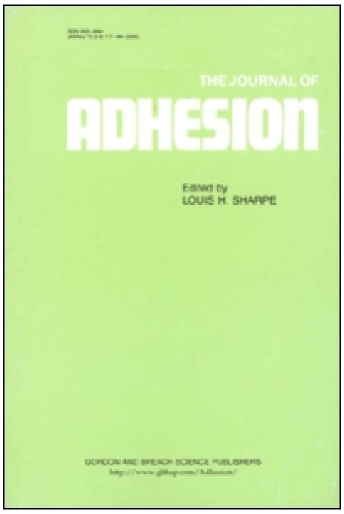

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Analysis of Ink/Coating Penetration on Paper Surfaces by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in Conjunction with Principal Component Analysis (PCA)

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Analysis of Ink/Coating Penetration on Paper Surfaces by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in Conjunction with Principal Component Analysis (PCA)

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Time-of-Flight Secondary ion mass Spectrometry (ToF-SIMS), in conjunction with Principal Component Analysis (PCA), has been used to characterize the spatial distribution of the chemical components of ink, both on the surface and in the Z-direction of coated papers. Preliminary work was performed on commercial ink-jet printing paper and on commercially available photopaper to establish that ToF-SIMS, in conjunction with PCA, could help characterise ink/coating distribution. To illustrate further that ToF-SIMS/PCA could differentiate the individual components making up the ink, pigment-based and dye-based inks were applied to two coated papers (PCC + SA and PCC + starch + PVA) using an inkjet printer. This approach shows that high spatially resolved images obtained by ToF-SIMS allows a depth profile to be obtained, thereby allowing the correlation between ink distribution at the surface and in the Z-direction to be evaluated in relation to the coating formulation.

Keywords: Coated paper; Coating penetration; Depth profiling; Dye-based ink; Pigment-based ink; Principal component analysis (PCA); Spatial ink/coating distribution; Surface analysis; ToF-SIMS

1. INTRODUCTION

There is a demand for improved print quality on surface-treated and coated papers. Many papers, such as those used for high-grade

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magazines, inkjet paper, board, and newspaper inserts, meet extremely high requirements for brightness, finish, and printability. By refining surface treatments and/or coating formulations, it should be possible to diminish the use of ink, thereby reducing costs without compromising print speed and quality. To optimize the coating formulation, it is necessary to investigate its relationship with ink penetration/adhesion, as well as with the paper substrate. Methods are, thus, required to fully characterise, both chemically and spatially, ink penetration/adhesion on the coating, the quality of printing thereon, and the coating/paper substrate interface.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has emerged as one of the most important and versatile surface analytical techniques available for advanced materials research. This is due to its excellent mass resolution, sensitivity, and high spatial resolution providing both chemical and distributional information for a wide variety of materials and applications. In ToF-SIMS [1], a pulsed primary ion beam generates secondary species, a small percentage of which come off as positive or negative secondary ions. These are mass analysed by measuring ToF from the sample to the detector. The mass spectra and secondary ion images can be used to obtain composition, distribution, and molecular information of the surface constituents. Depending on primary ion source and mode of operation chosen [2], high mass resolution (*ca.* 9000 for ^{29}Si), spatial resolution ($\sim$200 nm), or a combination thereof (5000 for ^{29}Si/$\sim$250 nm) can be obtained.

To date, there has been only limited application of ToF-SIMS to the study of paper surfaces and its effect on print quality and performance. This is surprising, given the strength and versatility of the technique which has been applied to many other systems [3]. Studies on paper have included studies on sizing agents [4–8], surface defects [9,10], surface morphology [11,12], and characterisation and distribution of inks [13–15]. This may arise quite simply because the wealth of information that ToF-SIMS provides can itself be problematic. A ToF-SIMS spectrum consists of numerous peaks resulting from the fragmentation of the surface molecules. A breakdown of this pattern allows identification of the material at the surface by comparison with model compounds or with the aid of library spectra [16]. However, it is not feasible to identify all fragments, and a few characteristic peaks are often all that is needed to identify the compound, or more importantly in the context here, follow its distribution. In spite of this, however, analysis of ToF-SIMS spectral data can remain overwhelming. Recently, multivariate analysis methods [17]; and, in particular, principal component analysis (PCA), have been applied to simplify the data analysis and improve chemical contrast.

PCA is a statistical method used to find the combination of the variables that describe the most important trends in the data sets. PCA results are displayed mainly by score and loading plots [18]. The score plots allow classification of similar species, whilst the loadings give an indication of which ion species correlate (or anti-correlate) with a particular principal component (PC). Application of PCA to ToF-SIMS data, both imaging and spectral, has had considerable interest over the last few years. PCA allows for a fair degree of automation in analysing a data set, and can allow distinction between spectra that nominally look very similar and where unique secondary ions may not be present. For example, Castner's group has used PCA to distinguish the spectra of various adsorbed protein films, which would be virtually impossible to separate visually [19–21], whilst Vanden Eynde and Bertrand have applied PCA analysis to quantify polystyrene blends [22]. PCA has proven valuable in analysing and improving contrast in ToF-SIMS images. By grouping together all spectral features for a component, one can greatly increase the signal-to-noise ratio (S/N) and acquire meaningful images. This is especially important if it is necessary to remain within the "static limit" (sputtering of no more than 0.1% of the top monolayer) [2]. Further, topographic effects can be extracted (typically from the first PC) enhancing any chemical information that may be masked [23]. For example, Biesenger *et al.* have applied PCA image enhancement to Langmuir-Blodgett films, thereby allowing chemical variations to be separated out where it was essential that the static limit not be exceeded [24].

In this article, the use of ToF-SIMS to characterise the chemical distribution of ink components (vehicle, binder, modifier, and pigment) on coated paper will be explored. PCA will be applied to analyze the ToF-SIMS imaging data in order to simplify data analysis and to enhance the chemical contrast between the ink and the coating. In addition, PCA analysis will be applied on a cross-section to enhance the contrast between the ink, coating, and paper. Previous studies [15] on ink penetration into coated paper have made use of unique marker components [13] in the ink formulation in conjunction with depth analysis *via* sputter profiling. Use of the latter can raise the question of chemical modification, which can occur due to the sputtering process. Application of PCA, along with the high spatial resolution capabilities, allows the determination of the distribution of the various components (ink, coating, and paper) into the paper without the modification in chemistry that accompanies sputter profiling, and without the need to perform a full chemical assignment.

2. EXPERIMENTAL

2.1. Paper Sample Preparations

In order to establish that ToF-SIMS in conjunction with PCA can enhance chemical contrast and help characterise ink/coating distribution on and into paper, three types of samples were used:

1. A commercial ink-jet printing paper on which a test pattern of a 4-colour semicolon array was printed using an ink-jet printer (HP Business Inkjet 2200, Hewlett Packart, Houstou, TX, USA).
2. A commercially available photo-paper where the top-coating consisted of silica and polyvinyl alcohol (PVA). A cross-section was obtained by a freeze-fracture method in which the sample was held in a custom made Cu vice and plunged into a nitrogen slush (Emitech K1220VTS, Ashford, Kent, UK) to freeze the sample. The fractured surface was prepared by simply striking the exposed part with a metal object.
3. Two custom-coated papers, the coating of the first of which consisted of precipitated calcium carbonate (PCC) and styrene acrylate (SA) latex (PCC + SA), while the coating of the second paper consisted of PCC, starch and polyvinyl alcohol (PVA) (PCC + Starch + PVA). (coatings prepared by V. Li and S. Janardhnan at the university of Toronto). Two types of inked lines were printed using the ink-jet printer. For the first, a black (pigmented type) ink was used, while a yellow (dye type) ink was used for the second.

For the analysis, the samples were simply held on the sample-platen using clips, or in the case of the freeze-fractured surface, the vice itself was placed on the platen with the exposed fracture surface at the top.

2.2. ToF-SIMS

All spectra were obtained on the ION-TOF ToF-SIMS IV instrument (ION-TOF, Münster, Germany) located at Surface Interface Ontario in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto. A pulsed Ga liquid metal ion gun at 25 keV was used, operated in either a high-mass resolution mode or in a high-spatial resolution imaging mode. Full details of the experimental set-up for these modes are provided in Reference [2]. Charge neutralisation was achieved using the electron flood-gun supplied with the instrument. Other specific details are given in Section 3, Results and Discussion.

2.3. PCA

PCA [17,18] was performed using PLS_Toolbox 3.0 (Eigenvector Research Inc., Manson, WA), USA operating on Matlab 6.5 (The Mathworks Inc., Natick, MA), USA. Peaks with a relatively large area (above an arbitrarily chosen threshold) were selected from the SIMS spectra (normalised to total counts) using the auto-peak function of the software. For the 4-colour semicolon array and the printed lines on the coated surfaces, the auto-peak search function was used on the positive high-mass resolution spectra to generate a peak list of 186 peaks. The binary data matrix of these SIMS images, together with "sum of rest" (S) were transformed to a Matlab readable form, autoscaled (*i.e.* mean-centered and then divided by its standard deviation [24]), and finally processed using the PCA software. For the paper cross-sections, 15 peaks were selected from the negative SIMS spectra, which were collected in a high spatially resolved mode [2]. The main peaks were in the low mass range and there was little interference from neighbouring mass fragments, in spite of the low mass resolution which is obtained when using this mode. The negative spectra were used in these cases, since they gave the clearest results and the layers were well defined in spite of the limited number of peaks.

3. RESULTS AND DISCUSSION

3.1. PCA Images of the 4-Colour Semicolon Array

To demonstrate that PCA can help simplify SIMS data analysis and enhance chemical image contrast, initial studies were conducted on the 4-colour semicolon array [2]. The array consisted of 3 pairs of semi colons printed with dye-based inks (yellow, blue, and red) and one pair printed with black ink which is pigment based [2]. The spectrum obtained was typical of a paper surface and no effort was made to separate out possible ink fragments within the mass spectrum. Figure 1 shows the total ion image obtained from the positive ion SIMS spectrum. No clear contrast between the ink distribution and paper surface is discernable. While individual components could be identified and used to ascertain distribution, this can be time consuming. PCA provides an easy way of improving the image contrast and highlighting chemical differences, as can be seen also in Fig. 1. The principal components that contribute to this image are shown. PC1, which is similar to the total ion image, is primarily associated with topographic, as opposed to chemical, effects in that the loadings (not shown) are predominantly positive and, thus, most of the peak intensities are influenced evenly [24]. On the other hand, the chemical differences between the ink components and the paper surface are

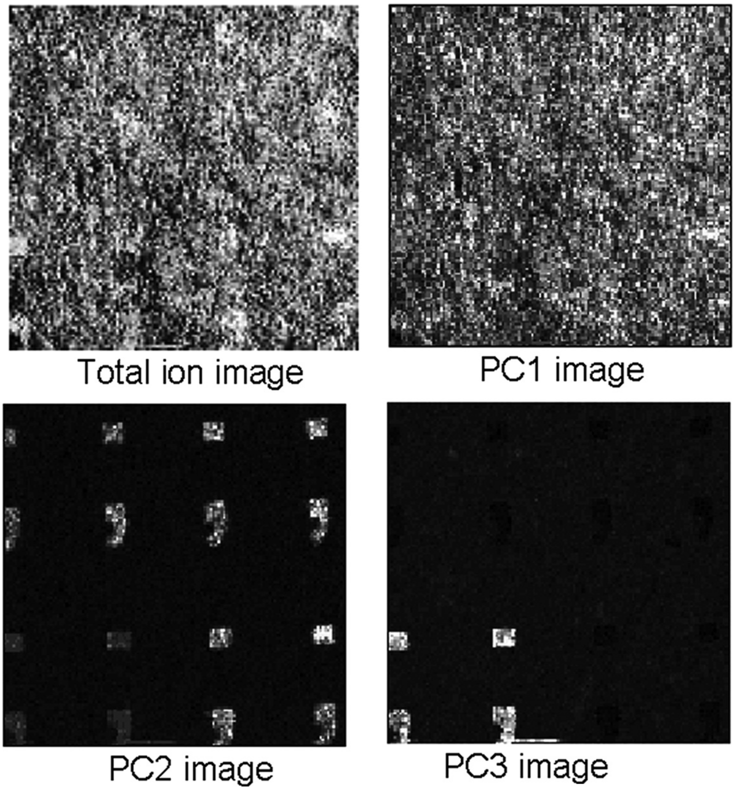

FIGURE 1 PCA image enhancement of ink on paper surface: The array consists of four pairs of semicolons. Three pairs are printed with dye-based inks (yellow – upper left pair; blue – upper right pair; red – lower right pair) and one printed with black (pigment-based) ink (lower left pair) [2]. Shown are the total (positive) ion image and the first three principal components.

highlighted in PC2, while PC3 further distinguishes the black ink (lower left quadrant) from the other coloured inks. From the loadings it should be possible to identify what contributes to the chemical differences and work is in progress to ascertain this.

In summary, PCA can improve the chemical imaging contrast between the various constituents without the need to perform a full chemical assignment or identify individual molecular markers.

3.2. PCA Image Analysis of Paper Cross-Sections

Positive and negative SIMS spectra collected in the high mass resolution mode for (i) uncoated paper (the back-side of the photo-paper); (ii) the

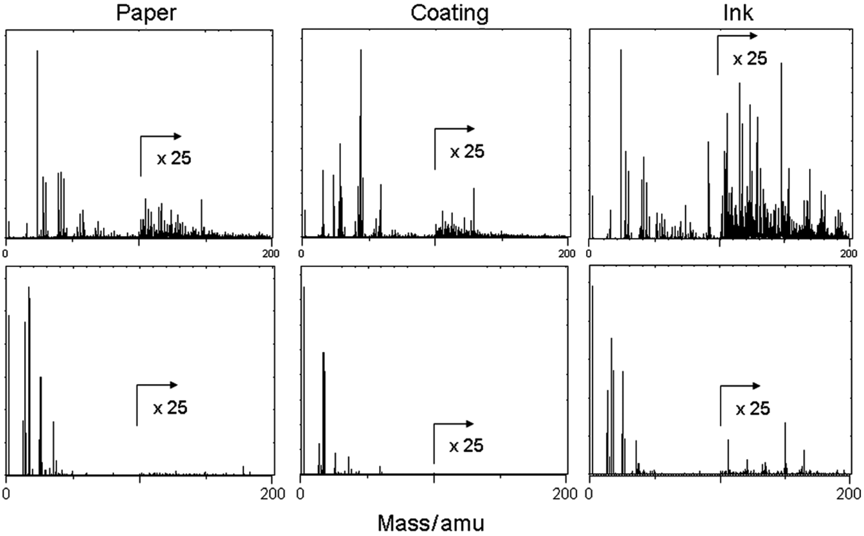

FIGURE 2 Positive (upper) and negative (lower) mass spectra for paper, coating, and the dye-based ink. The mass range is 0–200 amu, and the spectra were collected in the high mass resolution mode.

coated-side; and (iii) the inked surface are shown in Fig. 2. Apart from a prominent Na peak (mass 23), the positive spectrum for the back-side is characteristic for that of paper. It can be seen that differences do exist in the spectra of the different layers. Peaks for the subsequent PCA analysis of the paper cross-sections were selected from these spectra.

To illustrate that ToF-SIMS in conjunction with PCA can provide depth information on coated papers, negative ion SIMS images of the cross-section of a commercially available photo-paper were obtained. Figure 3 shows the first two principal components, along with their respective loadings, for the cross-section prepared by using a freeze-fracture method. Loadings for PC1 were all positive and, as discussed above, this indicates that topographical information is being displayed. PC2, however, shows positive values for masses 16 (O^-), 17 (OH^-), 28 (Si^-), 29 (SiH^-), and 32 (O_2^-), which will, hence, contribute most to the brightest regions, consistent with the coating layer having a composition of silica and PVA. To further justify this correlation, mass spectra (as opposed to loadings) were taken using a region of interest (ROI) analysis. Two regions of the same area were chosen—centre of the paper cross-section and the coating as indicated from PC2. The ROI are shown in Fig. 4 along with a reconstructed mass spectrum using the peak list, the intensities of which were

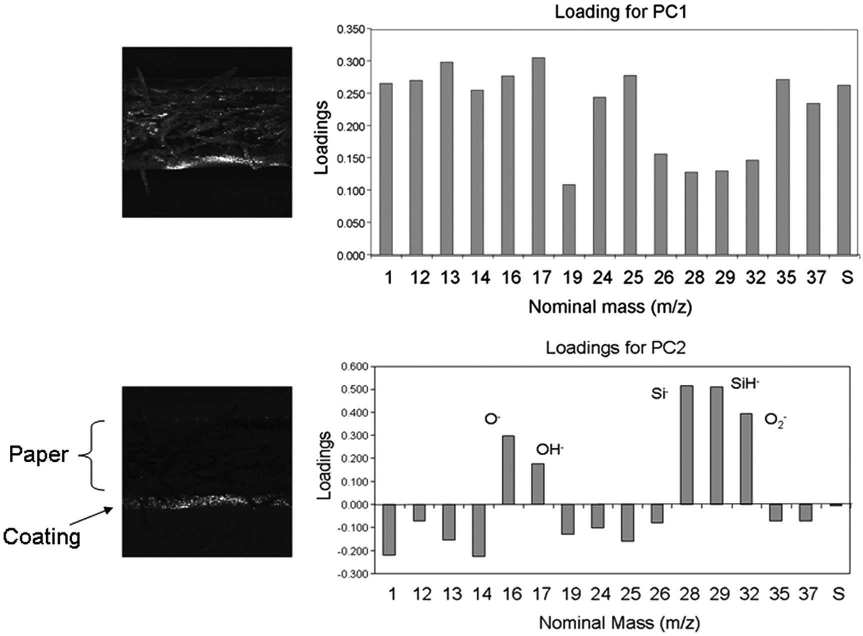

FIGURE 3 Images and loadings for PC1 (upper) and PC2 (lower) for the coated paper cross-section. Field of view for the image is $500 \times 500\,\mu m^2$.

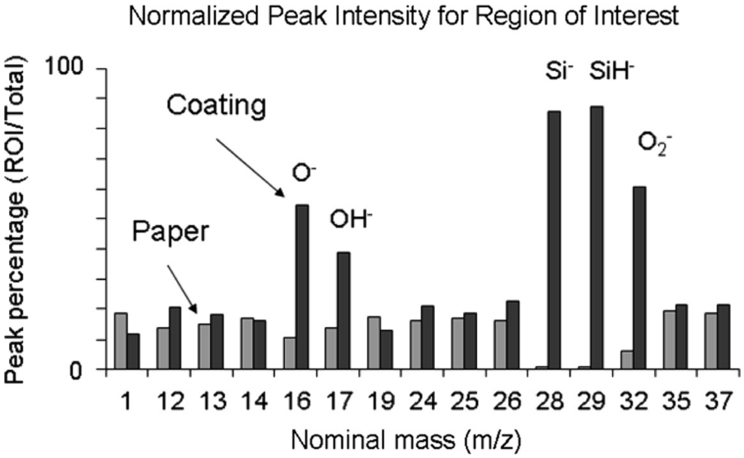

FIGURE 4 ROI analysis for the coated paper cross-section. The whole area of the coating (see PC2 in Fig. 3) was used for the Coating ROI, while a similar-sized strip at the centre of the paper cross-section was used as the Paper ROI. See text for details of the ROI analysis.

normalised by the spectrum of the whole paper for each individual ion (peak intensity of each ion in ROI spectrum is divided by the peak intensity of same ion in the whole sampling area). This has the effect of enhancing the variations in the image as opposed to showing the absolute intensities. For these spectra, the peak intensity is replaced by the peak percentage, which allows the unique peaks in that specific area to be quickly identified. From this it is seen that the O^-, OH^-, Si^-, SiH^-, and O_2^- peak intensities for the coating region are distinctively higher than those peaks associated with the hydrocarbon components, whereas the reverse is true for the paper region.

Similar analysis was performed on an inked region of the coated paper. It showed that PCA can distinguish an ink-layer on top of the coating. In this case, the cross-section was prepared simply by cutting the stiff paper with a sharp razor, to avoid problems arising from the different fracturing properties of the layers produced by the fairly crude freeze-fracturing method employed. Figure 5 shows the ROI for the ink-coated paper cross-section. The ROI analysis confirmed the relative increase in carbon-containing species (13 (CH^-), 24 (C_2^-), and 25 (C_2H^-)), which can be associated with the different (hydrocarbon) composition of the ink layer (and paper) from that of the coating and also reconfirms an increase in the Si associated with

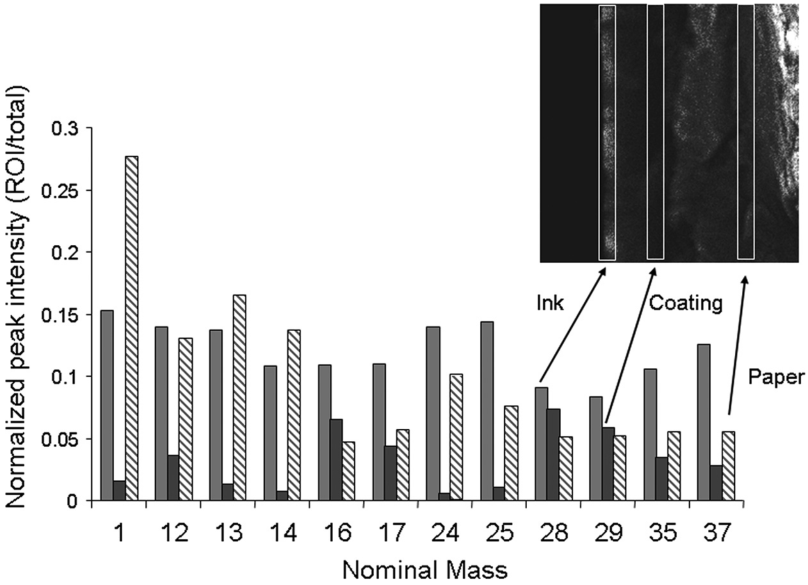

FIGURE 5 ROI analysis for the ink/coated paper cross-section. ROI locations are indicated by the arrows and white boxes.

the coating layer, consistent with results arising from PCA analysis performed on the cross-section.

3.3. PCA Image Analysis of Ink Distribution on Different Coating Formulations

While it has been demonstrated that ToF-SIMS with PCA can distinguish between the various layers, it is of primary interest to establish that it is capable of providing detailed information about chemical distribution, in particular, for the individual components of ink. To study this, two kinds of inked lines were analysed and compared, the first made with black (pigmented type) ink and the second with a yellow (dye type) ink. Further, based on the line shape and contour at the edge, the quality of printing on different coatings could be evaluated.

Figure 6 shows positive SIMS images (collected in high-mass resolution mode) of four selected fragments (selected from loadings) and two principal components for the black line printed on PCC + SA SA coated paper. From the SIMS images three distribution profiles are

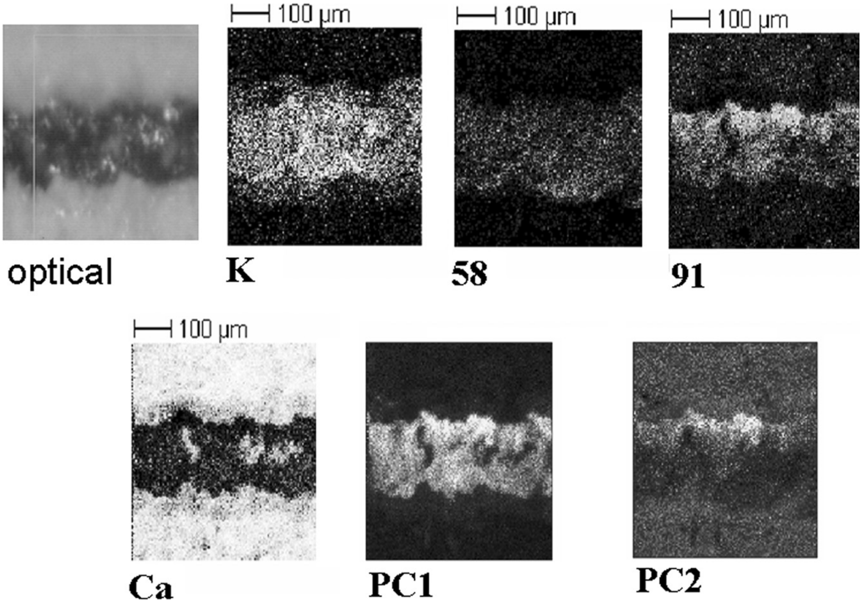

FIGURE 6 Positive SIMS images of black ink on PCC + SA coated paper. Also shown are the two first principal components and the optical image.

apparent, indicated by (i) K (39); (ii) mass 58 ($C_3H_8N^+$); and (iii) mass 91 ($C_7H_7{}^+$) image distributions. These have been associated with the ink vehicle, binder or modifier, and pigment, respectively. The presence of a thick layer of ink is also indicated in the Ca (40) image, in which the dark region shows masking of the Ca-containing coating. Further evidence of the different distributions is provided by the PCA analysis. Topographic information in this case is given by PC2 (positive loadings–not shown), whereas PC1 provides chemical information. The PC1 image shows that the central region of the inked line in bright contrast represents the pigment layer. A shadow region is apparent on either side of this layer (which is also evident in the Ca SIMS image), and it represents the binder and vehicle diffusion regions. While these assignments are based on what might reasonably be expected, previous work [25] has suggested that vehicle/binder

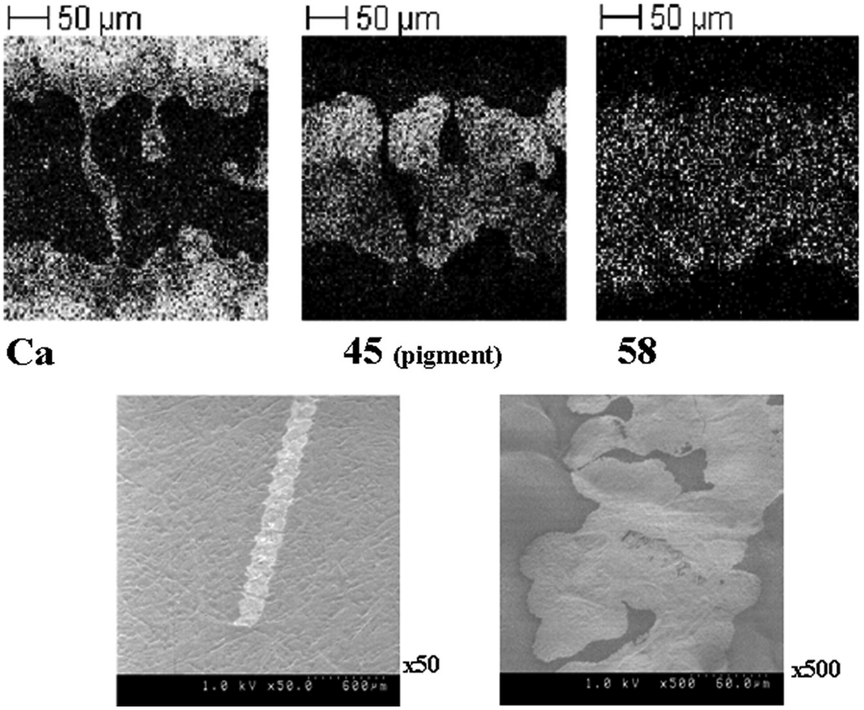

FIGURE 7 Positive SIMS images (top) of black ink on PCC + SA coated paper – as for Fig. 5 except images obtained in high spatial resolution mode [2]. Mass 45 has been chosen to represent the pigment distribution. Also shown are the SEM images (bottom).

does diffuse more into paper. Positive assignment of the various fragments to different components, however, would require full knowledge of the chemical composition of the inks.

Further confirmation of the ink distribution can be obtained from images taken in a high spatial resolution mode. These are shown in Fig. 7. The pigment distribution is clearly revealed in the dark regions of the Ca image, which matches the distribution of mass 45 ($C_2H_5O^+$) which, like mass 91, is also associated with the pigment. Since the pigment would be on top of the coating, its presence should be detectable by SEM. Images using a field-emission SEM are also shown in Fig. 7. The same patchy structure seen in the SIMS image for the pigment layer is clearly evident.

Figures 8 and 9 show selected positive SIMS and PCA-treated images for the yellow ink on PCC + SA coated paper, respectively. The images were obtained in a high spatial resolution mode. Since this is a dye-based ink, its behaviour will differ from that of the black pigment-based ink. As with the previous example, the dark region in the Ca (40) image represents the presence of the inked line. The clearest chemical contrast between the coating and the ink is

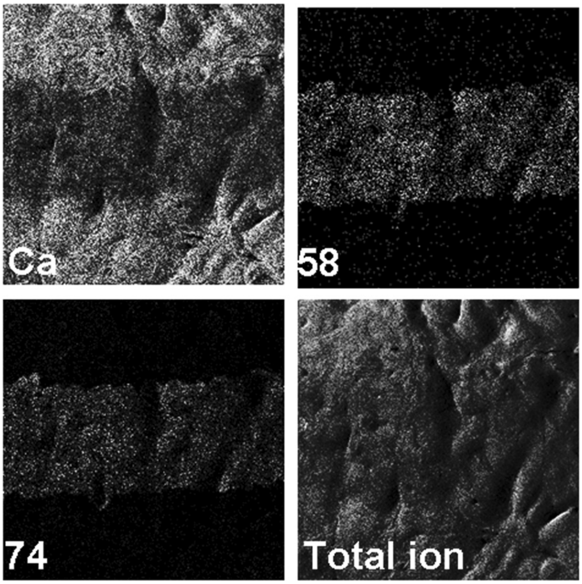

FIGURE 8 Positive SIMS images of selected fragments obtained in high spatial resolution mode on the yellow ink line printed on PCC + SA paper. Selected fragments were obtained from the loadings (see Fig. 9).

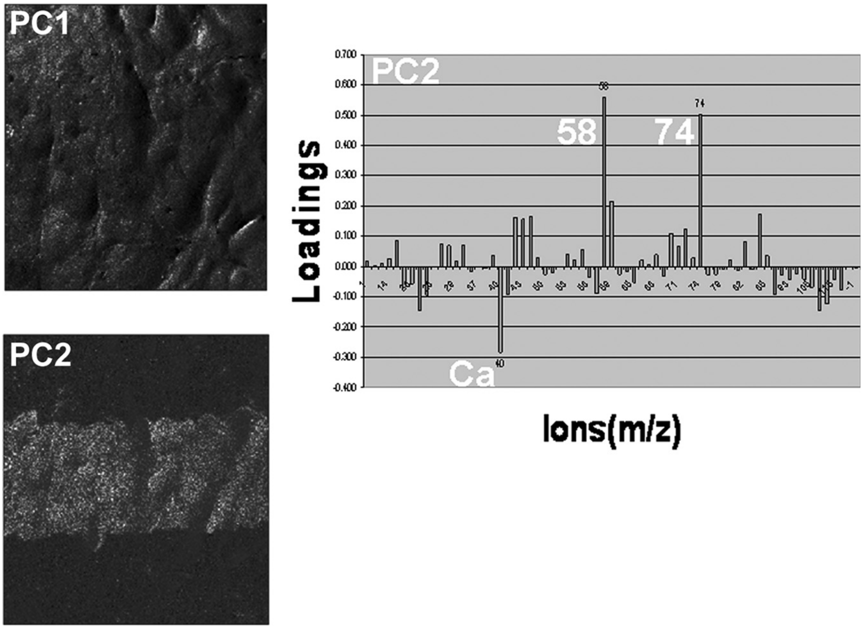

FIGURE 9 First two principal components for the images presented in Fig. 7. Loading plot for PC2 is also presented.

provided by masses 58 and 74, which show large positive loadings (Fig. 9). These match the dark area in the Ca image and, hence, there is no apparent separation of components as was found for the pigment-based ink. Also shown in Fig. 8 is the total ion image, which matches the image obtained from PC1 and reveals the topographical information. PC2 shows the chemical contrast between the ink and the coating. No difference in contrast or significant changes in line-width or the ink are ascertainable from these plots. SEM images were also obtained; however, no contrast could be observed between the ink and coating, which is not surprising since the yellow ink is dye-based.

Both the black and yellow inked lines were also printed on PCC + Starch + PVA coated paper and characterised by ToF-SIMS. Figure 10 shows positive SIMS images for masses 58 and 91 for the black ink on the two different coating formulations. When compared with the same lines printed on PCC + SA coated paper, these lines were less sharp and had a lower ink density. Similar results were obtained for the dye-based ink. Thus, the PCC + SA coating has a better printing quality than the PCC + Starch + PVA coating.

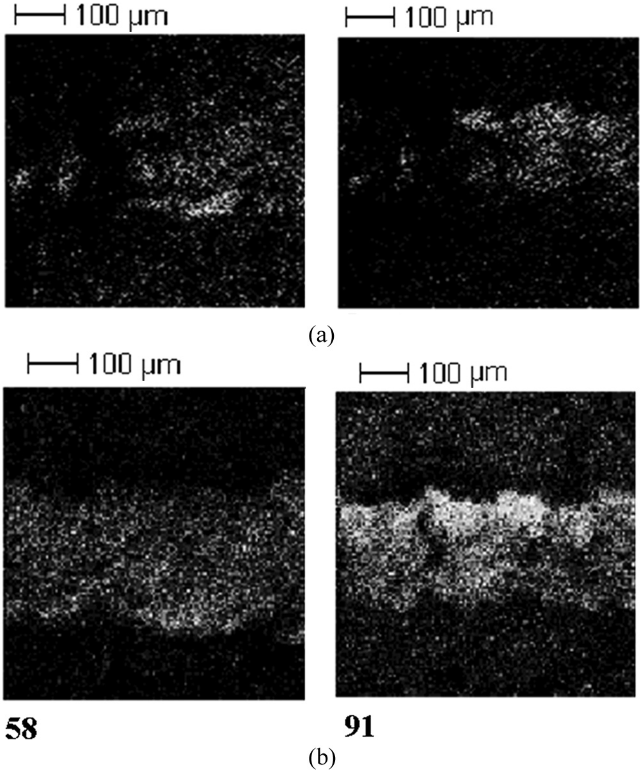

FIGURE 10 Binder (mass 58) and pigment (mass 91) distribution for the black ink line printed on (a) PCC + Starch + PVA and (b) PCC + SA.

4. CONCLUSION

It is seen that the imaging capabilities of ToF-SIMS, in conjunction with the chemical information the technique provides, allows for a convenient means of analysing ink spreading on, and penetration into, coated paper surfaces. Both elemental and chemical information is obtained and, hence, similar chemical components can, in theory, be separated, particularly with the high mass resolution that is achievable. This allows the various ink constituents within the formulations to be followed. While all the chemical information is retained, analysis of the data can be daunting. PCA was seen to greatly simplify the analysis and allowed an easy means of separating and identifying various components, including those chemically similar, without the need to perform a full chemical assignment.

Of the two different inks, one pigment-based and the other dye-based, ToF-SIMS was able to follow the distribution of both, unlike techniques such as SEM, which could only follow part of the pigment-based ink. Further, the technique was able to separate out the components. Specifically:

- The ink vehicle, binder/modifier, and pigment for the pigment-based ink were clearly identifiable and had a different distribution.
- No separation of components was apparent on the dye-based ink.
- Lines printed on the PCC + SA coatings were sharper than the corresponding lines printed on the PCC + Starch + PVA coatings.

With reference to depth distribution, the use of this methodology provides a convenient means of obtaining such by imaging the cross-section, since both elemental and chemical information is retained, as opposed to the more general means of obtaining depth information by sputter profiling. In the latter, the sputtering process destroys the sub-surface structure, effectively removing any chemical (as opposed to elemental) information normally available via ToF-SIMS even though the sputtering process is decoupled from that utilized for spectral acquisition. However; this may be less of an issue with the advent of the C60 cluster source which, for some systems, allows retention of molecular information [26]. However, the depth information obtainable by imaging the cross-section alone is limited to the spatial resolution of the technique, which is much larger than what would be obtainable by depth profiling though, given the scale of the penetration, this may not be of concern.

Thus, in summary, ToF-SIMS with PCA image analysis can map out the chemical distribution of individual components of ink on coated paper surfaces, thereby allowing the study of the interaction of ink, and its specific components, with coated paper. While this paper has specifically dealt with ink on coatings, the methodology will be equally applicable to adsorption and interaction of various species on different substrates.

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