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ABSTRACT

Time of flight secondary ion mass spectroscopy is a new technique for probing the chemistry of surfaces. Applying the technique to many papers and papermaking problems shows that it is a powerful tool for analysis and problem solving. The authors discuss various applications in detail with emphasis on problems involving defects and runnability. The technique helped resolve a sizing problem where pitch was a highly effective desizing agent. This brought new insight to an old problem—why some pulps are more difficult to size than others.

Application:

SIMS is a simple and valuable tool for paper analysis. Detection of the presence of desizing agents is an example.

Probing paper surfaces with ToF SIMS: A new problem solving tool

RUSSELL J. KULICK AND JACOB S. BRINEN

TIME OF FLIGHT (TOF) SECONDARY ion mass spectroscopy (SIMS) is a surface analysis technique used to obtain mass spectra and mass images of organic and inorganic constituents present on the surfaces of materials *(1)*. The technique works by pulsing a primary ion beam onto the sample surface. The impact of the primary ion beam on the surface causes sputtering of atomic and fragment species and desorption of molecular ions for subsequent detection according to their masses.

Storing the data in a computer allows retrieval in various ways including a mass picture of the surface under examination using any or all the ions released from the surface as **Fig. 1** shows.

ToF SIMS can analyze positive and negative ions and is sensitive to organic and inorganic ions. The instrument we use has high mass resolution capability and can provide compositional information on the secondary ions produced by the primary ion beam. SIMS can answer some important questions:

- What is a material?
- Where is it on the sample?
- Approximately how much exists?

Several studies on paper samples have used SIMS. The earlier work involved laboratory treated samples *(2–4)*. SIMS recently examined two commercial papers with special problems—print mottle in coated paper and contamination on label paper *(5)*.

EXPERIMENTAL

ToF SIMS spectra were obtained with the Charles Evans & Associates TFS ToF SIMS spectrometer using 25 KV ^{69}Ga ions for a primary beam and operated in the microprobe mode. An unbunched beam of 20–30 ns pulse width capable of lateral resolutions of 2000 Å optimized the spatial resolution rather than mass resolution (1000 at ^{28}Si). Charge compensation was effected by an electron flood gun that pulsed out-of-phase with the ion gun. The ToF SIMS images and spectra were obtained under static SIMS conditions *(6–8)*.

EXAMPLES

We have conducted many SIMS investigations of commercial papers and problems. SIMS has proven extremely versatile and has given answers where conventional techniques might have difficulty. To illustrate the use of SIMS, we offer some examples as follows.

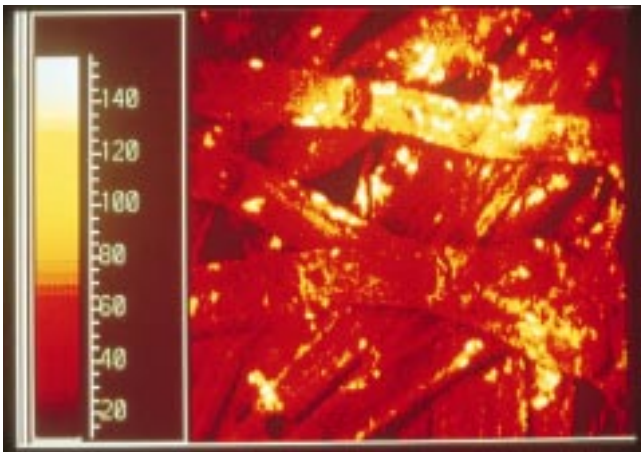
Fish eyes

Our first example concerns a machine making uncoated alkaline free sheet. SIMS analysis examined two types of defects. Both were fish eye defects consisting of crushed, transparent spots approximately 5 mm in diameter. Type 1 had a clear center. Type 2 was primarily clear but also contained black specks in the transparent area. Although the defects appeared similar, the customer believed that they had different origins. SIMS analysis proved this was true.

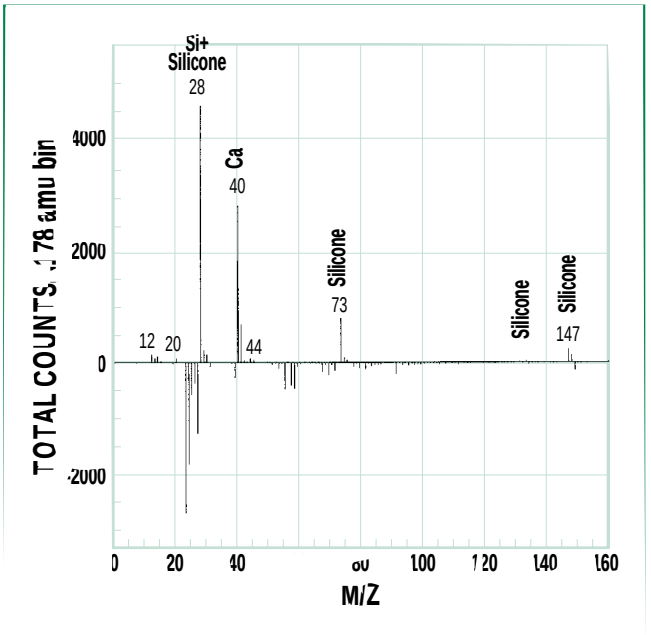
In analyzing the fish eye defects, we obtained SIMS spectra from the transparent area and from a nearby uncrushed area—blank. The difference spectrum resulted by subtraction of the blank spectrum from the defect spectrum. Mass species enriched in the defect compared with the base sheet showed a net positive number of counts in the difference spectrum.

Figure 2 is a positive ion difference spectrum of the Type 1 fish eye with a clear center. The defect is highly enriched in calcium (mass 40) and in silicone fragments (mass 28, 73 and 147). This suggests that Type 1 defects result from poor dispersion or agglomeration of a silicone-based defoamer and filler—calcium carbonate.

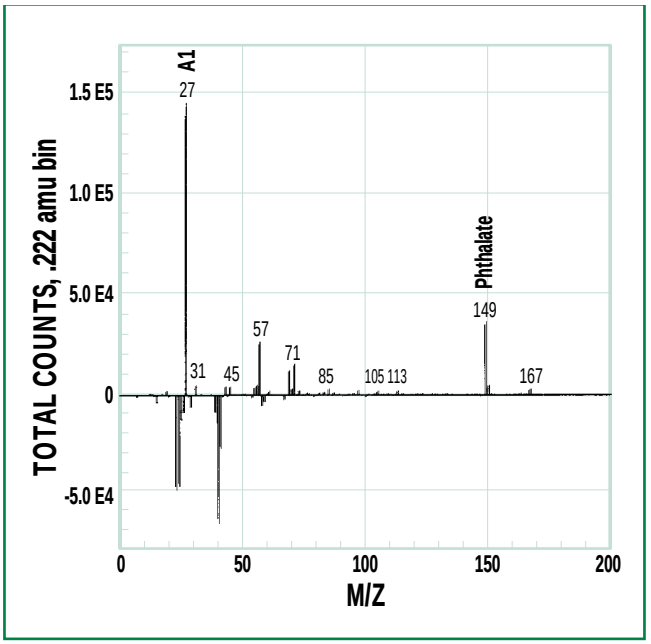
Type 2 defects are dramatically different. **Figure 3** shows the positive ion difference spectrum. This defect has a very intense peak from aluminum (mass 27) and no enrichment of calcium. In addition, the spectrum shows a strong peak at mass 149. This peak is a phthalate fragment from polyethylene terephthalate plastic or a phthalate plasticizer. This machine uses a small quantity of thin stock alum. The customer should look at alum dilution and mixing and plastic contamination as potential sources of Type 2 fish eyes.



1. Positive ion SIMS mass picture of a paper surface from mass 0 to 175



2. A positive ion difference spectrum of Type 1 fish eye showing excess calcium and silicone in the defect



3. A positive ion difference spectrum of Type 2 fish eye showing excess aluminum ion and phthalate ion in the defect

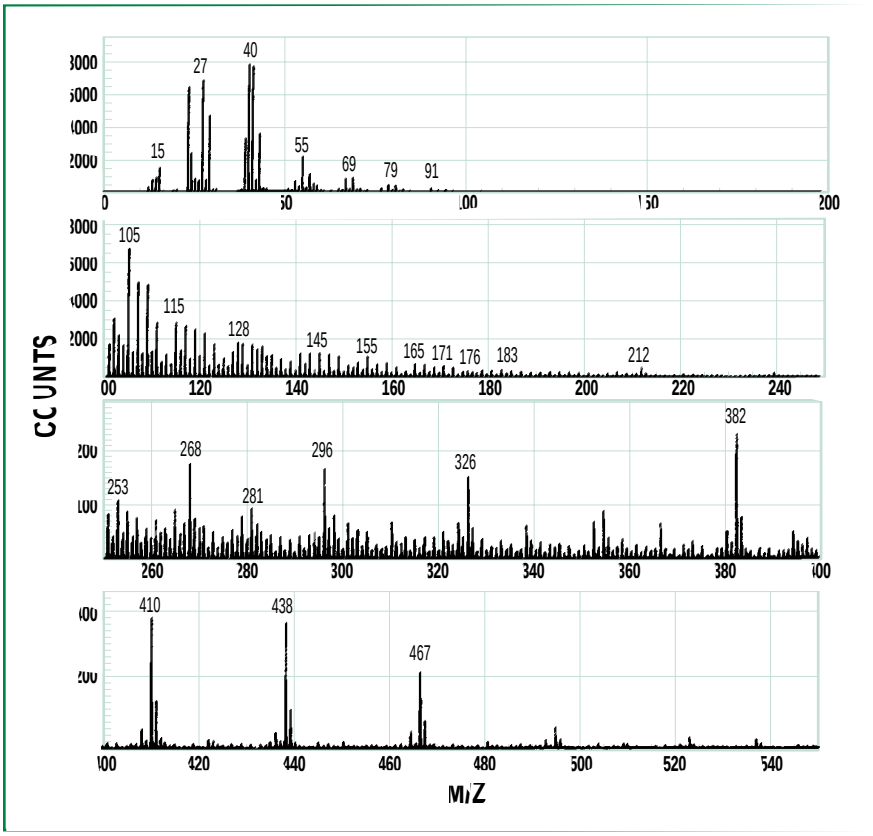
Brownish specks

This customer was producing a yellow-dyed grade of alkaline fine paper. The defects in question were small, irregular, brownish specks approximately pinhead size. They were surface defects located exclusively on one side of the sheet. Washing the machine did not alleviate the problem. SIMS difference spectra did not show any significant organic ions in the specks. A big difference existed in the inorganic content. The specks were rich in sodium, magnesium, and iron. A negative ion SIMS difference spectrum showed the specks were rich in chloride. Because the specks were rich in sodium and chloride, we suspected they originated at the size press or in the after section. Sodium chloride addition at the size press gave static control. Since the defects were only on one side, the after dryers were the prime suspects. The presence of iron suggested corrosion. Since magnesium is a common ion in this sulfite pulp system, its presence is usual. The most probable cause of the speck problem was pitting or etching on the after dryer cans. The site was probably the first top can since the specks were all on the wire side. The first top can did indeed show etching. Prompt correction of this eliminated the specks.

Sizing problems

This investigation was more detailed than the previous ones. Our customer was making alkaline fine paper sized with alkenyl succinic anhydride (ASA). When using regular bleached kraft pulp, modest doses of ASA gave good sizing. One grade presented a problem. When making a totally chlorine free (TCF) grade with purchased, bleached sulfite pulp, the dosage of ASA required increase by a factor of two or three to meet sizing specifications. The customer asked us as the size supplier to investigate this problem.

A chromatographic method provided a key to understanding the problem. We suspended a sheet of the problem paper with the long side (machine direction) vertical in a chromatography chamber having a small quantity of reagent grade acetone in the bottom. The acetone rose by capillary action approximately halfway up the sheet. We then removed the sheet from the chamber and allowed it to air-dry. We could easily see the position of the solvent front in the dried paper as a slightly transparent zone several millimeters wide due to migration of acetone soluble material with the solvent front (R_f = 1.0). We made sizing



4. SIMS positive ion spectrum of P 277 with the top spectrum using a 1 min acquisition and the others using 20 min

measurements on three regions of the paper:

- The region swept by acetone below the solvent front
- At the solvent front
- The region not exposed to acetone above the solvent front.

We did this by a standard penetration method using green-dyed water buffered to pH 7.0 (80% reflectance).

Sizing in the unexposed area remained unchanged (277 s). The region swept by acetone had considerably improved sizing (405 s). In the solvent front region, the sizing was effectively destroyed (11 s). This paper clearly contained acetone soluble desizing materials.

The three areas of the paper—designated by their sizing values of P 277, P 405, and P 11—underwent SIMS analysis. **Figure 4** shows the positive ion ToF SIMS spectrum of the untouched paper (P 277). The feature of interest is the presence of many high mass peaks that are absent in paper made in the laboratory with standard bleached kraft pulp. The most prominent of these peaks are at mass 326, 382, 410, 438, 466 (shown in the spectrum as 467 but with actual mass 466.5), and 494.

Figure 5 shows a comparison of the three regions in the high mass area of 300–550. The P 405 region is depleted in these peaks. The region with the worst sizing (P 11) is highly enriched in this material. A few peaks could be assigned formulas using the observed mass and calculated ion mass. The peaks at 397 and 339 have tentative identification as cerotic acid ($C_{26}H_{52}O_2$) and erucic acid ($C_{22}H_{42}O_2$), respectively.

Another way to display the SIMS data is a mass picture. **Figure 6** shows the total positive ion picture from the P 277 region. **Figure 7** shows the same field limited to ions of mass 370–500. The desizing material is distributed in patches on the surface of the paper.

We extracted the paper and the bleached sulfite pulp used to make it with room temperature acetone and obtained 0.14% and 0.23% extractables. The extracted materials had virtually identical Fourier transform infrared (FTIR) spectra. We applied the pitch from the pulp to the P 405 region from a dilute acetone solution. A sizing test showed that sizing was almost destroyed. Pitch from the pulp acting as a desizing agent was responsible for the sizing problem.

We ran a SIMS spectrum on both extracts. The paper extract had all the mass peaks present in the pulp and contained some additional peaks. Peaks at mass 466, 438, 410, 382, 354, and 326 appear related by deletion of C_2H_4 units from a parent molecule or could represent a homologous series of molecules. The molecular formula of the mass 466 ion fits $C_{31}H_{63}NO$ best, and the 326 ion fits $C_{21}H_{43}NO$ best. The origin of the M/Z 326 nitrogen containing molecule is unknown, but it is present in the sulfite pulp. (The others do not occur in the pulp). Another publication provides a more detailed description of the SIMS and other work on this paper *(9)*.

Besides the paper studied here, many other paper samples have undergone testing by the acetone chromatography technique. Hard to size papers made with mechanical pulp, bleached aspen sulfite pulp, TCF kraft

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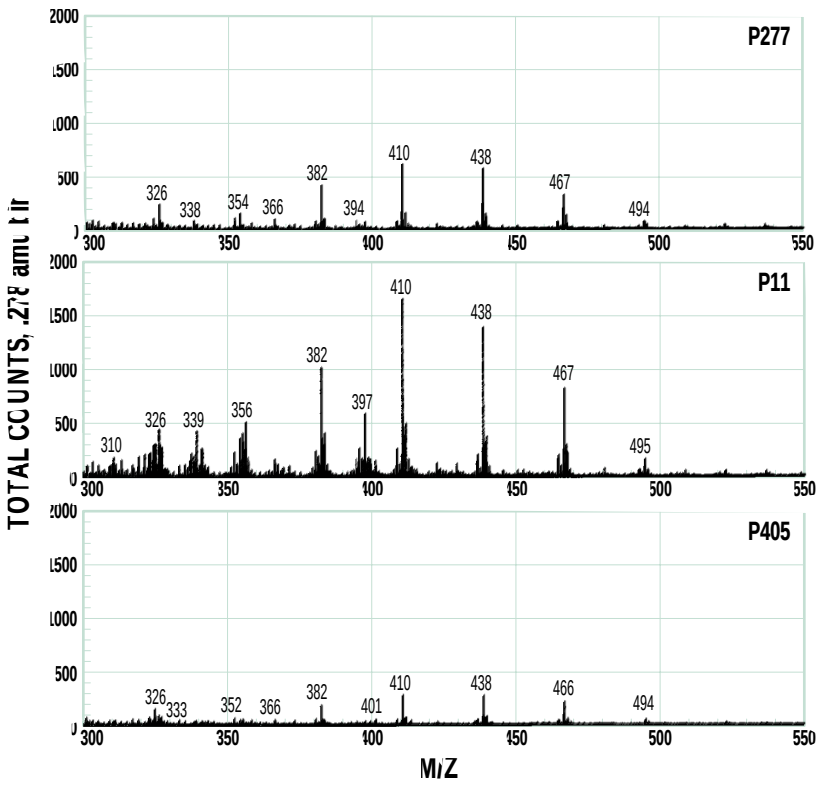
Chemistry, defects, mass, spectroscopy, pitch, problem solving, properties, runnability, science, sizing, surface properties

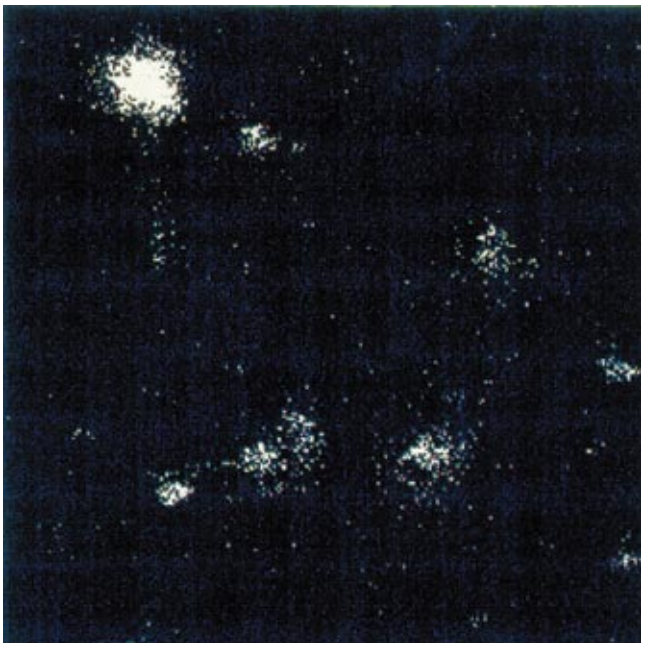
pulp, and recycled pulp with a high proportion of mechanical fiber contained high levels of desizing pitch. The nature of the sizing agent—ASA or alkyl ketene dimer (AKD)—made no difference. If desizing pitch was high, both sizing agents produced poor sizing. The worst situation yet encountered was a sheet that had 631 s of sizing in the acetone-washed region vs. only 14 s in the unexposed region.

To clarify which components in pitch are damaging to sizing, we obtained some pure lipids—monsteroyl-rac-glycerol, 1,3 dierucin, linoleic acid, stearyl alcohol, tri linolein, cholesteryl linoleate, and stearic acid oleyl ester. We prepared a dilute solution of each compound in acetone and applied them to an acetone cleaned paper. Sizing tests on the contaminated areas showed that all the compounds had a negative impact on sizing. The biggest impact appeared to come from linoleic acid and tri linolein. These compounds reduced sizing to zero while the others left from 2–24 s of sizing in paper that began with 47 s.



5. Comparison of the high mass positive ion spectrums of P 277, P 11, and P 405 showing intensity difference with all spectra using the same conditions with identical acquisition times

6. Total positive ion SIMS mass picture of the P 277 region



7. The same field as Fig. 6 but limited to positive ions of mass 370–500

Ordinary corn oil contains more than 50% tri linolein. When tested as above, it was also highly destructive of sizing. Corn oil is an easily obtained model compound for future studies.

The sizing interference displayed by all the lipid model compounds suggests that desizing is a general phenomenon. When unoriented hydrocarbons bearing polar groups interact with oriented hydrophobic sized surfaces, it is reasonable to expect that the resultant surface will be less hydrophobic, have a lower contact angle, and be more easily disrupted by aqueous penetrants.

CONCLUSION

SIMS is a valuable new tool for paper analysis. Sample analysis requires little or no time-consuming preparation. SIMS analysis often provided excellent diagnostic results—some reported here.

The analysis of the sizing problem is particularly important. Sizing difficulties with certain pulps is common knowledge but rarely explained. The presence of desizing pitch in the pulp represents a new insight. Acetone chromatography is a simple and quick method of screening for the presence of desizing agents. TJ

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