Spectroscopic Evaluation of the Efficacy of Two Mass Deacidification Processes for Paper

Andrew N. Maclnnes and Andrew R. Barron*  
Department of Chemistry and Materials Science Laboratory, Harvard University, Cambridge, Massachusetts 02138, USA

Paper samples treated by either a diethylzinc (DEZ) or a magnesium butoxytriglycolate (MG-3) mass deacidification process have been subjected to spectroscopic analysis, using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), Rutherford back-scattering (RBS), X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS) to identify the nature of the alkaline reserve buffer. In the case of uncoated 'plain' paper, the DEZ process produced a uniform distribution of ZnO buffer throughout the paper depth. In contrast, treatment with MG-3 resulted in incomplete buffer MgCO₃ formation; however, rectifying methodology for the uniform formation of MgCO₃ buffer is discussed and established. Neither process is, at present, effective in providing a buffer within the core of glossy, kaolin-coated paper.

Keywords: Paper; Deacidification; X-Ray photoelectron spectroscopy; Rutherford back-scattering; Scanning electron microscopy

In this age of computer-based information technology, much materials chemistry has been aimed at the synthesis, characterisation and testing of new materials to support and develop this class of technology (e.g. superconductors, semiconductors). Little work has been aimed towards the employment of modern surface spectroscopic techniques to what is undoubtedly the original information technology system, i.e. that of the printed page. It is problems associated with this latter technology, however, that offers interesting applications in the application of materials-chemistry techniques.

The deterioration of paper in books and archival material due to acid hydrolysis has been recognised since the turn of the century. The source of the acidity, the hydrolysis of the aluminium sulfate sizing agents, was identified in the late 1950s, and as a consequence alkaline paper size became commercially available. Further progress has recently been made with the development, in 1984, of an American National Standard for Permanent Paper, along with its subsequent revision to include coated paper. This US standard is the basis for an international standard now under development.

Although the movement towards the exclusive alkaline-sized paper will inhibit the degradation of future volumes, it does not solve the immediate problems associated with retrospective collections. Approximately 3 million of the 11.7 million volumes in the book collection at Harvard suffer from the effects of acid degradation, i.e. the atmospheric hydrolysis of the aluminium sulfate sizing resulting in the formation of sulfuric acid, which attacks the cellulose fibres of the paper, leading to the loss of strength and embrittlement of the pages.

\[ Al_2(SO_4)₃ + 3H₂O \rightarrow Al₂O₃ + 3H₂SO₄ \]  

Depending on the initial strength and fibre content of the paper comprising an individual book, this process can occur in as little as 50 years.

Several processes have been developed over the last 30 years to treat books en masse, as opposed to single item treatment) to neutralize the acid in the paper, and leave an alkaline reserve to buffer against future acid attack from the environment. While a number of previous studies have, and are being, performed by vendor companies and independent groups, these have (are) focused on the physical effects of the deacidification process. Typical studies involve the measurement of paper strength by the MIT fold test or degree of polymerisation. Equally important, however, is a determination of the quantity, chemical identity, and distribution of the alkaline reserve buffer. We have, therefore, instituted a spectroscopic analysis using complimentary techniques to gain insight into chemical nature of two current mass deacidification processes. As such, we propose to evaluate the morphological and bulk chemical changes within treated papers by both cross-sectional and planar scanning electron microscopy (SEM) with associated energy dispersive X-ray analysis (EDX). Similar analysis of chemical (i.e. elemental) modifications in a near surface (Å) layer is examined by Rutherford back-scattering (RBS). This technique, which relates mass and depth of the elements within this layer can provide insight as to how the treatments have been taken into the paper, i.e. distributed evenly throughout the page depth versus surface segregation. Finally, by use of the surface analysis techniques X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary-ion mass spectrometry (ToF SIMS) we aim to determine the chemical nature of the elemental species present and thus elucidate the exact nature of the alkaline reserve buffer available within deacidified paper. Thus, as part of Harvard's evaluation of two commercial processes, Akzo Chemical's DEZ process using diethylzinc (1) and FMC's process using MG-3 magnesium butoxytriglycolate (2), we have undertaken and present here, a comprehensive spectroscopic investigation of the relative chemical effects on both uncoated paper and 'glossy' coated paper (such as used in this journal, for this page and the cover, respectively) of both deacidification processes.

Experimental

Paper Treatment

Two consecutive pages of each of the two types of paper chosen for study: uncoated and coated high-quality book paper with cotton fibre were removed from the binding. A portion of each page was retained, along with a third whole...
page of each type, as a control, the remainder was subjected to treatment along with batches of whole books by either the DEZ process by Akzo Chemicals, Inc., Deer Park, Texas, U.S.A., or the FMC process by FMC Corporation (Lithium Division) Bessemer City, North Carolina, U.S.A. A sample of the uncoated paper was also treated at Harvard with iso-propylmagnesium chloride (Pr'MgCl), as a control for the detection of magnesium.

DEZ Process
During treatment by the DEZ process books are placed within trays inside a vacuum chamber. After removal of air, the books are dried at 20 Torr to reduce their moisture content from ambient (ca. 6-8% H₂O) to ca. 0.5%. Diethylzinc (DEZ, 1) gas is then pumped into the vacuum chamber to a pressure of 20 Torr. After an exposure time of 12 h (depending on the quantity and types of papers treated), the untreated DEZ is removed in vacuo. The chamber is finally flushed with moist nitrogen to ensure complete hydrolysis of the residual organozinc compounds and rehydration of the paper (ca. 3-4% H₂O).

FMC Process
The FMC deacidification process is solvent based, using either CFC-113 (as in the present studies) or heptane to provide a carrier for the magnesium butoxytriglycolate (MG-3, 2) reagent. Books are placed in the treatment chamber and dried to ca. 2% residual moisture using 1-100 mHz radiofrequency irradiation. The chamber is then filled with the solution of MG-3 for ca. 5 min after which the solution is drained, and the books rinsed with pure solvent. Finally the solvent is removed under vacuum and the books rehydrated to ca. 4% H₂O. Variations on this standard treatment procedure were performed by FMC, at our specific request and these are detailed in the results and discussion.

Treatmente with Pr'MgCl
Small samples (1 cm × 2 cm) of uncoated paper were placed into a Schlenk-type flask, and dried under vacuum, at 100 °C for 12 h. After cooling to ambient temperatures, dry nitrogen was introduced into the flask, and a solution of Pr'MgCl in Et₂O (50 cm³, 2 mol dm⁻³ Aldrich) was added via a syringe through a rubber septum. The paper samples were stirred in the solution for 5 h after which the excess magnesium reagent was removed by filtration and washed with dry, degassed, Et₂O (2-40 cm³), and hexane (2×50 cm³). Drying under vacuum ensured all volatile hydrocarbons were removed.

Spectroscopy
Scanning electron microscopy (SEM) was performed on a JEOL JSM 6400 microscope with a Noran Z-Max windowless energy dispersive X-ray (EDX) system and associated software. Analysis was typically performed at 15 kV for EDX analysis on both gold-coated and as-received paper coupons. No noticeable attenuation of X-ray signal due to the gold coating was observed. X-ray photoelectron spectroscopy (XPS) was performed on a surface science SXS-100 spectrometer using monochromated Al-Kβ X-rays. The problem of specimen charging, due to the insulating nature of the papers examined, was overcome by the combination of electron flood gun and additional large particulate matter (1-30 μm in diameter). The latter's identity is consistent with an aluminium silicate used as sizing material determined by EDX and XPS. No zinc or magnesium was detected in this specific sample of paper; however, some low-quality uncoated paper was found to contain localised trace quantities of Mg due to the tale magnesium alumino-silicate) used as a whitener.

The RBS spectra [Fig. 2(a)] of a sample coated with ca. 20 Å of gold showed the presence of aluminium, silicon and oxygen. The presence of a plateau for the Al and Si edges is consistent with the even distribution of sizing throughout the analysis depth of the paper.

Results and Discussion
Three consecutive pages were removed from a single book for each sample of paper. For each type of paper one page was treated by Akzo (DEZ), one by FMC (MG-3) and the third retained. In addition, a corner sample from the pages to be treated was retained, in case it became critical to know whether they had come from different rolls of paper. Several samples of both coated and uncoated paper were investigated. The results presented here are for two representative examples: uncoated high-quality book paper with cotton fibre, and Kaolin coated 'glossy'.

Uncoated Paper
Untreated
The SEM of the untreated and uncoated sample [Fig. 1(a)] shows the paper to consist of interwoven fibres, 5-30 μm in diameter and particulate matter (1-30 μm in diameter). The latter's identity is consistent with aluminium silicate used as sizing material determined by EDX and XPS. No zinc or magnesium was detected in this specific sample of paper; however, some low-quality uncoated paper was found to contain localised trace quantities of Mg due to the tale (magnesium alumino-silicate) used as a whitener.

DEZ-treated
Since diethylzinc (DEZ) readily reacts with acid, it has been assumed that in the DEZ process, the organometallic will react with both the sulfuric acid formed from the hydrolysis of the alum sizing (see above), and the residual moisture present in the paper [eqn. (2) and (3)], the former reaction neutralising the paper, and the latter providing a zinc oxide buffer to neutralise future acid attack. However, previous spectroscopic studies have failed to confirm the chemical identity of the zinc.

\[
\begin{align*}
\text{ZnEt}_2 + \text{H}_2\text{SO}_4 & \rightarrow \text{Zn(SO}_4) + 2 \text{ EtH} \quad (2) \\
\text{ZnEt}_2 + \text{H}_2\text{O} & \rightarrow \text{ZnO} + 2 \text{ EtH} \quad (3)
\end{align*}
\]

Visually the surfaces of the papers treated by DEZ show no noticeable difference from their untreated counterparts. Under higher magnification SEM analysis shows that no degradation of the fibre structure has occurred, and no additional large particulate material is present. However, it is possible to see some slight webbing between overlapping fibres [Fig. 1(b)]. Quantitative EDX indicates the presence, in addition to those elements present prior to treatment, of zinc (ca. 0.3 atom%). Furthermore, EDX maps and point analyses

\[1 \text{ Torr} = 133.322 \text{ Pa.}\]
of the page cross-section show the presence of Zn throughout the page interior.

RBS analysis of a treated page [Fig. 2(b)] exhibits a Zn feature consisting of a narrow 'hump' with a constant tail, suggesting the enrichment of Zn on the surface and then uniform concentration through the analysis depth (<4 μm).

Typical XPS survey results for the DEZ-treated page are shown in Fig. 3. In addition to peaks due to C, O, Al, and Si (observed in the untreated paper), peaks due to Zn are observed. Note that the zinc content does not diminish significantly after sputtering with Ar ions, consistent with its presence throughout the sample depth.

High-resolution XPS of the elemental peaks to elucidate their chemical state by normal peak-shift information is hampered in this particular case, in that analysing the insulating, inhomogeneous paper leads inevitably to surface charging effects. We have therefore identified the Zn species present by use of the charge-independent Auger parameter,12 which utilises relative shifts of both photoelectron and Auger peaks present and thus, by observation, negates the peak shift due solely to surface charging. In this case, the modified Auger parameter, $\alpha^*$, is defined in terms of the kinetic energy ($T$) of the LMM Auger peak and the binding energy ($E_b$) of the Zn 2p photoelectron peak:

$$\alpha^* = T(\text{LMM}) + E_b(2p)$$  

From recorded spectra we have ascertained the values of $E_b(2p) = 1023.9 \pm 0.1$ eV and $T(\text{LMM}) = 983.9 \pm 0.2$ eV. The Auger parameter $\alpha^*$ correspondingly gives a value of 2009.8(±0.3) eV. This is consistent with the $\alpha^*$ value of ca. 2010 eV reported for ZnO.13 Thus, from our spectroscopic results we have shown that in the case of uncoated paper the DEZ process does indeed produce ZnO (ca. 1.5–2.0%) as a buffer. Importantly, since zinc is detected within the core of the paper as well as the surface it appears that the DEZ process provides a uniform distribution of buffer.

**FMC-treated**

The magnesium butoxytriglycolate reagent (2) is proposed to react with acid present in the paper in an analogous manner to that for DEZ, i.e.

$$\text{ROMgOCO}_2\text{R} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{CO}_2 + 2 \text{HOR}$$  

$$\text{R} = \text{Bu(OCH}_3\text{)}_3$$

However, the desired buffer, MgCO$_3$, is thought to be formed as a consequence of the reaction of the CO$_2$ liberated from the hydrolysis of the carbonylated butoxyglycol ligand and the magnesium oxide formed as the primary hydrolysis product:14

$$\text{ROMgOCO}_2\text{R} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{CO}_2 + 2 \text{HOR}$$  

$$\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$$

Thus, according to FMC the treated paper should contain a uniform distribution of MgCO$_3$.

Although the majority of samples of uncoated paper showed no visual change as a consequence of treatment, the ink constituents in some samples had undergone chromatographic separation, while other samples showed a slight change (for the better) in their visual 'whiteness'.

The SEM of the treated paper surface is indistinguishable from that of the untreated paper, i.e. no new particulate material or webbing is observed. Quantitative EDX analyses on different samples examined in plane section indicated that variable, but low, levels of Mg are present (≤0.2%), while no magnesium was detected by RBS above the background; the RBS spectra of treated and untreated samples were superimposable. XPS of the Mg-treated papers indicate variable amounts of Mg on the analysed surfaces, ranging from 0 to 4% [Fig. 4(a)]. However, brief argon-ion etching resulted in any Mg signal diminishing below the detection limits of the spectrometer (ca. 0.1%) [Fig. 4(b)]. Thus, it would appear that
the treated papers contain no magnesium, except for a small surface residue. However, ICP Atomic Absorption analysis of the sample indicates the presence of magnesium to a total concentration to be 0.45%. Since this magnesium is not detected within the outer layer of the paper it is presumably within the core (see below).

Since the low quantities of Mg detected for many of the samples, makes interpretation difficult, and the quantity of Mg, as determined by quantitative EDX varies depending on the paper type, we further investigated a sample of paper found to have the greatest Mg content by ICP AA, a high-quality book paper, with cotton fibres. Quantitative EDX of the core (i.e. cross-section) indicates a bulk Mg content of ca. 0.4 atom%, while from XPS the content of Mg on the surface was again, if at all present, below the detection limit of the technique (<0.1%). RBS, likewise, did not detect the presence of Mg in this surface layer consistent with our observations on all the uncoated papers studied.

The disparity between bulk (ICP-AA, EDX) and surface region results (XPS, RBS) for all the MG-3 treated papers is intriguing, and therefore was subjected to further investigation by exposing the internal surface of the paper (cohesive fracture) followed by XPS analysis. Fig. 5 shows the wide scan of the exposed internal surface. In this region we can clearly identify the presence of magnesium. High-resolution XP spectra of the Mg 2p and Mg KLL regions were recorded to ascertain an Auger parameter based on the relative shift of these photoelectron and Auger peaks, and hence give an indication of the chemical states of the magnesium buffer present. However, unlike the zinc case, no extensive library of Auger parameters could be found for magnesium. We, therefore, ran standards of MgCO₃ and MG-3, dried under argon, in our spectrometer to compare with the exposed paper body. The recorded Auger parameter values determined from eqn. (8)
were $\alpha^*$ MgCO$_3$ = 1230.5 (±0.3) eV, $\alpha^*$ MgG-3 = 1230.7 (±0.3) eV, $\alpha^*$ Mg in paper = 1230.3 (±0.3) and 1228.7 (±0.3) eV (two forms of magnesium were observed to be present within the exposed paper).

$$\alpha^* = 7\text{(Mg KLL)} + E_d(\text{Mg 2p})$$  (8)

The chemical shifts observed by this analysis could be used, by inspection with reported shifts, to identify one of the forms of Mg present [corresponding to $\alpha^* = 1228.7(±0.3)$ eV] in the paper viz. magnesium oxide MgO. The second form of Mg could not be uniquely identified by the analysis owing to the similarity of Mg peak shifts exhibited by both the original treatment precursor and the possible product MgCO$_3$.

The inability to distinguish chemical state shifts between these two compounds (presumably due to the similar nature of their Mg bonding environment) led us to the use of secondary ion mass spectrometry (SIMS). The SIMS technique identifies mass fragments produced after energetic ion bombardment of the sample surface and can, therefore, indicate the combined elemental forms that constitute the surface compounds. By use of high-resolution time-of-flight (ToF) SIMS over a cross-section of treated paper we could identify fragments at 39.95 u corresponding to MgO$^+$ but could find no fragment at a value of 83.97 u, attributable to [MgCO$_3$]$^+$. The presence of fragments (albeit amongst a great many others) at 28.03 u (CH$_2$CH$_2$) and 57.07 u (C$_2$H$_5$) corresponding to glycolate links and butyl groups of the magnesium butoxytriglycololate precursor would thus suggest that the magnesium species present after deacidification is a combination of magnesium oxide (or hydroxide) and the original precursor which has simply not reacted (hydrolysed) owing to insufficient reaction time, ca. 5 min.

From the forgoing it would appear, therefore, that while the magnesium reagent penetrates the page core much of the complex is removed, presumably in the subsequent washing step (see Experimental), prior to its conversion to magnesium oxide or carbonate. Based on the results of treatment with Pr'MgCl (see below) and the chemical characterisation of the magnesium present within the page we can conclude that it is the slow reactivity of the MG-3 reagent with water that causes the surface depletion of Mg in the final papers. Two obvious solutions to this defect have been investigated. First, the localisation of magnesium content a result of the solution treatment employed, versus the gas-phase process used for DEZ? Secondly, does the lower reactivity of the magnesium alkoxide (2) towards protic acid (including water) as compared to the pyrophoric DEZ (1) account for the difference in buffer distribution? In an attempt to shed some light on these questions we have investigated the treatment of the uncoated paper with a Grignard reagent in hydrocarbon solution. The Grignard, Pr'MgCl, was chosen for two reasons. First, the reactivity of the Mg–C bond with acidic groups is much higher than the Mg–O bonds in MG-3. Secondly, the Mg–Cl bonds present in Pr'MgCl should be retained in the paper after treatment. This provides a second element for detection, since the Cl edge in RBS, and peak in EDX, are distinct from those of the other elements

Isopropyl magnesium chloride

The localised concentration of magnesium found in the MG-3-treated paper, i.e. only within the core of the page, posed the following questions. First, is the localisation of magnesium content a result of the solution treatment employed, versus the gas-phase process used for DEZ? Secondly, does the lower reactivity of the magnesium alkoxide (2) towards protic acid (including water) as compared to the pyrophoric DEZ (1) account for the difference in buffer distribution? In an attempt to shed some light on these questions we have investigated the treatment of the uncoated paper with a Grignard reagent in hydrocarbon solution. The Grignard, Pr'MgCl, was chosen for two reasons. First, the reactivity of the Mg–C bond with acidic groups is much higher than the Mg–O bonds in MG-3. Secondly, the Mg–Cl bonds present in Pr'MgCl should be retained in the paper after treatment. This provides a second element for detection, since the Cl edge in RBS, and peak in EDX, are distinct from those of the other elements

![Fig. 6 Survey XP spectra of MG-3 treated but unwashed (see text) Williamsburg uncoated paper](image)

![Fig. 7 Scanning electron micrograph of Williamsburg uncoated paper after treatment with MG-3-CO$_2$ (B, see text for experimental details)](image)
in the paper, Al, Si, O and C. FMC have announced that when the use of freons is banned within the USA they will switch to a hydrocarbon solvent. We, therefore, used hexane as a model solvent. The samples of paper were placed in a Schlenk flask and heated to 80 °C under vacuum (10⁻³ mmHg) for 36 h, and subsequently treated with Pr'MgCl in hexane (see Experimental). The treated samples were visually indistinguishable from their untreated equivalents, and no blurring of the inks was observed. However, SEM images [Fig. 1(c)] revealed that large deposits had formed between the fibres. These deposits were found to be rich in Mg and Cl.

Given the higher concentration of Mg throughout the page from treatment with Pr'MgCl as compared to MG-3, and the presence of Mg on the surface, we can conclude that the surface depletion of Mg from MG-3 treated samples is due to removal of the Mg complex by washing prior to its full hydrolysis and subsequent conversion to the insoluble MgCO₃ (see above). Given these results it is surprising that in a commercial process FMC have made no attempt to detect Mg in the washings from the MG-3 treatment.

Coated Paper

Untreated

The micrograph of the untreated kaolin-coated sample is shown at two magnifications in Fig. 8(a) and (b). The surface is porous and micaceous, consisting of kaolin platelets 1–2 μm in size. The pores in the surface are ca. 1 μm in diameter; however their depth is unclear. SEM of the paper in cross-section reveals the kaolin coating to be ca. 20 μm thick with no apparent contiguous path of porosity. Elemental analyses using RBS [Fig. 9(a)] EDX and XPS [Fig. 10(a)] are consistent with the coating being a calcium aluminosilicate with significant quantities of TiO₂.

DEZ-treated

Although the treated papers did not appear visually different from the untreated, significant changes are discernible from the SEM images shown in Fig. 8(c) and (d) as compared to their untreated analogue. At the lower magnification [x·1000, Fig. 8(c)] it can be clearly seen that the porous surface of the untreated paper [Fig. 8(a)] has been covered, or in-filled, to give a uniform featureless zinc-rich coating, presumably ZnO (see below). At higher magnification [x·10 000, Fig. 8(d)] the ZnO coating consists of near uniform grains ca. 0.1 μm in diameter. However, none of the pores present in the untreated sample are retained, but infilled by the ZnO. SEM and EDX analysis of the cross-section reveals that, whereas the uncoated paper showed the presence of Zn throughout the page, there is no Zn detected within the coated papers.

The RBS spectra of the DEZ-treated sample is shown in Fig. 9(b). The magnitude of the Zn edge is such to obscure the presence of Ti and Ca while the shift in the Al and Si edges [c.f. Fig. 9(a)] suggests the presence of a Zn rich overlayer.

The XPS of the treated papers surface [Fig. 10(b)] consists almost entirely of Zn and O constituent with its formulation as ZnO. This assignment was confirmed from the measured value of the Auger parameter x*, 2010.3 (±0.3) eV (see above). The Zn content is reduced considerably after 2 min argon-ion etch [Fig. 10(c)], suggesting the purely surface nature of this Zn rich layer, i.e. simply a surface residue on the kaolin platelets which is observed to be removed after brief etching.

The detection of ZnO on the surface of the kaolin coating but none beneath the kaolin or within the paper core suggests that the diethylzinc did not diffuse through the coating prior to hydrolysis. First kaolin is a hydrated aluminosilicate, which in the present case contains calcium ions. It is likely, therefore, that ZnEt₂ will react with the hydroxy groups resulting in
the incorporation of zinc into the kaolin surface. Thus, the diethylzinc may react more rapidly with the hydroxides and residual water than the rate of its diffusion through the kaolin coating. Secondly, although the kaolin coating is clearly particulate, there may not be a contiguous path to the paper core, thus preventing diffusion of the diethylzinc through the coating. The diethylzinc then only reacts with the hydroxides present on the surface, subsequent hydrolysis giving a coating of ZnO.

**FMC-treated**

The EDX and RBS of the treated samples showed no Mg to be present in the bulk of the pages, while XPS indicated a surface content of Mg lower than the detection limit of the spectrometer (i.e. <1%). In addition, SE micrographs of the treated pages were absolutely identical to those of the untreated samples. We can presume from our prior analysis on uncoated paper that the MG-3 precursor, if present on the kaolin surface, is simply removed by the heptane rinse.

**Conclusions**

By the use of a range of spectroscopic techniques we have shown that the DEZ mass deacidification treatment is effective in providing a uniform distribution of zinc oxide buffer throughout the page of uncoated paper. In contrast, although the MG-3 process as currently practised commercially does provide small quantities of magnesium within the paper core, none is observed on the paper surface. This would leave the latter open to acid attack. In addition, the magnesium is present as a mixture of species, including the unhydrolysed complex, but not as the carbonate which is required as an active buffer! Thus, the commercial FMC deacidification process is totally ineffective at providing sufficient buffer within the treated paper. However, we have demonstrated that the problem of poor dispersion of Mg through the page may be overcome by omitting the final washing step. More importantly, the formation of a uniform concentration of magnesium carbonate buffer may be promoted by irrigating with CO₂ prior to washing. It is this latter modification which leads to the successful deacidification of uncoated paper using MG-3. However, to our knowledge no such improvement has been adopted by FMC, questioning the MG-3 process technical validity.

We believe the most important result from this study is that, in the case of glossy coated paper, neither process is at present effective in providing a buffer within the paper core. Thus, at the present time it is ineffective and therefore economically pointless to treat coated paper. However, we note the following. While the DEZ process does not deacidify coated paper, it may be used to provide a buffer coating on basic core coated paper so as to preclude attack by external atmospheric pollutants, and in this regard we see future applications. We also expect that with correct drying conditions the DEZ process has the best potential for the successful deacidification of coated acid core paper.
We are indebted to Richard Miller (Akzo) and Dr. Robert Wedinger (Lithco) for their invaluable assistance and cooperation in the treatment of samples. John Chervinsky (Harvard), Professor Thomas Gilbert and Jason Li (Northeastern University), and Dr. Tim Carney (Kratos, U.S.A.) are acknowledged for assistance with RBS, atomic absorption and SIMS measurements, respectively. Partial financial support for this work was provided by the Harvard Libraries and the Aluminum Research Board. We acknowledge Ms. Carolyn Morrow and her colleagues in the Harvard Preservation Office for their support and encouragement.

References
2 W. J. Barrow, Manuscripts and Documents: Their Deterioration and Restoration, University of Virginia Press, Charlottesville NC, 1955 and references therein.
9 (a) R. Naoumof, Paper Z., 1905, 30, 2802; (b) R. Korn, Papier Fabrik., 1937, 35, 33; (c) G. Van Nederveen and A. H. H. Van Royen, Papierwereld, 1951, 6, 41; (d) O. Andersson, Stensk Papperstid., 1951, 54, 591.

Paper 2/02150A; Received 27th April, 1992