JOURNAL OF MATERIALS SCIENCE **38** (2003) 2171 – 2177

Surface analysis of softened paper by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and the Kawabata evaluation system

M. PARFITT, J. C. VICKERMAN
Department of Chemistry, UMIST, P.O. Box 88, Manchester M60 1QD, UK

R. MITCHELL
CSMA Ltd., Armstrong House, Oxford Rd., Manchester M1 7ED, UK

C. M. CARR*
Department of Textiles, UMIST, P.O. Box 88, Manchester M60 1QD, UK

N. INCE, P. KNIGHT
Hercules Ltd., Widnes, WA8 8UD, UK

Smoothness is an important factor in consumer perception of tissue quality, with physical modification and chemical additions to the paper able to enhance tissue handle. Therefore objective measurement of the papers mechanical properties in developing new products and maintaining existing quality is vital. In this study the surface chemical composition of the softener treated paper is investigated using ToF-SIMS, and related to the surface frictional properties of the paper.

1. Introduction

The softness and smoothness of paper is important to the consumer and is therefore vitally important to the paper manufacturer. Facial tissues, paper towelling and napkins are all being marketed on the basis of softness/smoothness, which is mainly assessed by subjective panel testing either by the Magnitude Estimation Method or the Paired Comparison Test [1, 2]. However, there has always been an underlying need to develop an objective measurement system to provide quantification of the papers mechanical properties under appropriate non-destructive conditions. The Kawabata Evaluation System for Fibres (KES-F) is widely used in the Textile industry for objective measurement and communication of the textiles mechanical properties [2, 3]. However, although the KES-F System has achieved some acceptance in the paper industry it is far from being an industrial standard, partly due to the testing conditions and instruments not being optimised for paper samples. Nevertheless the system will allow paper products to be developed, improved and ultimately related to consumer panel testing.

The use of softeners and debonders are widespread in the paper industry and the effect of additives on the papers mechanical properties can be gauged. However, little research has been undertaken to demonstrate chemical delivery to the paper surface where the consumer perception of smoothness is relevant and where bulk additions may not reflect surface composition.

Previous ToF-SIMS studies have probed the surface of paper to investigate the distribution of organic additives and the nature of localized paper defects [4–6]. In this study the potential for combining surface analysis with objective measurement of the smoothness of softened paper is demonstrated.

2. Experimental

2.1. Materials

A series of printing paper quality samples, 35 g/m^2, were manufactured from a mixture of hard and soft woods on pilot scale machinery. A cationic dialkyl dimethyl quaternary ammonium softener (Softener A) was incorporated at levels of 0.1%, 0.2%, 0.3% and 0.4%, respectively, into the paper pulp prior to manufacture. A cationic dialkyl imidazoline (Softener B) and a cationic diester dialkyl quaternary ammonium softener (Softener C) were similarly incorporated into paper samples.

2.2. ToF-SIMS analysis (7)

The surface analysis of the paper samples was performed on a MS 2000 Bio-ToF-SIMS instrument. The spectra were obtained under *static* conditions using a Ga^+ ion source (25 keV, pulse length 50 ns) and a pulsed electron flood (50–70 eV) for charge compensation. The operating pressure was less than 4×10^{-8} torr. The intensity ratios calculated for surface softener concentration were the average

* Author to whom all correspondence should be addressed.

of duplicate measurements with a typical error of ±5%.

For each sample analysis, a total primary-ion dose of less than 1×10^{-12} ions cm^{-2} was used, well below the threshold of 1×10^{13} ions cm^{-2} for static SIMS. Both positive and negative ion spectra were acquired from an area of 250 μm × 250 μm in the mass range $m/z = 0$–1000.

2.3. Kawabata evaluation system for fabrics (KES-F) (7)

The samples, 20 × 20 cm, were conditioned at 65% R.H. and 20°C for 24 hrs prior to testing. Although the KES-F system measures bending, shear, tensile, compression and surface properties only the surface analyser was utilized. The test conditions for the paper were 10 gf pressure for the surface roughness probe and 50 gf for the friction probe. The data presented were an average of ten measurements per sample. The statistical analyses were performed using the Microsoft Excel package and the Student t-Test values determined.

3. Results and discussion

The subjective perception of smoothness of textiles is closely related to softness, with the MMD value being strongly correlated to the subjective perception of smoothness [8]. With paper, smoothness/softness has been correlated with surface roughness, SMD [9], although the perception of smoothness will also be influenced by the slip/stick effect of the variation in the coefficient of friction, MMD. Therefore the effect of softeners will be important in subjective analysis by lubricating the surface and enhancing surface deformation to create the impression of smoothness/softness.

ToF-SIMS is an excellent technique for characterizing surface chemistry and in particular fibre surface absorbates [7, 10]. The surface sensitive technique, with its sampling depth of 1–2 nm, provides both elemental and molecular mass spectral data by bombarding the sample surface with a primary ion beam and analysing the masses of the sputtered secondary ions emitted from the surface. The experiment is performed under ultra-high vacuum in order to allow the efficient passage of the ions through the Time-of-Flight mass spectral analyser. Thus both positive and negative ion mode data can be obtained. The control non-softened paper showed a relatively high intensity ToF-SIMS positive ion spectrum in the $m/z = 0$–100 range, typical of the fragmentation of organic material. No ion intensity was observed in the $m/z = 450$–700^+ region.

Examination of the positive ion ToF-SIMS spectrum of the cationic dialkyl dimethyl quaternary ammonium Softener A film and treated paper showed three strong signals at $m/z = 494^+, 522^+, 550^+$, Figs 1 and 2. These signals confirm that the softener is a mixture of C_{18} and C_{16} derivatives with the molecular ion structures shown, Scheme 1. Both stearyl and oleyl C_{18} derivatives are evident from the ToF-SIMS spectrum.

Quantification of ToF-SIMS data can present difficulties due to the relatively high proportion of neutral secondary particles produced in comparison to positive and negative secondary ions. However, previous ToF-SIMS studies have successfully monitored the relative surface changes on a number of organic systems using the formula $I_A/(I_A + I_B)$, where I_A and I_B are measured intensities of ions A and B, respectively [11–13]. For the calculations I_A corresponds to the peak intensity of the softener ion of interest and I_B to the peak intensity of the signal at $m/z = 41^+$ ($C_3H_5^+$), a non-specific ion characteristic of organic surfaces. Analysis of the softened paper under identical experimental conditions has shown that the softener A ion intensity, $m/z = 550^+$, similarly increases as the softener addition to the pulp increases, Fig. 3. In addition to the cationic species the negative ion ToF-SIMS spectra of the softener film and paper also indicate the presence of the fatty palmitic ($C_{15}H_{31}CO_2^-$), oleic ($C_{17}H_{33}CO_2^-$),

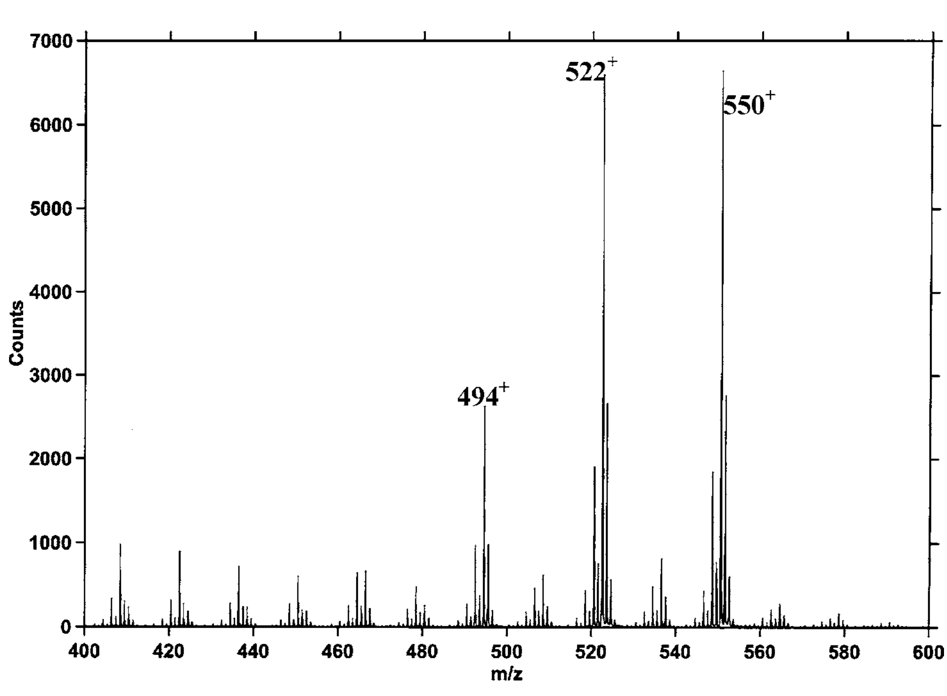


Figure 1 Positive ion ToF-SIMS spectrum of softener A film on aluminium foil.

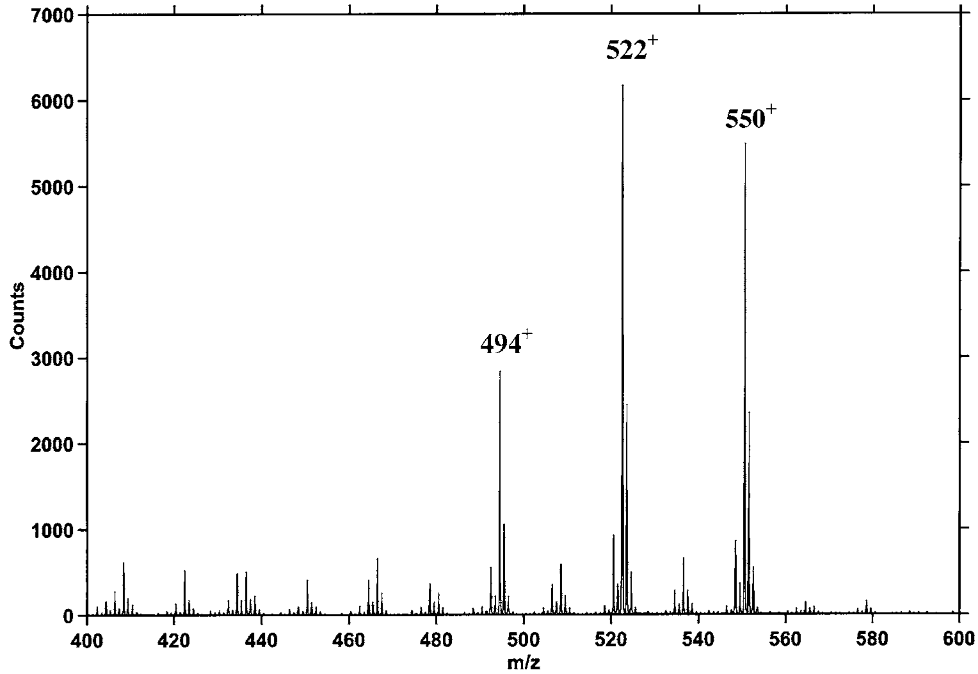
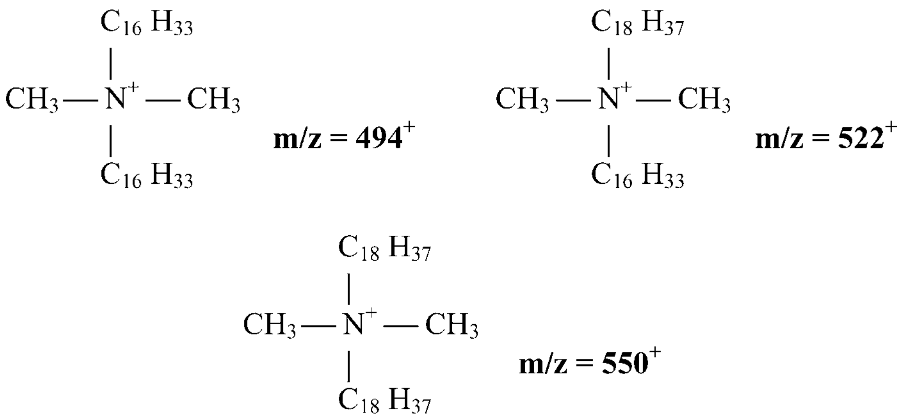


Figure 2 Positive ion ToF-SIMS spectrum of softener A treated (0.4% wt/w) paper.



Scheme 1 Ion assignments in positive ion ToF-SIMS spectrum of softener A (dialkyl dimethyl quaternary ammonium ion).

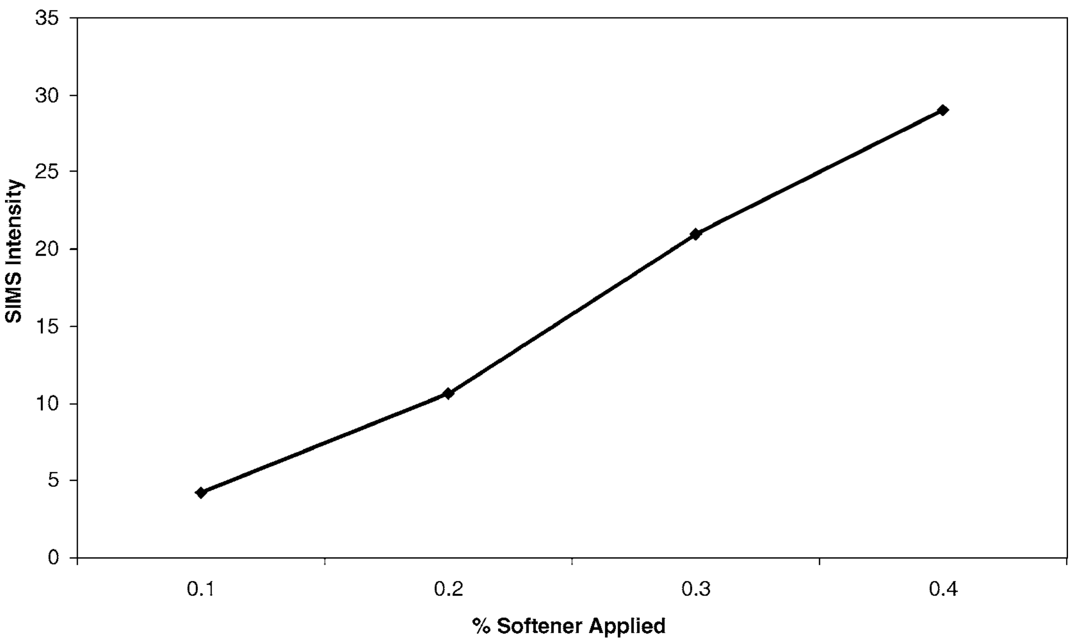


Figure 3 Effect of application concentration of softener A on ToF-SIMS intensity ratio (I_A, *m/z* = 550^+).

TABLE I KES-F analysis of the mean deviation of coefficient of friction, MMD, of paper

	MMD value									
	Control		0.1% softener A		0.2% softener A		0.3% softener A		0.4% softener A	
	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD
Mean	0.0271	0.0326	0.0230	0.0258	0.0197	0.0216	0.0168	0.0176	0.0143	0.015
SD	0.0027	0.0018	0.0020	0.0037	0.0051	0.0042	0.0040	0.0034	0.0010	0.0010

MD = Machine direction; CD = Cross direction; SD = Standard deviation.

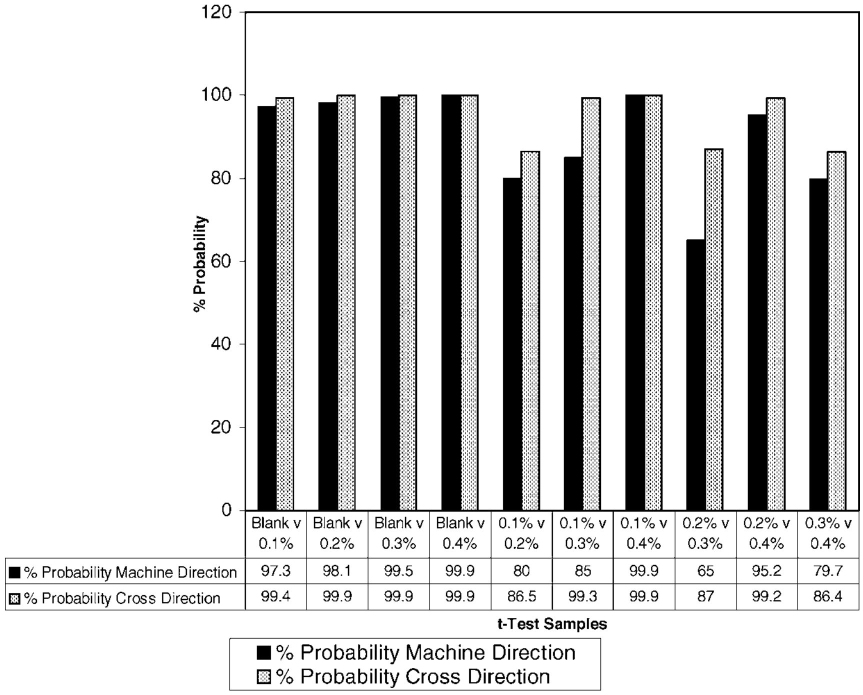
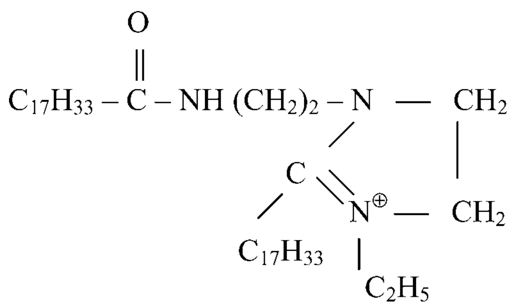


Figure 4 Student *t*-test analysis of effect of softener concentration on paper smoothness, MMD.

and stearic ($C_{17}H_{35}CO_2^-$) acids at $m/z = 255^-$, 281^- and 283^-, respectively.

The mean deviation of the coefficient of friction, MMD, in the KES-F analysis of textiles has been shown to correlate closely with subjective perception of smoothness [8]. In this study the effect of increasing the levels of Softener A was to progressively reduce the MMD value, Table I. Statistical analysis of the data indicates that there is a high probability that the differences between unsoftened and softened samples are significant, greater than 99%, Fig. 4. However, when the application levels of softener are similar the statistical differences are not as clear. This data analysis could be improved by larger sampling but again the final stage of product development will require subjective analysis to validate the objective measurement.

ToF-SIMS analysis of the Softener B film and treated paper revealed a dominant signal at $m/z = 642^+$ which can be assigned to a dioleate imidazoline species, Figs 5, 6, and Scheme 2. The negative ion ToF-SIMS of softener B revealed the presence of palmitic (C_{16}), oleic (C_{18}) and stearic acid (C_{18}) ions at $m/z = 255^-$, 281^- and 283^-, respectively. Thus indicating that the ions at $m/z = 646^+$, 644^+, 614^+, 616^+, 618^+ were in fact softener derivatives based on varying the palmitic, oleic and stearic substituents. Since fragmentation of amides occurs during ToF-SIMS analysis it is not certain whether these fatty acid ion signals are due to actual "free" fatty acids in the softener formulation as in Softener A, or are fragmentation ions of the amide molecule.



Scheme 2 Structure of softener B, a cationic dioleate imidazoline ($m/z = 642^+$).

In order to further establish the relationship between the applied softener concentration and surface softener ToF-SIMS ion intensity a series of standard samples were prepared. Again an approximately linear relationship between ion intensity and softener loading was observed, Fig. 7.

Examination of the softener C treated paper positive ion ToF-SIMS spectra shows the presence of a series of high molecular mass ions, Fig. 8. The proposed ion assignments, Table II, are based on the diester dialkyl quaternary ammonium structure in Scheme 3. The

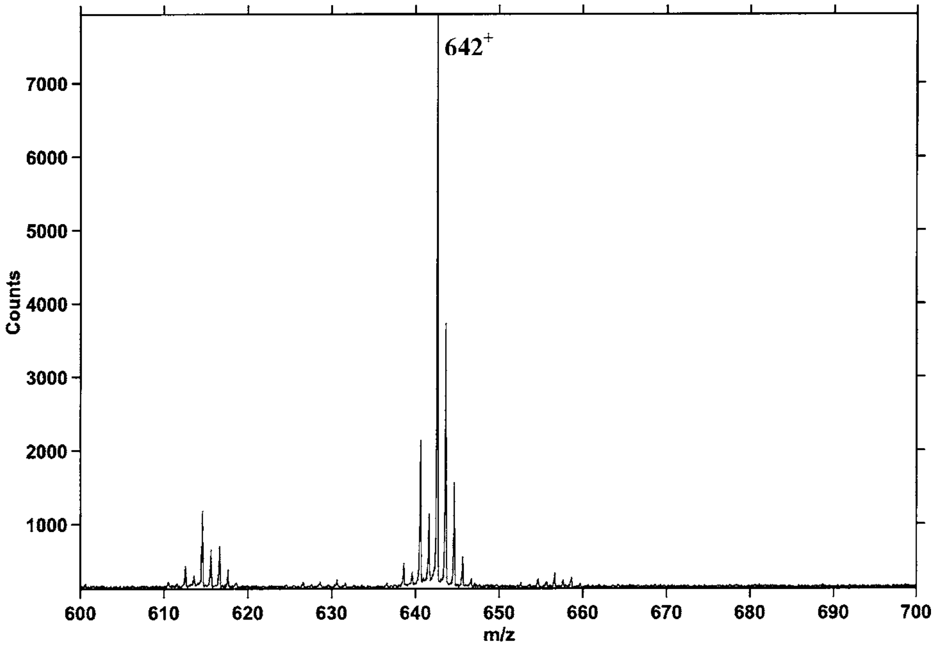


Figure 5 Positive ion ToF-SIMS spectrum of softener B film on aluminium foil.

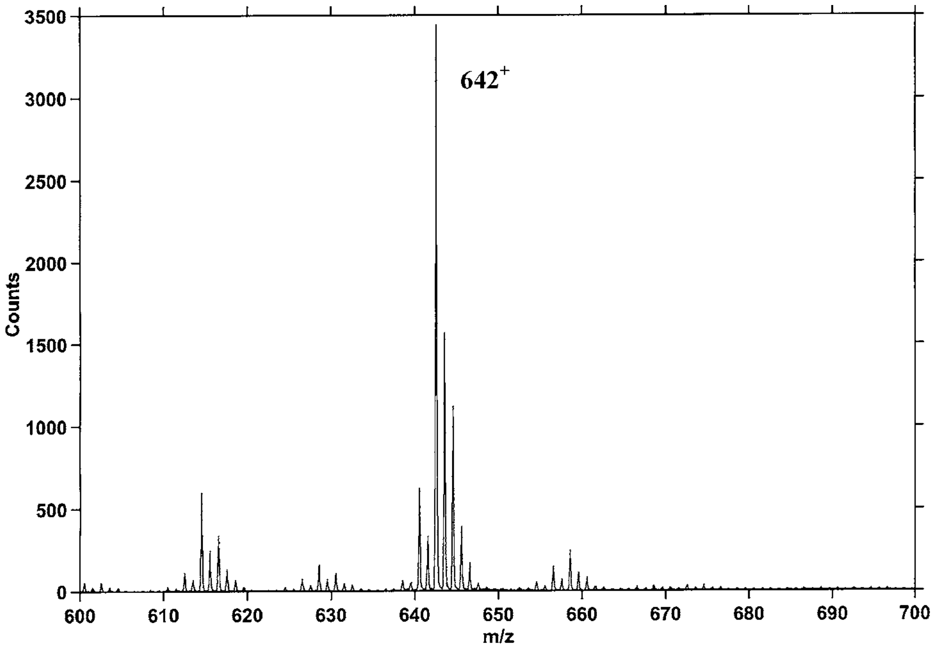


Figure 6 Positive ion ToF-SIMS spectrum of 0.4% (wt/wt) softener B treated (0.4% wt/wt) paper.

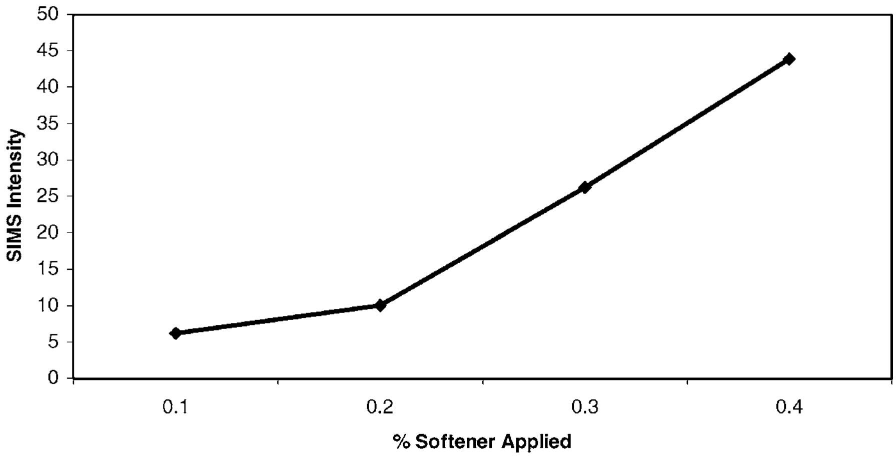


Figure 7 Effect of application concentration of softener B on ToF-SIMS intensity ratio at paper/surface (I_A, $m/z = 642^+$).

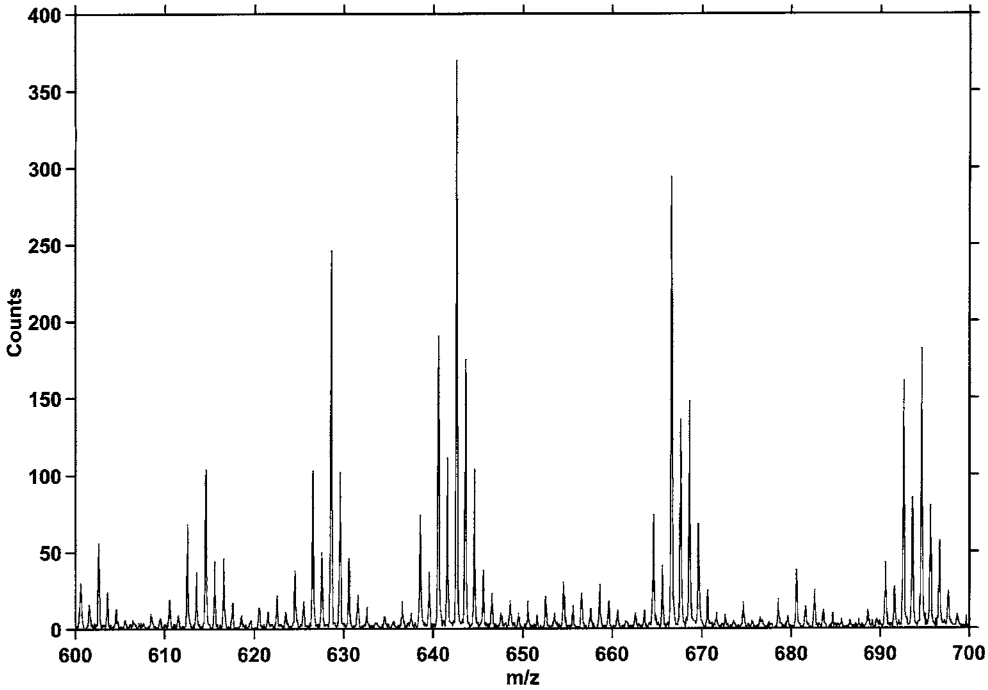
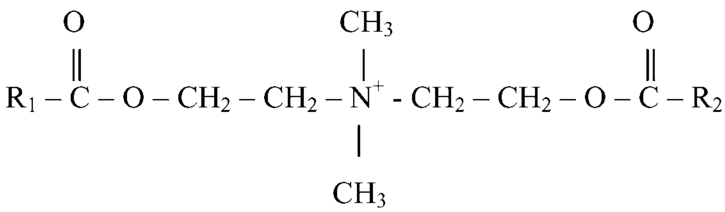


Figure 8 Positive ion ToF-SIMS spectrum of softener C treated (0.4% wt/wt) paper.



Scheme 3 Proposed structure of softener C, a cationic mainly C_{18}/C_{16} diester dialkyl type quaternary ammonium softener.

negative ion ToF-SIMS spectrum of the softener treated paper indicate that palmitic, stearic and oleic fatty acids are all present, but again it is uncertain whether they are present as "free" acids or as a result of fragmentation of the parent molecular ion. The dominant molecular ion occurs at $m/z = 642^+$, suggesting the C_{16}/C_{18} derivative is the major softener component.

Into the future while the "traditional" softeners will still maintain market share, combination softeners will be developed for paper which offer softness/smoothness with functionalities such as enhanced strength or substantivity "built-in" to the molecular structure. Croda has already developed such products in the hair care market and opportunities for transferring these systems will be explored.

TABLE II Proposed ToF-SIMS ion assignment of softener C structure

Alkyl substitute		
R_1	R_2	*m/z*
$C_{17}H_{35}$	$C_{17}H_{35}$	666^+
$C_{17}H_{35}$	$C_{17}H_{33}$	664^+
$C_{17}H_{35}$	$C_{15}H_{31}$	642^+
$C_{17}H_{33}$	$C_{15}H_{31}$	640^+
$C_{15}H_{31}$	$C_{15}H_{31}$	614^+
$C_{15}H_{31}$	$C_{15}H_{29}$	612^+
$C_{19}H_{39}$	$C_{17}H_{35}$	694^+
$C_{19}H_{39}$	$C_{17}H_{33}$	692^+

4. Conclusions

The ToF-SIMS analysis of typical softeners applied to paper has been successfully demonstrated with characteristic ion species observed at the paper surface. Increasing the softener incorporation into the paper produces a concomitant increase in the surface softener spectral intensity, as detected by ToF-SIMS. The combination of ToF-SIMS and the KES-F surface analyser is potentially useful in relating softener delivery to the paper surface to the surface frictional properties.

Acknowledgements

The author would like to thank A. Harvey for the KES-F analyses and Dr. H. Gong for helpful KES discussions. In addition thanks to Croda Colloids, UK, for continuing to fund research into the application of the KES system for paper analysis and novel softener development.

References

1. H. HOLLMARK, "Mechanical Properties of Paper and Paperboard," edited by R. E. Mark (Marcel Dekker, New York, 1983) Chap. 11, 497.
2. M. K. RAMASUBRAMANIAN, "Handbook of Physical and Mechanical Testing of Paper and Paperboard," Vol. 1, 2nd ed. (Marcel Dekker, New York, 2000).

3. S. KAWABATA, "The Standardization and Analysis of Hand Evaluation," 2nd ed., (The Hand Evaluation and Standardization Committee, The Textile Machinery Society of Japan, July, 1980).
4. J. S. BRINEN, *Nordic Pulp Paper Res. J.* **8**(1) (1993) 123.
5. Y. OZAKI, *ibid.* **12**(4) (1997) 260.
6. R. J. KULICK and J. S. BRINEN, *Tappi J.* **81**(2) (1998) 152.
7. J. C. VICKERMAN and A. J. SWIFT, "Surface Analysis—The Principal Techniques," edited by J. C. Vickerman (J. Wiley and Sons, 1997).
8. E. FINNIMORE and A. KONIG, *Melliand Textilberichte* **67**(7) (1986) 516.
9. J. J. KIM, I. SHALEV and R. L. BARKER, *Tappi J.* **77**(10) (1994) 83.
10. S. VOLOOJ, C. M. CARR, R. MITCHELL and J. C. VICKERMAN, *Surf. Interface Anal.* **29** (2000) 422.
11. M. C. DAVIES, S. R. LEADLEY and N. M. FRANSON, *Polym. Adv. Technol.* **3** (1992) 293.
12. G. N. BATTS and A. J. PAUL, *Langmuir* **10** (1994) 218.
13. M. R. ALEXANDER and F. R. JONES, *Carbon* **33** (1995) 569.

*Received 2 August
and accepted 11 November 2002*