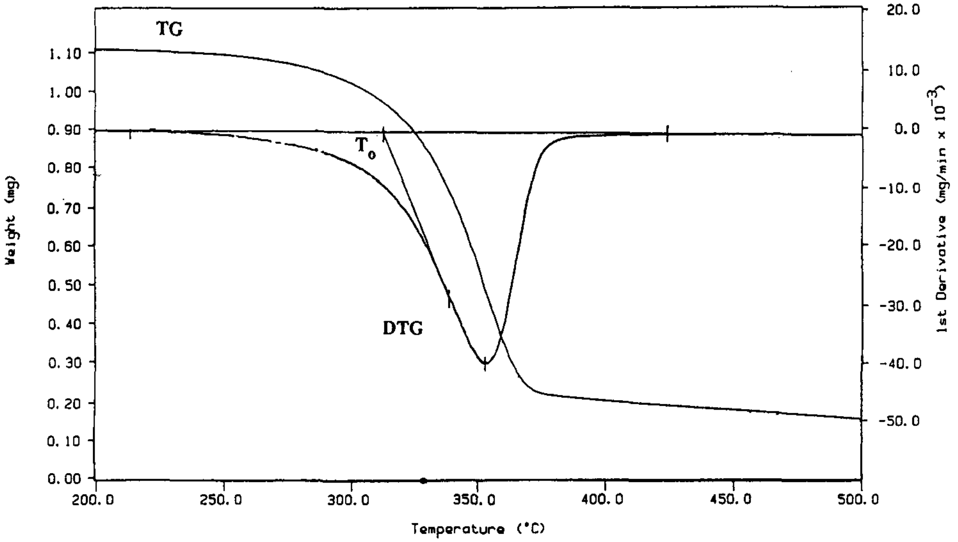

Fig. 13 TG and DTG curves of sample 2 before treatment

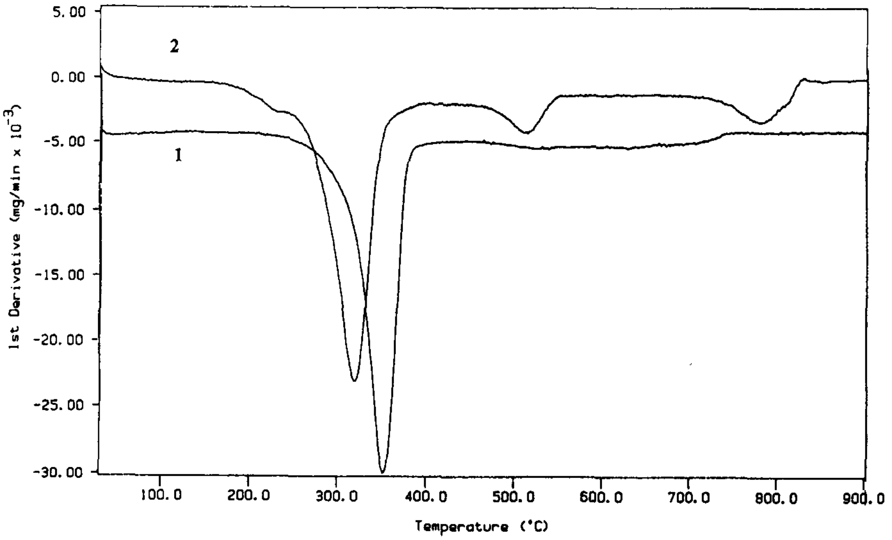

Fig. 14 DTG curves of (1) sample 1 before treatment, (2) sample 1 after treatment

After conservation treatment values of T_o in all cases were significantly reduced (sample 1, T_o = 279°C; sample 2, T_o = 278°C; sample 3, T_o = 269°C). The TG curves gave, in addition to the main characteristic peak which corresponds to cellulose degradation, smaller peaks at higher temperatures in the vicinity of 500° to 550°C and then 750° to 800°C. Magnesium carbonate and calcium carbonate are known to decompose in air at temperatures of 600° and 760°C respectively [10]. Figure 14 shows the DTG curve for treated sample 1 where the additional features are clearly seen. As it has already been shown from XPS data that conservation treatment increases both the magnesium content and carbonate content in sample 1, and then the calcium content in sample 2, it is reasonable to conclude that the peaks represent decomposition of carbonates deposited in the papers.

Fourier transform infrared spectroscopy (FTIR)

A Perkin Elmer 1710 infrared spectrometer fitted with a beam condenser to give an effective spot size of 1.8 mm^2 and a diamond cell was used to record spectra (4 cm^{-1} resolution) in the 400—600 cm^{-1} region. The spectrometer was equipped with a TGS detector. The diamond cell requires a small sample size and so it was possible to use samples of the order of about 1 mm^2. All samples showed a peak in the region of 1650 cm^{-1}. For aged cellulose samples this could be attributed to the following: carboxyl and aldehyde absorption bands [11] (the original *pH* of the papers was in the vicinity of *pH* 5), primary amides (contribution from the proteinaceous size present in all samples), O–H stretching vibration of adsorbed water [11] (a small peak in this region also occurred in Whatman filter paper), and C=C streching vibration (C=C bonds are formed during the aging

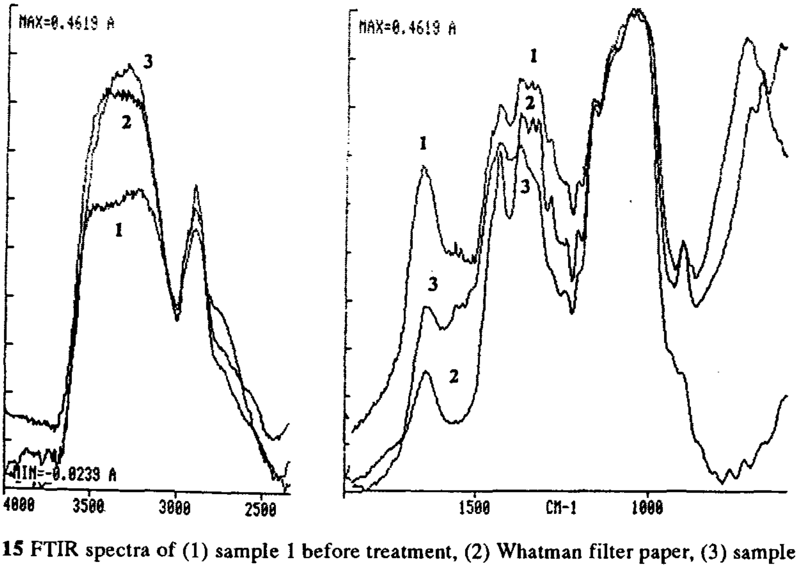

Fig. 15 FTIR spectra of (1) sample 1 before treatment, (2) Whatman filter paper, (3) sample 1 after treatment

of cellulose [8]). After conservation treatment there was an increase in intensity of the O–H stretching vibrational peak for samples 1 and 3 accompanied by smaller changes in the C–H stretching vibration, a decrease for sampe 1 and an increase for sample 3. For sample 1, however the peak at 1650 cm^{-1} was reduced in intensity (Fig. 15), this probably resulting from the loss of both amide and carboxyl groups. (The final *pH* of treated sample 1 was in the region of 9, considerably higher than for samples 2 and 3 where it was about 7.) Other changes which were observed after conservation treatment occurred in the 1600–800 cm^{-1} region where cellulose is known to contain a large number of frequencies characteristic of its structure (e.g. the band at 1426 cm^{-1} which declines in intensity on conversion of cellulose 1 to cellulose 2 [12], and the band at 1372 cm^{-1} which has been used together with the band at 2900 cm^{-1} as an indicator for the relative degree of crystallinity of cellulose [11]. Figure 16 shows that the spectrum of treated sample 3 in this region shows significant changes, as was also the case for sample 2; sample 1 by comparison was relatively unaffected. This implies that aqueous decidification may affect the structure and the degree of crystallinity of cellulose, a phenomenon which has already been reported in the aqueous treatment of textiles [3].

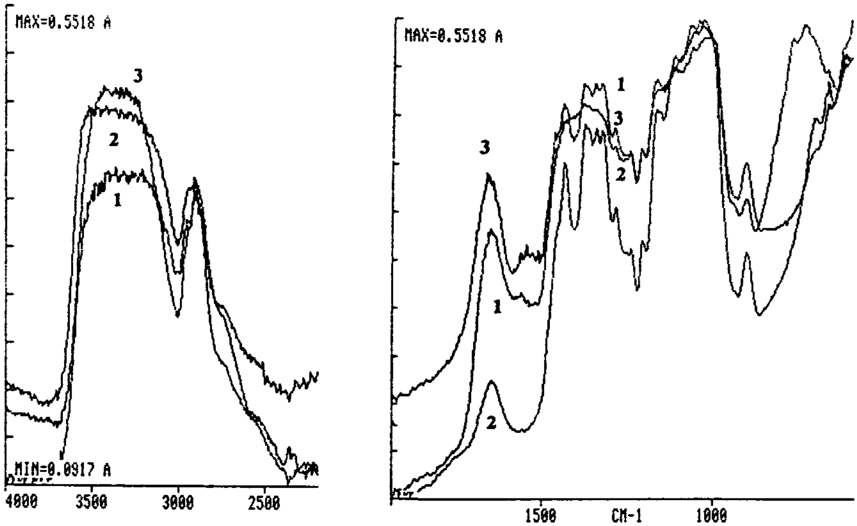

Fig. 16 FTIR spectra of (1) sample 3 before treatment, (2) Whatman filter paper, (3) sample 3 after treatment

Conclusions

These preliminary investigations have shown that it has been possible to confirm what was expected from the non-aqueous method of treatment, i.e. the inclusion of increased cellulosic material and the deposition of possibly magnesium carbonate on the fibres. As far as the aqueous treatments are concerned, the results indicate that the $Ca(OH)_2$ treatment increased levels of calcium, and that possibly calcium carbonate was deposited on the paper. With the light magnesium carbonate treatment (sample 3) there was also a slight indication of some carbonate deposition (TG) accompanied by indications of some negative aspects such as reduced degree of crystallinity (FTIR) and some alteration in the fibre morphology (SEM). Another negative aspect of the aqueous treatment was the noticeable fading of the iron gall inks. The latter confirms what has been recently reported [13]. Results have to be interpreted with a certain degree of caution since tests involved such small sample sizes, particularly in the case of XPS and FTIR (1 mm^2). Measurements need to be repeated with samples from different areas of the manuscripts. With the recent development of an ATR objective which can be used with the FTIR to record spectra directly from the surface of manuscripts, the need for sampling will be altogether eliminated [14]. Work is in progress to develop this application.

The presentation of this paper at the 10th ICTA Congress at Hatfield is particularly appropriate since Sir Richard Fanshawe was born in Ware, Hertfordshire, in 1608. After his death in Madrid in 1666 his body was brought back to England in a Spanish coffin by his wife, Lady Ann Fanshawe, and he was buried in the Church of St.Mary the Virgin, in Ware.

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The authors acknowledge the assistance of the Curator of Valence House, Susan Curtis, for making part of the archive available for scientific analysis and conservation treatment. The authors also acknowledge the conservation work which was carried out by Keith Dean, Senior Conservator, Essex County Record Office. We would also like to thank the following for their assistane: University of London Intercollegiate Research Service (TG, TMA), A. Beard Department of Geology, Birkbeck College (SEM), G. Widmann Mettler Application Laboratory (DLTMA), Dr. R. West, The centre for Surface and Materials Analysis (XPS), Dr. P. Larcey and J. Arthur, Polymer Laboratories (DETA).

References

1 M. Wentz, 'Experimental Studies on the Effect of Aqueous and Nonaqueous Treatments on Historic Textiles' in Historic Textile and Paper Materials, ed. H. L. Needles and S. H. Zeronian, American Chemical Society, Washington, DC 1986, pp. 211–230.

2 W. A. Deer, R. A. Howie and W. Zussman, An Introduction to the Rock-forming Minerals, Longman, Harlow, UK, 1966.

3 D.-S. Hon, 'Fourier Transform IR Spectroscopy and Electron Spectroscopy for Chemical Analysis-Use in the Study of Paper Documents' in Historic Textile and Paper Materials, ed. H. L. Needles and S. H. Zeronian, American Chemical Society, Washington, DC 1986, pp. 349–361.

4 P. Waters, 'Archival Methods of Treatment for Library Documents' in *Preservation of Paper and Textiles of Historic and Artistic Value II*, ed. J. C. Williams, American Chemical Society, Washington, DC 1981, pp. 13–23.

5 V. Daniels, 'Aqueous Deacidification of Paper' in Conservation of Library and Archive Materials and the Graphic Arts, ed. G. Petherbridge, The Society of Archivists and the Institute of Paper Conservation, London 1980, pp. 121–125.
6 H. G. Wiedemann, Thermochim. Acta, 100 (1986) 283.
7 G. Hedley, M. Odlyha, A. Burnstock, J. Tillinghast and C. Husband, Cleaning, Retouching and Coatings, IIC, Brussels 1990, pp. 98–105.
8 D. Dollimore and J. M. Hoath, Thermochim. Acta, 45 (1981) 87.
9 D. Dollimore and B. Holt, Polymer Sci., 11 (1973) 1703.
10 G. Widman and R. Riesen, Thermal Analysis: Terms, Methods. Applications, Hüthig Verlag, Heidelberg 1987.
11 G. M. Berry, S. P. Hersh, P. A. Tucker and W. K. Walsh, 'Reinforcing Degraded Textiles, Part: Properties of Naturally and Aged Cotton Textiles' in Preservation of Paper and Textiles of Historic and Artistic Value, ed. J. C. Williams, American Chemical Society, Washington, DC 1977, pp. 228–248.
12 J. Blackwell, 'Infrared and Raman Spectroscopy of Cellulose' in Cellulose Chemistry and Technology, ed. J. C. Arthur, Jr., American Chemical Society, Washington, DC 1977, pp. 206–218.
13 A. Liénardy and P. Van Damme, Studies in Conservation, 36 (1991) 155.
14 A. Strawn, (Private Communication).

Zusammenfassung — Vor der Behandlung von Briefen von 1665-66 wurden diese mittels SEM, FTIR, ESCA/XPS, TG und TMA/DLTMA charakterisiert. Alle drei Schriftstücke hatten eine ähnliche Zusammensetzung und bestanden grundlegend aus Zellulosematerialien. Die zwei aus Lissabon abgesandten Schriftstücke enthielten Spuren von Fe und Cu; diese Verunreinigungen waren auch in dem aus Dublin abgesandten Schriftstück enthalten. Alle drei Briefe wurden Eisengallfarbe geschrieben. Als besonderes Merkmal wies die Tinte des Briefes aus Dublin kleine Glimmerpartikel auf. Nach der Konservierungsbehandlung wurden die Schriftstücke mittels der gleichen Methoden untersucht, um festzustellen, ob und in welchem Ausmaß Änderungen während der Behandlung auftraten. SEM zeigte eindeutige Veränderungen der Oberfläche der behandelten Schriftstücke. Mittels XPS gelang es, die infolge der Behandlung eingetretene Änderung der Oberflächenzusammensetzung der Schriftstücke zu messen. In allen drei Fällen wurde die thermische Stabilität durch die Behandlung gesenkt.