

# The observation and distribution of organic additives on paper surfaces using surface spectroscopic techniques

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**SUMMARY:** Incorporation of low levels of organic reagents into paper generally leads to improved performance properties in formation, wet strength, sizing and printability. The development of surface spectroscopic techniques provides a means of detecting the presence and distribution of these additives on the paper surface. The information content of ESCA and SIMS for characterizing paper surfaces is compared for both internal and surface sized paper surfaces.

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Incorporation of organic reagents into paper results in improved performance properties in areas such as formation, wet strength sizing and printability. In general, the reagent concentrations used are low and are difficult to detect using conventional spectroscopic techniques. However, the development of surface spectroscopic techniques such as X-ray Photoelectron Spectroscopy (XPS or ESCA) and Secondary Ion Mass Spectroscopy (SIMS) provides a means for detecting and identifying the presence of these additives. Since most conventional sizing agents contain long chain aliphatic functionalities, their presence may be detected in XPS by examination of the C 1s spectrum (Dorris, Gray 1978; Gray 1978; Takeyama, Gray 1982; Borch, Miller 1988; Brinen et al. 1989). The presence of heteroatoms provides an additional means of monitoring the additives (Brinen et al. 1989). SIMS, in addition to providing another means for detecting the additive presence, is much more specific in its ability to identify the chemical nature of the additive.

In addition to detecting and identifying the presence of additives, both of the above spectroscopies may be used to obtain information regarding their spatial distribution. In previous publications, dynamic SIMS imaging (Brinen et al. 1991) has been used to obtain spatial information on inorganic species on paper surfaces and both dynamic and static SIMS imaging (Brinen, Proverb 1991) have been used to show the distribution of organic surfactants on paper surfaces. Initial attempts to image the fluorinated surfactants reported by Brinen and Proverb (1991) using ESCA have been made in collaboration with S. F. Davies and D. Briggs (ICI). While successful (Davies, Briggs 1992), the spatial resolution is considerably poorer than that attainable using SIMS imaging.

In the present study the comparison of the information content between ESCA and SIMS is made for paper surfaces treated with commercial and experimental sizes, both internal and surface. The identification of molecular species attributable to paper additives on paper surfaces using SIMS has yet to be reported until the present study. To demonstrate this could be done, unusual methods of application were employed, i.e., higher than normal concentrations and a high solubility solvent to introduce the sizes to the paper surface. Uniform

distributions of additives would be expected via a vis introduction via aqueous dispersions. Experiments of this type and as a function of concentration are in progress in our laboratory.

## Experimental

### Sample preparation

Two different paper preparations were used in this study, one for the internal sized paper samples and the other for the surface size studies. The preparation of the samples used in the surface size study were made using a pilot paper machine and was reported in a previous publication (Brinen, Proverb 1991). In the present study a styrene-acrylic type resin surface size was applied in the size press while a fluorinated (in the acrylic moiety) styrene acrylic type resin surface size was prepared and was applied to the handsheet via tub sizing. ASA and surface size were used at the 0.1% and 0.1-0.2% levels, respectively.

The other paper handsheets were made in a hand sheet mold with 50150 hardwood/softwood pulp and 20% calcium carbonate. The sheets were tub sized using reagent grade toluene as a solvent at a dose of 0.4% real polymer on fiber (8 lbs/ton of sizing agent). The sheets were air dried for 10 minutes at room temperature and drum dried for 45 sec at 116°C prior to spectroscopic examination.

### Spectroscopy

The SIMS data reported in this work were obtained using a Time of Flight (ToF) SIMS instrument, the Charles Evans & Associates TFS spectrometer using 25kV <sup>69</sup>Ga ions for excitation in the microprobe mode. Spectrometer conditions were chosen to optimize the spatial distribution at the expense of not operating under maximum mass resolution. Charge compensation was effected with an electron flood gun which was pulsed out of phase with the ion gun. The ToF SIMS images and spectra shown were all taken under static SIMS conditions [see references in (Brinen, Proverb 1991)]. XPS experiments were performed using an HP 5950A ESCA spectrometer with Al k alpha radiation (Brinen, Proverb 1991).

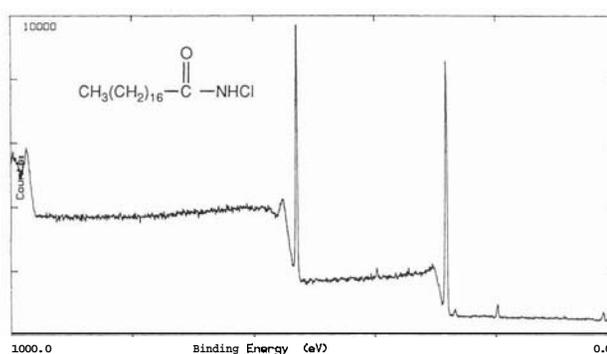


Fig. 1. ESCA survey scan of paper tub sized with a toluene solution of N-chloro stearamide.