

Microscopy of ink particles after repulping of electrostatic and mixed office post-consumer paper furnishes

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ABSTRACT: *An environmental scanning electron microscope (ESEM) permits the effect of the deinking process variables on ink particle size and geometry to be determined qualitatively. Larger, more three-dimensional ink particles are more easily removed in fine screens and forward cleaners than smaller and flatter ink particles. Certain deinking chemicals promote formation of relatively large three-dimensional ink particles during repulping of post-consumer office paper. ESEM analysis of residual ink particle morphology also can help elucidate the physical and chemical processes occurring in deinking laser-printed and photocopy paper. ESEM studies of different ink types show that iron-containing electrostatic inks can be differentiated from other (iron-free) inks remaining in deinked fibers. The study reveals that many of the residual ink particles left after pilot mill deinking of one grade of office post-consumer paper are actually the result of fusion of different ink particles. Energy dispersive X-ray spectroscopy analysis can also identify paper fillers remaining after flotation deinking.*

KEYWORDS: *Deinking, electrostatic copying, fillers, impurities, ink, lasers, mixed waste papers, particle size, printers, scanning electron microscopy, toners.*

The widespread use of photocopiers and laser printers has resulted in recovered office paper con-

taining increasing levels of difficult-to-remove electrostatic inks. These furnishes include mixed office post-

consumer paper (MOP), various ledger grades, computer printout (CPO), and mixed post-consumer paper. Removing the photocopier- and laser-printed paper from these furnishes is expensive. Also, it leaves a large supply of photocopier- and laser-printed paper for landfill disposal or recycling. The alternative to sorting is to develop chemicals and process equipment effective in removing electrostatic inks from repulped paper.

Electrostatic printing processes and the composition of toner inks is described in references (1-3) and in references cited therein. Deinking of laser-printer, photocopier, and MOP furnishes is being studied extensively in our laboratories. A better understanding of processes occurring in the deinking of laser-printed and photocopier-printed paper will aid in designing improved deinking agents. Therefore, our studies also include research into how electrostatic inks are detached from the fiber and separated from the pulp slurry. The nature and role of surfactant-ink interactions is also being studied. Of particular interest is whether electrostatic ink particles interact with other ink particles and what effect these interactions have on the deinking process.

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ESEM basics

In studying ink particles, the greater depth of field the scanning electron microscopy provides compared to conventional optical microscopy is an advantage. In conventional scanning electron microscopy, insulating samples such as cellulose require a conductive coating to prevent surface charging. This is not necessary when using the environmental scanning electron microscopy (ESEM). Thus the natural surface properties of samples can be studied using the ESEM technique (4, 5). Fine detail often obscured by coating materials is visible using the ESEM technique.

References (6) and (7) describe the principles of the ESEM in detail. Key differences between environmental scanning electron microscopy and conventional scanning electron microscopy are detailed in reference (4).

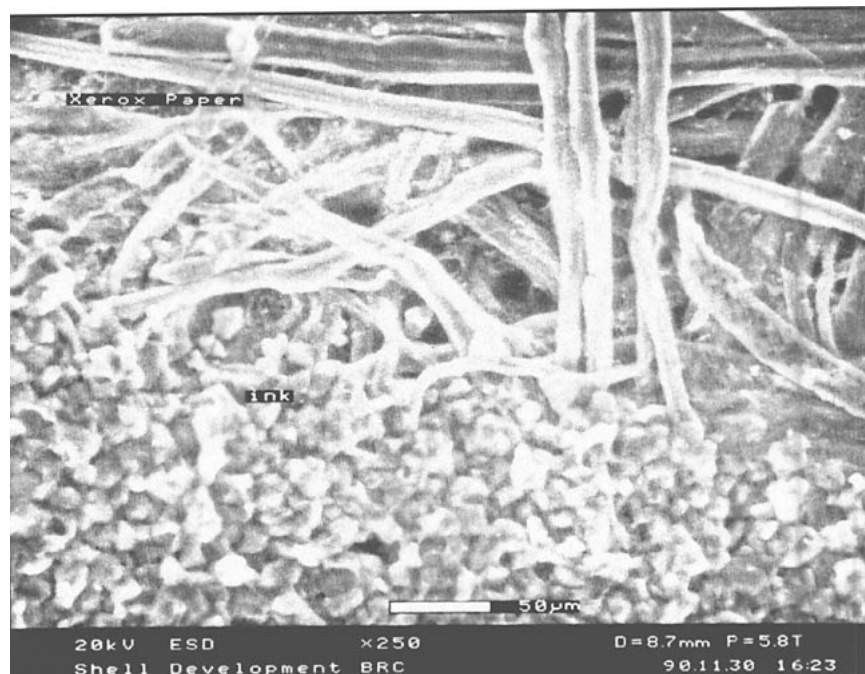
Unlike conventional scanning electron microscopes, the ESEM instrument does not require test samples to be under high vacuum. A typical vacuum in a scanning electron microscope is *ca.* 1.0×10^{-5} torr (mm Hg). The pressure in the ESEM sample chamber is typically 2–20 torr. This higher pressure can be tolerated because pressure limiting apertures separate the sample chamber from the upper column of the instrument (6, 7). The upper column is maintained at high vacuum by a separate pumping system.

As a result of the higher operating pressures, volatile materials such as liquid water are often amenable to ESEM study. The ESEM is capable of imaging while the sample chamber is saturated with water vapor. Near the saturation point, water condensation onto fiber samples can be induced by cooling the sample or increasing the water vapor pressure.

1. ESEM image of flexographic printing on newsprint



2. ESEM image of photocopier printing. The toner was a styrene-acrylate copolymer.



Pulp and paper applications of the ESEM

The ESEM has proven very useful in studying pulp and paper samples (4). Water present in a sample need

not evaporate. Water can also condense onto cellulose from the chamber atmosphere and be adsorbed. (This adsorption and absorption can cause cellulose fiber swelling.) The degree of fiber swelling can be quan-

3. Enlargement of Fig. 2. Note the partial fusion of toner particles and their attachment to fibers.



4. ESEM image of a residual photocopier styrene-acrylate toner ink particle after laboratory pulping and flotation at 110°F using SDA-30.



tified and related to fiber surface wettability and sizing agent requirements. This allows the study of the wettability and swelling of cellulose fibers. Fiber swelling upon absorption of water vapor can be directly

measured. The effect of adsorbed deinking surfactant, sizing agents, and other process chemicals on fiber wettability can be studied in a reproducible and quantitative way (4).

The ESEM technique has been used to study newspapers printed using letterpress, offset, and flexographic inks (3, 8). However, printed and unprinted areas of newspapers are not distinguishable under conventional ESEM operating conditions. As a result, special imaging procedures using low sample chamber pressures had to be developed (8). Laser-printed paper and photocopier printed paper have also been imaged using the ESEM (3). The ESEM technique has also been applied to detergency studies (9).

Results

Imaging electrostatic inks

Unlike newsprint inks, special ESEM techniques are not required to image laser or photocopy inks. Electrostatic ink morphology is in sharp contrast to that of the newsprint inks. Newsprint inks appear to exist as a thin film on cellulose fibers (Fig. 1). Figures 2 and 3 represent an ESEM examination of a photocopier printed page. The appearance of laser-printed sheets is similar. These inks exist as a thick layer of partially fused beads. This morphology makes it easy to identify electrostatic ink in ESEM images.

Residual electrostatic ink particles remaining after flotation are much easier to image and identify than newsprint ink. The three-dimensional character of residual photocopier ink and laser printer ink is clearly evident in Figs. 4 and 5, respectively. Using carefully designed deinking agents, electrostatic ink particles in repulped paper can be fairly large, 100 μ or more on their long axis. The impressions of cellulose fibers on many residual styrene-acrylate toner ink particle surfaces are clearly evident (Fig. 4). The upper arrow of Fig. 4 indicates an impression in the ink particle apparently left by the partially detached fiber in the lower right of the micrograph. The lower arrow indicates an impression in the ink par-

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ticle still occupied by a cellulose fiber. An impression from which the cellulose fiber has been completely removed may be seen in the upper right of Fig. 4.

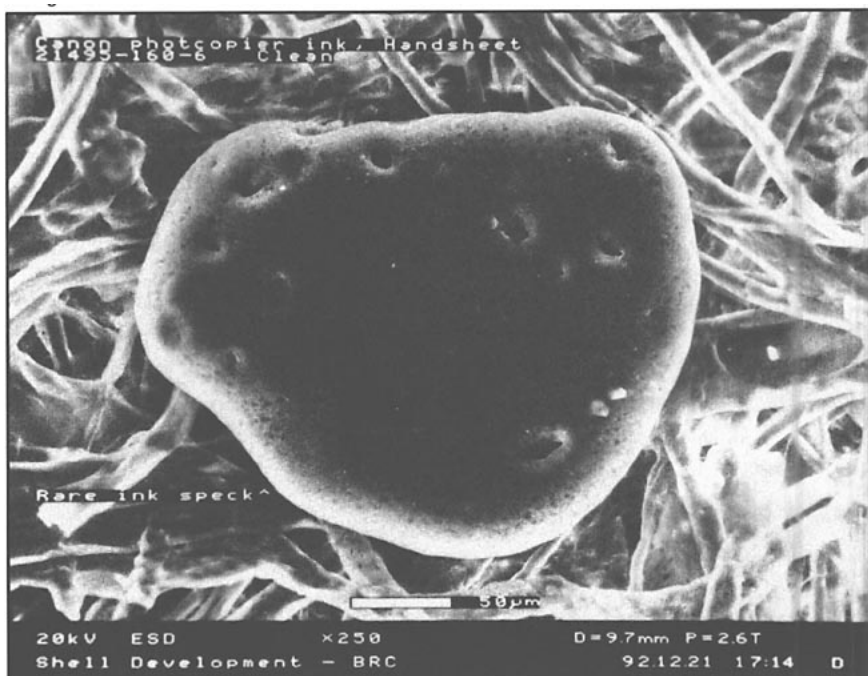
These fiber impressions were not observed when deinking paper printed using a polyester toner ink (Fig. 5). The arrow in Fig. 6 indicates a clean fracture in the lower left of a toner ink particle. This fracture suggests that toner ink particles are hard and perhaps brittle after repulping. Without a deinking agent, styrene-acrylate toner ink particles after repulping are smaller and appear more two-dimensional, i.e., more like flakes and less like spheres (Fig. 7). Similar results were observed for a polyester toner ink.

Deinking of a PS-40¹ grade furnish was studied in a pilot mill. (Results of this study will be reported separately.) This furnish was estimated to contain about 80% photocopy- and laser-printed papers. Figure 8 is a typical image of an ink particle remaining after flotation. Figure 8 suggests that ink particles remaining after flotation were softened (in the pulper) and then hardened. Neither the styrene-acrylate copolymer-based toner inks or the polyester-based toner inks alone ever presented this appearance after laboratory repulping.

Figure 9 is the ESEM image of one of the few ink particles remaining in the forward cleaner accepts after pilot mill deinking. This ink particle also has the appearance of a melted and rehardened plastic. In addition, it appears very elongated compared to typical ink particles remaining after flotation. Most, but not all, of the few ink particles in the cleaner accepts presented this elongated appearance. ESEM images of smaller particles usually appeared more spherical.

¹PSD-40 is a term for a grade of post consumer paper. It is a designation used by mills and paper brokers. The term PS-40 is defined in the post consumer grades listed in the PIMA catalog.

5. Residual polyester resin toner ink particle after laboratory repulping at 160°F and flotation using SDA-24.



6. ESE micrograph of a residual polyester resin laser ink particle after laboratory repulping and flotation at 200°F using SDA-30.

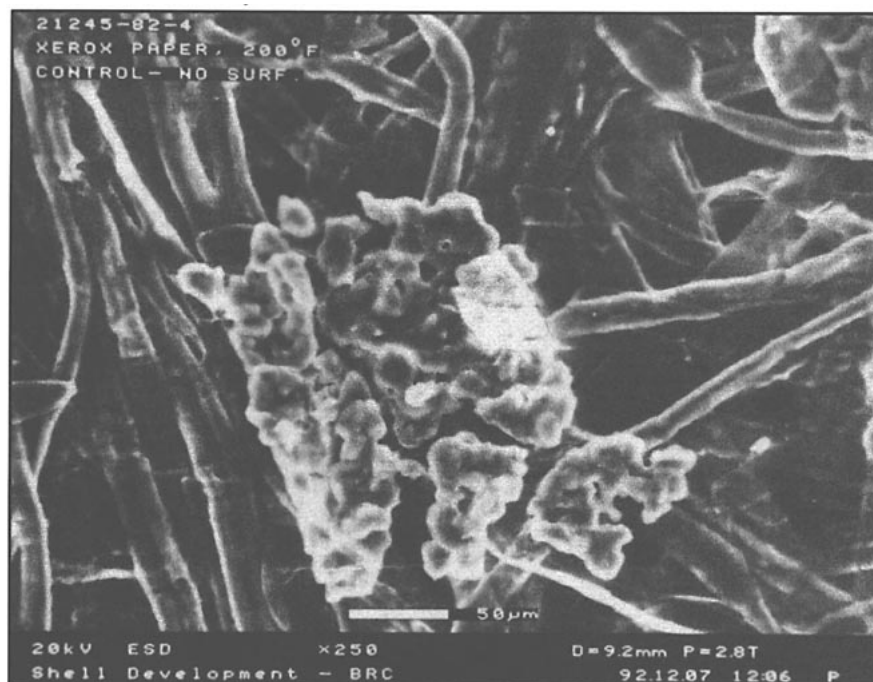


EDS analyses

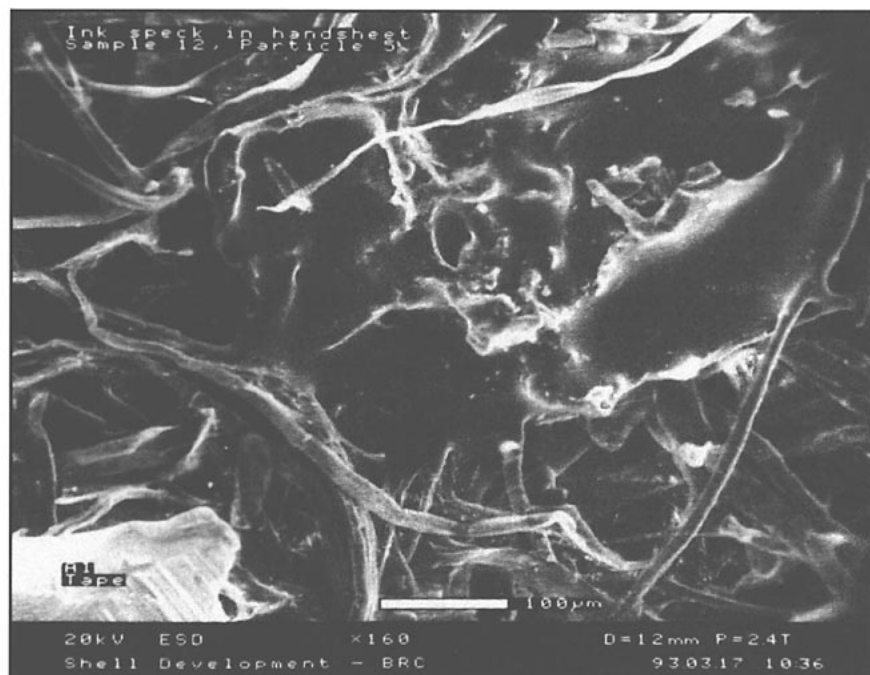
Energy dispersive X-ray spectroscopy (EDS) analyses of residual inks can be useful because many electrostatic inks contain iron. The EDS

spectra make these inks readily identifiable. Figure 10 indicates the residual office paper ink on the left-hand side of Fig. 11 contains iron compounds. These submicron iron particles are visible as very bright

7. ESEM image of a residual styrene-acrylate toner ink particle after laboratory pulping at 200°F and flotation using no surfactant.



8. ESEM image of a MOP ink particle after pilot mill pulping at 160°F and flotation using SDA-31.



spots on the ESEM image (Fig. 11). However, iron absorption peaks are not present in the EDS spectrum of the right-hand side of the ink particle. This part of the ESEM image is nearly devoid of bright spots.

Occasionally, PS-40 grade office paper residual ink particles such as that in Fig. 12 were found containing other metals. EDS analysis indicates that most of the bright spots in

this ESEM ink particle image are copper minerals. Some calcium, perhaps from a small filler particle, is also apparent in the EDS spectrum.

Imaging residual filler particles in deinked paper

Many filler and coating particles are removed in deinking. However, the retention of some fillers in flotation deinking of newsprint/magazine furnishes can improve deinked sheet opacity and brightness. Filler retention can also be an issue in deinking office post-consumer paper. Fillers can be imaged using the ESEM technique. The bright spot in the center of the fiber imaged in Fig. 13 appears to be a filler particle. In Fig. 14, the ratio of the aluminum (Al) and silicon (Si) peaks in the EDS spectrum indicates that this residual filler particle is kaolinite. The aluminum and silicon EDS peaks were not present when other parts of this image were subjected to EDS analysis. The furnish was photocopier paper which was subjected to flotation deinking. Thus, EDS analysis can determine the elements present in residual filler particles and aid in identifying retained fillers.

Discussion

Impressions of cellulose fibers are clearly engraved in the surface of the photocopy ink particle imaged in Fig. 4. These indentations have been seen in many experiments on both residual photocopy and laser printer inks. These impressions are particularly noticeable when the electrostatic inks are based on styrene-acrylate copolymers. Fiber impressions were observed at pulping temperatures as low as 100°F. This is significantly below the accepted glass transition temperature, T_g , or softening point of electrostatic inks (150–160°F). However, T_g of styrene-acrylate copolymer toner ink separated from flotation cell rejects was about 104°F.

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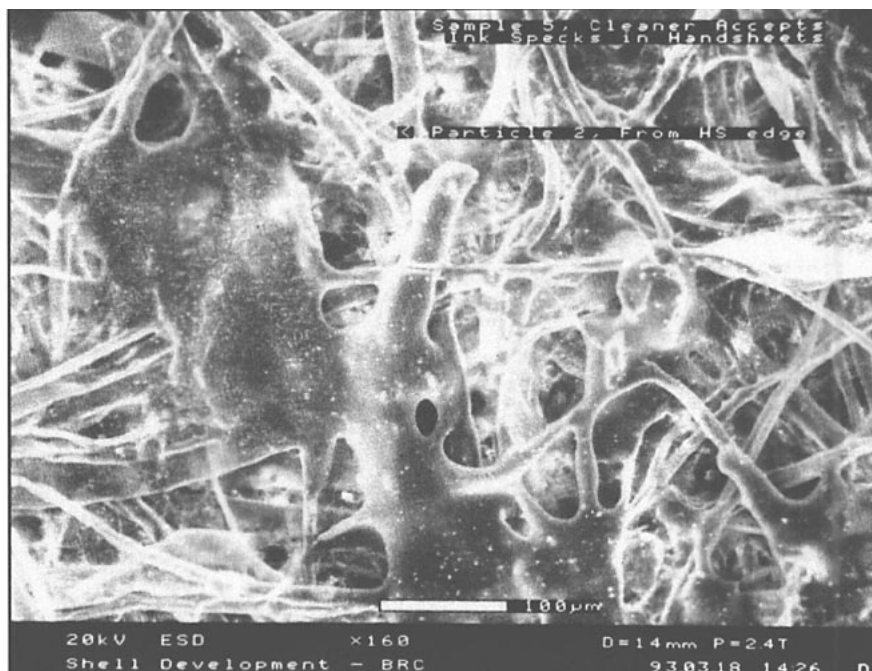
These impressions are probably where the ink was originally attached to the paper. In the ESEM image of Fig. 4, a fiber is still embedded in the ink particle. Detachment of these fibers would leave impressions similar to the other impressions observable in Fig. 4. A cellulose fiber partially detached from a photocopier ink particle is apparent in Fig. 4. What appears to be a fiber impression extends from the point of fiber attachment along the surface of the ink particle. (An alternative explanation is that these impressions are left by cellulose fibers which collided with softened electrostatic ink particles. However, Fig. 4 would seem to render this hypothesis less likely unless collision forces are strong enough to re-attach the fiber to the ink particle.)

These impressions imply a deinking mechanism in which a large, somewhat softened ink particle is detached from the cellulose surface. Softening is sufficient to assist ink particle detachment but not sufficient to erase the indentations left by cellulose fibers once in contact with the ink. The detached ink particles could be in the form of fairly large flakes. In the absence of a deinking agent (Fig. 7), mechanical action alone did not promote conversion of two-dimensional ink flakes into more three-dimensional objects. This was true even when the pulping temperature (200°F for Fig. 7) was well above the toner T_g .

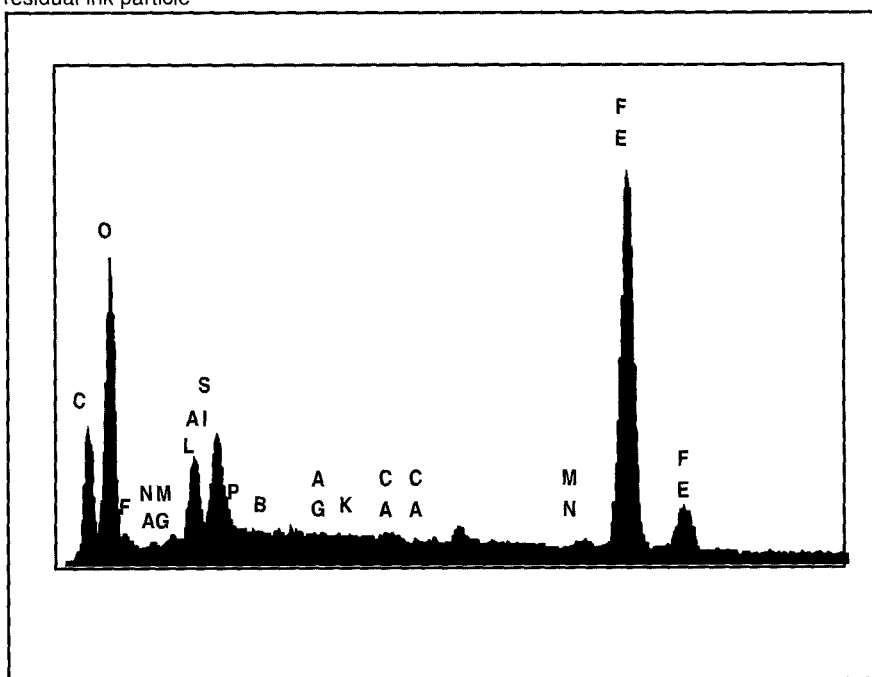
Effects of forward cleaners

The temperature of the PS-40 pulp slurry passing through the pilot mill forward cleaners was approximately 70°F. This is well below the T_g of both the toners (150–160°F) and photocopy ink rejects from a laboratory deinking test (ca. 104°F). However, mixing an electrostatic ink with a conventional ink vehicle might reduce the ink T_g further. A considerable percentage of the few ink particles remaining in the cleaner accepts presented an elongated ap-

9. ESEM image of a residual MOP ink particle after pilot mill pulping at 160°F and forward cleaning using SDA-24.



10. Energy dispersive X-ray spectroscopy analysis of the right-hand portion of the Fig. 11 residual ink particle



pearance. Could mixing of electrostatic inks and conventional inks reduce the ink T_g enough so shear forces in the forward cleaners elongate ink particles? This would explain the appearance of the ink particle in Fig. 8.

However, the ink particles in the flotation froth immediately after removal from the flotation cell were quite hard. This suggests that the ink particles were below their T_g both during flotation and forward clean-

11. ESEM image of a residual MOP ink particle after pilot mill pulping at 160°F



12. ESEM image of a residual MOP ink particle after pilot mill pulping at 160°F



ing. So it is unlikely that shear forces in forward cleaners caused elongation of softened ink particles. A more probable explanation is that a few almost two-dimensional elongated ink particles were present after

repulping. As the more three-dimensional particles were removed by flotation and forward cleaning, these elongated particles became more apparent.

Shear forces probably played a role in determining ink particle size and geometry. However, this role was most likely greatest in the pulper. There the shear forces were high and the pulping temperature (160°F) was at or above the toner T_g . The fracture observed in a laser ink particle after pulping (Fig. 6) could have been induced by shear forces. Had shearing continued, this particle could have been broken up into smaller ones. The distorted shape of the ink particles depicted in Figs. 8 and 9 suggests that shear forces during pulping were breaking these particles apart. These particles are representative of many of the particles observed after pilot scale repulping of PS-40 furnish in the presence of several different proprietary deinking agents. When using carefully designed deinking surfactants, the combination of chemical and mechanical action promoted conversion of electrostatic ink flakes to more three-dimensional objects during pulping.

The hydrophobic nature of ink surfaces can be a driving force to minimize ink surface area and assist the conversion of flat ink particles into more three-dimensional objects. Some deinking agents can reduce the electrostatic ink T_g . The measured T_g value for a styrene-acrylate copolymer toner ink collected from flotation deinking rejects was about 104°F using SDA-24². Ink softening would promote conversion of ink flakes into more three dimensional objects. However, the essentially two-dimensional ink particles observed at 200°F (well above the toner T_g) in the absence of surfactant, Fig. 7, suggests that ink softening is insufficient to convert detached ink into three-dimensional particles. Some specific chemical interactions with the electrostatic inks are required.

²The Shell deinking surfactants used are synthesized from petroleum feedstocks and are designated SDA, Synthetic Deinking Agent, followed by an identification number.

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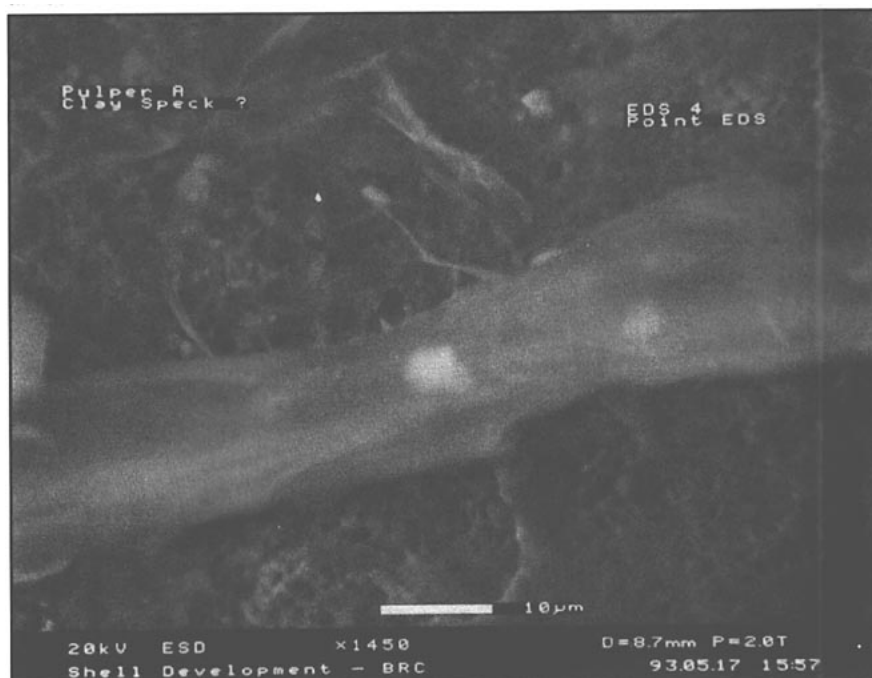
The localized iron mineral content of the Fig. 11 ink particle is high on the left-hand side and low on the right-hand side. This combined with an apparent ridge dividing the iron-mineral rich and poor areas, suggests that two softened ink particles have collided and fused. It is difficult to imagine this fusion occurring unless at least one of the ink particles were softened.

This interpretation is consistent with the deinking mechanism presented above. Residual ink in the PS-40 grade furnish pilot mill study presented a more plastic appearance than 100% electrostatic furnishes deinked in the laboratory. (The same deinking agents, process temperatures, and pH were used in the laboratory and pilot mill tests.) Could the ink vehicles of the conventional inks present in the furnish have promoted ink softening? This possibility will be examined in a future report.

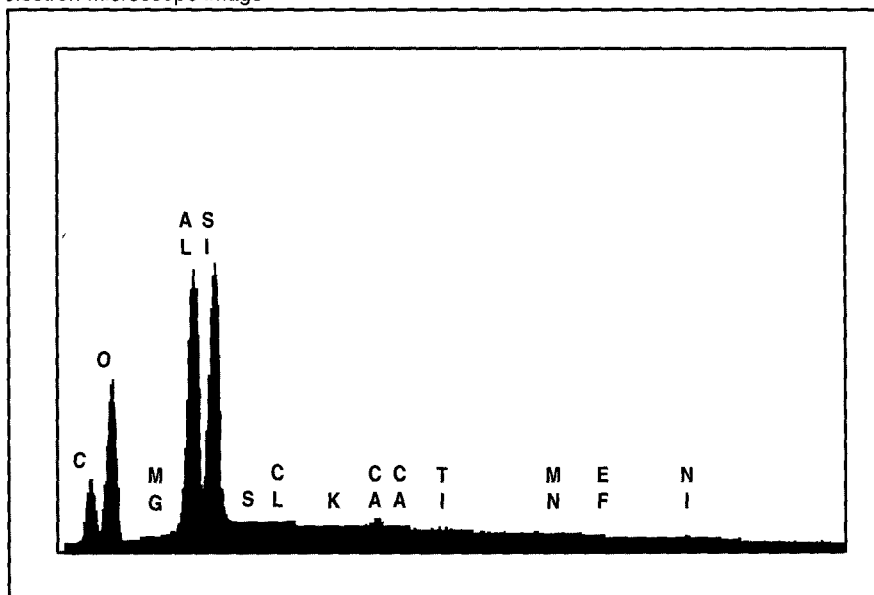
Conclusions

ESEM analysis permits effects of deinking process chemicals, process design, and process conditions on ink particle size and geometry to be qualitatively determined. These analyses suggest that electrostatic ink particles are softened during pulping of 100% electrostatic ink furnishes and MOP furnishes containing high levels of photocopier- and laser-printed paper. The EDS capabilities of ESEM can be used to identify iron-containing electrostatic inks and differentiate them from other (iron-free) inks remaining in deinked fibers. ESEM images and EDS analysis suggest that many of the residual ink particles left after deinking PS-40 grade office post-consumer paper are actually the result of fusion of different ink particles. Prior to fusion, some of these ink particles contain iron while some do not. EDS can also be used to identify paper fillers remaining after deinking. ■

13. ESEM image of a clay particle attached to a fiber after pilot mill pulping of a MOP furnish at 160°F



14. Energy dispersive X-ray spectroscopy analysis of the light spot in the Fig. 13 scanning electron microscope image



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