

# SIMS Studies of Ink Jet Media

*Jerry Pinto*

*International Specialty Products*

*1361 Alps Road, Wayne, New Jersey 07470*

*Mark Nicholas*

*Evans East*

*666 Plainsboro Road, Plainsboro, New Jersey 08536*

## Abstract

In this paper, we refine the present understanding of ink jet media and the performance advantages that certain polymers confer upon a variety of products, ranging from film transparencies to digital photographic paper. On the basis of time-of-flight secondary ion mass spectrometry (TOF-SIMS), we determine the extent of ink penetration in model coatings as well as in representative commercial media in an effort to correlate the effect of **PVP**, **PVP** blends, and **PVP** copolymers on dye binding. The exceptional performance attributes associated with **PVP** derive from the unique combination of hydrophilicity, polarity, and hydrophobicity contributed by the lactam ring, thereby enabling the complexation of polarizable, anionic organic dyes. **PVP** is utilized in both narrow and wide format coatings in order to inhibit dye diffusion, thus providing a critical mechanism for the control of dot gain, ink spreading, and inter-color bleed. This capacity to bind ink jet dyes is manifested by TOF-SIMS cross-sectional images of variously printed samples which show that the presence of **PVP** in the coating effectively restricts the ink to the media surface.

## Ink Jet Media

Inkjet media is constructed by coating an ink receiving layer onto a substrate, typically paper, film, or resin-coated paper. Additionally, backside coatings are also usually present, in order to provide static, curl, and friction control properties. Important substrate parameters include gloss/haze, opacity/clarity, stiffness, caliper, and color. Gloss control is ordinarily obtained by resin-coating the substrate which further impacts other properties, such as color, opacity, and stiffness. The ink receiving layer may be a simple *hydrophilic matrix* or a more complex *microporous network*. Examples

of microporous networks include paper, as well as paper and film coatings consisting of particulate fillers, such as silica gel or colloidal silica. Regardless of the particular construction, any porous medium is governed by *capillary phenomena* which induces ink penetration, allowing for rapid drying. Alternatively, aqueous liquid flow into a hydrophilic matrix proceeds by the slower process of molecular *diffusion*. Furthermore, the coating is ordinarily more sensitive to humidity and there may be greater ink dependency, in addition to the longer drying time.

## Polyvinylpyrrolidone & Dye Binding

Media formulators have successfully developed products which reconcile the conflicting requirements of rapid ink absorption and high optical density, often through the adoption of coating compositions that rely on the extraordinarily diverse properties of **polyvinylpyrrolidone (PVP)** and **PVP** copolymers. While the ability to imbibe excessive quantities of water is a natural consequence of the intrinsic hydrophilicity of the polymer chain, the truly spectacular performance reserved to **PVP** derives from the unique combination of hydrophilicity, polarity, and hydrophobicity contributed by the lactam ring, thereby enabling the complexation of polarizable, anionic organic dyes.<sup>1</sup> Indeed, **PVP** is utilized in both narrow and wide format coatings in order to inhibit dye diffusion, thus providing a critical mechanism for the control of dot gain, ink spreading, and inter-color bleed. This capacity to bind ink jet dyes results in highly resolved, circular dots. Furthermore, because the dye molecules are *preferentially* retained at the media *surface*, high optical densities are easily obtained. Moreover, **PVP** is a *unique* polymer in terms of its ability to accommodate *both water and solvent* in an ink jet film. This is nontrivial given the fact that thermal inks may contain between 10-30% solvent.

Understanding the role of water (and organic solvents) in the dye binding process is perhaps the central issue governing the performance of **PVP** in an ink jet coating. The critical feature embodied by the pyrrolidone ring is the (effective) *negative* charge at the oxygen atom. We believe that acidic protons from tightly bound water molecules promote dye binding at this *particular* site. Water is absorbed by hydrogen bonding to the basic carbonyl sites along the **PVP** chain. These hydrogen-bonded water molecules then become *acidic* sites, promoting additional hydrogen-bonding to the *negative* charge sites of *anionic* azo dyes. When the water content of the film reaches ~15 wt. %, the carbonyl sites are apparently fully saturated with *hydrogen-bonded* water molecules; nevertheless, the absorption capacity of **PVP film** is ~60 wt. %, based upon water vapor sorption measurements at 100% relative humidity. More-over, the adsorption isotherm displays a sharp inflection at ~15% water content, clearly suggesting a change in the adsorbed (adsorbed) *state* of water.<sup>2,3</sup>

Hence, while the initial binding mechanism is apparently determined by acidic hydrogen-bonded (non-freezing) water at the lactam carbonyl, the incorporation of *additional* dye molecules must depend somehow on *hydrophobic* interactions, mediated perhaps, by the excess (free) water that is absorbed by the film. It seems reasonable to assume that dye aggregation occurs along the polymer chain locus of previously bound dye molecules.<sup>4</sup> Based upon this premise, the promotion of hydrophobic interactions should necessarily enhance dye binding, otherwise dimer formation may actually occur within the mobile free water phase. The fact that cationic dyes and surfactants display negligible binding affinity to **PVP** indicates that solvent participation is a critical aspect mediating the association of dyes, which can be attributed to the *polar* character of *structured water* molecules at the carbonyl moiety. In fact, recent thermodynamic data has shown that the entropy of binding between **PVP** and **Direct Red 80** is *positive*, indicative of the role that water structure plays in dye binding.<sup>1</sup>

## TOF-SIMS

In this paper, we refine the present understanding of ink jet media and the performance advantages that certain polymers confer upon a variety of products, ranging from film transparencies to digital photographic paper. On the basis of time-of-flight secondary ion mass spectrometry (TOF-SIMS), we examine both model **ISP** coatings as well as representative commercial media in an effort to correlate the effect of **PVP**, **PVP** blends, and **PVP** copolymers on dye binding. **PVP**, as well as **PVOH**, appears to be implicated in a number of products. While wide format films seem to be

simple blends of water-soluble polymers, narrow format media is considerably more complex, consisting of *multiple* layers and often incorporating *diverse* materials, such as *silica gel* or *alumina gel*. Our endeavors are directed towards the establishment of physical models of ink jet media enabling the design of appropriate polymers *specifically* for ink jet applications.

## Experimental

All experiments were performed with a Physical Electronics PHI-Evans TFS-2000 instrument, in which the primary ion beam was generated with a 15kV <sup>69</sup>Ga<sup>+</sup> liquid metal ion gun. Charge neutralization was used in all cases. Typical primary ion doses during both positive and negative modes of the TOF-SIMS analyses were on the order of 10<sup>12</sup> ions/cm<sup>2</sup>. This assures that the data was collected within the static limit, i.e., less than 1% of a monolayer was sputtered. Thus, all molecular fragments are indicative of species existing on the surface prior to analysis. Under these conditions, the sampling depth of TOF-SIMS is 1 monolayer for molecular fragment ions and 1-3 monolayers for atomic species. Ion images present integral ion intensities as a function of X,Y location on the surface.

Laboratory films were coated out of water or isopropyl alcohol onto **ICI** white opaque polyester. These films were printed on an **HP 850C**, using a standard imaging test pattern which allowed each color to be separately analyzed. Cross-sections of ink jet prints were made by clamping each film in a vise-like sample holder and cutting the film flush with the holder surface using a razor blade cleaned with methanol and Kim-Wipes. The cut was made by moving the blade parallel to the surface as viewed in cross-section, thus assuring that the printed surface is prevented from curling back on the cross-section. The samples were examined by TOF-SIMS in which we used an energetic Ga<sup>+</sup> primary ion beam to bombard the surface *of* the film *cross-section*, thereby generating *secondary* positive *and* negative cluster ions related to chemical species on the (exposed) surface of the *cut film cross-section*.

## PVP Standards

**PVP K-90** powder from **ISP** was dissolved in methanol and the solution cast onto a clean silicon wafer. This produced a very thin, flat, transparent **PVP** film. Positive TOF-SIMS analysis indicates that peaks at **56** - C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, **86** - C<sub>4</sub>H<sub>8</sub>NO<sup>+</sup>, **112** - C<sub>6</sub>H<sub>10</sub>NO<sup>+</sup>, **124** - C<sub>7</sub>H<sub>10</sub>NO<sup>+</sup>, and **138** - C<sub>8</sub>H<sub>12</sub>NO<sup>+</sup> may be used to identify **PVP**. Alternatively, the three ions at **26** - CN<sup>-</sup>, **42** - CNO<sup>-</sup>, and **84** - C<sub>4</sub>H<sub>6</sub>NO<sup>-</sup> in the negative

mode are equally characteristic of **PVP**. Although laboratory films coated onto the **PET** substrate appear to contain some organic contamination, nevertheless, the **PVP-silicon** and **PVP-PET** spectra in both modes were quite similar, validating the use of the **PVP-characteristic** peaks in all subsequent analyses, including commercially printed product samples.

### PVOH vs. PVP

Despite the prevalence of **PVOH** in a diverse array of commercial ink jet media, this polymer lacks any noticeable affinity for dyes, as shown by the positive ion TOF-SIMS cross-section of the inked image in Figure 1. The integrated intensity of the **ink-characteristic** high mass peaks ( $480^+$ - $550^+$ ), arising from the **HP 850C magenta** dyes, is essentially *uniform* through the depth of the coating, right up to the **PVOH/PET** film substrate interface.<sup>5</sup> Other ions, equally indicative of the ink, such as  $\text{Na}^+$ ,  $\text{Mg}^+$ ,  $\text{Li}^+$ , and  $\text{K}^+$ , also show the same pattern. Alternatively, the ink profile is equally revealed by the  $\text{SO}_3^-$  ion, which emanates entirely from the *sulfonate* groups of the diazo dyes. Consistent with the positive ion data, the  $80^-$  image (Figure 2) shows that ink diffusion is *unrestrained*, resulting in a *uniform* dye concentration profile all the way from the air/coating interface to the **PVOH/PET** film interface.

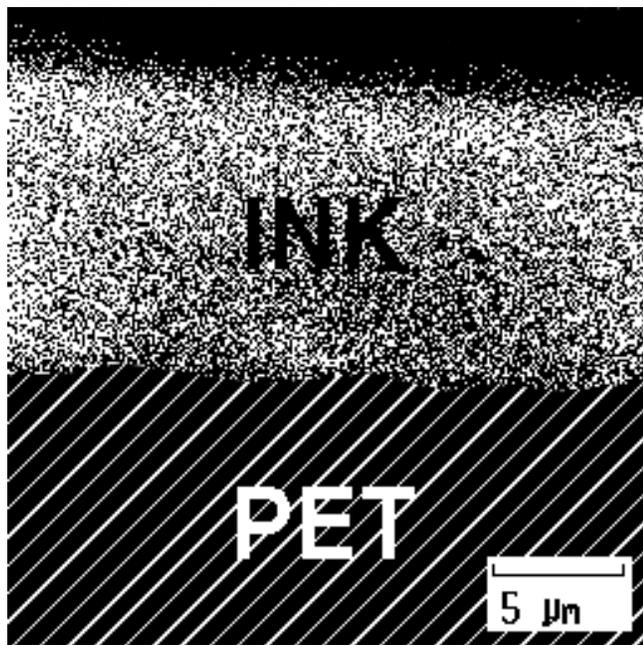


Figure 1. The positive ion mode cross-sectional image of the **ink-characteristic** ions ( $480^+$ - $550^+$ ) for the inked **PVOH** film.



Figure 2. The negative ion mode cross-sectional image of the magenta dye-characteristic  $\text{SO}_3^-$  ion at  $80^-$  for the inked **PVOH** film.

We obtain entirely different results with a pure **PVP**-coated film. In cross-section, the inked, **PVP** film exhibits the characteristic **PVP** ions at  $112^+$  and  $124^+$ , as shown in Figure 3, but essentially *no* signal from the **ink-characteristic** peaks at  $87^+$ ,  $89^+$ , and  $450^+$ - $555^+$  (not shown). The negative ion mode image in Figure 4 is consistent with the positive mode results. The **PVP-characteristic** ions at  $26^-$ ,  $42^-$ , and  $84^-$  are clearly visible, but there is almost *no* signal for the **ink-characteristic** sulfonate ion at  $80^-$  (not shown), notwithstanding the highly saturated portion of the magenta image that was used for the analysis.

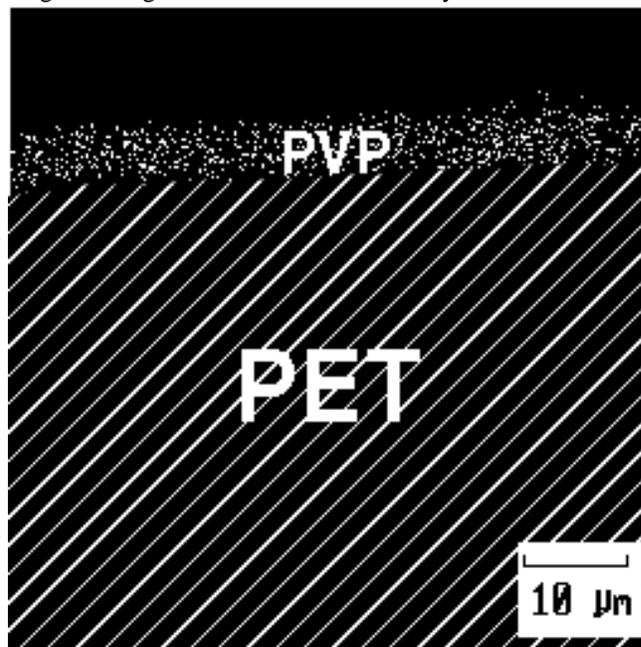


Figure 3. The positive ion mode cross-sectional image of the **PVP-characteristic** ions at  $112^+$  and  $124^+$  for the inked **PVP** film.

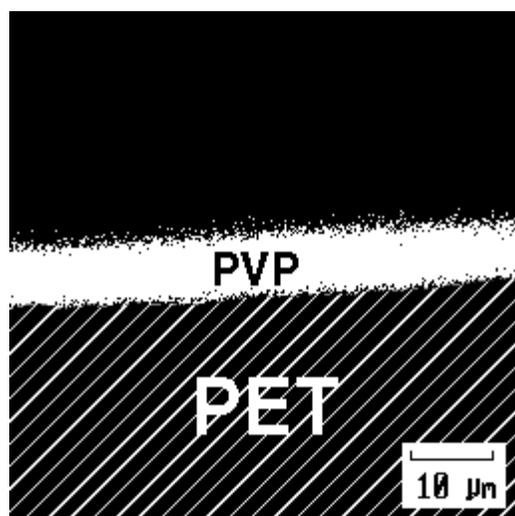


Figure 4. The negative ion mode cross-sectional image of the PVP-characteristic ions at 26, 42, & 84 for the inked PVP film.

Having already established our capability to identify and image the magenta dye from the HP 850C, we attribute the absence of a dye signal to the fact that PVP must immobilize the dye molecules in an extremely thin sub-micron region at the air/image interface. Indeed, visual images obtained by optical microscopy easily and directly confirm this interpretation. What's surprising, in the context of the extraordinary sensitivity of TOF-SIMS, is the inability to detect any dye signal within the bulk, even in the first few microns of the coating layer. Clearly, these results demonstrate the exceptional performance advantage that PVP confers to an ink jet coating in terms of its propensity to complex anionic dyes.

### HP Premium Glossy

In order to advance our understanding, we proceeded to analyze HP Premium Glossy film, which is known to contain PVP, as well as inorganic pigments, such as silica and alumina. The ~7 micron thick coating is manifested by an easily imaged, uniform PVP signal, as shown by the inked cross-sections in Figure 5. Interestingly, the relative ion intensities of the characteristic PVP signals at 112<sup>+</sup> and 124<sup>+</sup> are actually somewhat more intense compared to the pure PVP film, despite the fact that HP's product is a formulated composition which necessarily dilutes the PVP solid content. Because we were able to also detect Si<sup>+</sup> and Al<sup>+</sup> in the same coating band, we believe that the enhanced PVP signal may be a consequence of SIMS matrix effects, ultimately indicative of the fact that PVP is known to function as an extremely effective colloidal dispersant. Indeed, PVP provides an array of benefits in ink jet media.



Figure 5. PVP image at 112<sup>+</sup> + 124<sup>+</sup> for inked cross-sections of HP Premium Glossy film; ink signals at 87<sup>+</sup>, 89<sup>+</sup>, and 480<sup>+</sup>-552<sup>+</sup>.

The primary benefit, and the theme of this paper, is illustrated by the  $\Sigma$ ink signals at 87<sup>+</sup>, 89<sup>+</sup>, and 480<sup>+</sup>-552<sup>+</sup> (Figure 5). One can immediately appreciate how the ink is retained in a 2 micron thin region at the surface, a dramatic illustration of the affinity of ink jet dyes for PVP. Within this uppermost 2 micron ink region, the distribution of the dye appears to be rather uniform although a concentration profile may, in fact, exist but the sensitivity of our analysis precludes this degree of spatial resolution. (The background signal below the 2 $\mu$  band is artificially enhanced due to the transformation of the gray-scale image to B&W.)<sup>6</sup> The negative ion mode images, illustrated in Figure 6, are consistent with the positive mode results. The PVP-characteristic ions at 26, 42, and 84 are easily detected in the entire coating while the sulfonate ion intensity at 80<sup>-</sup> is actually more intense at the surface.

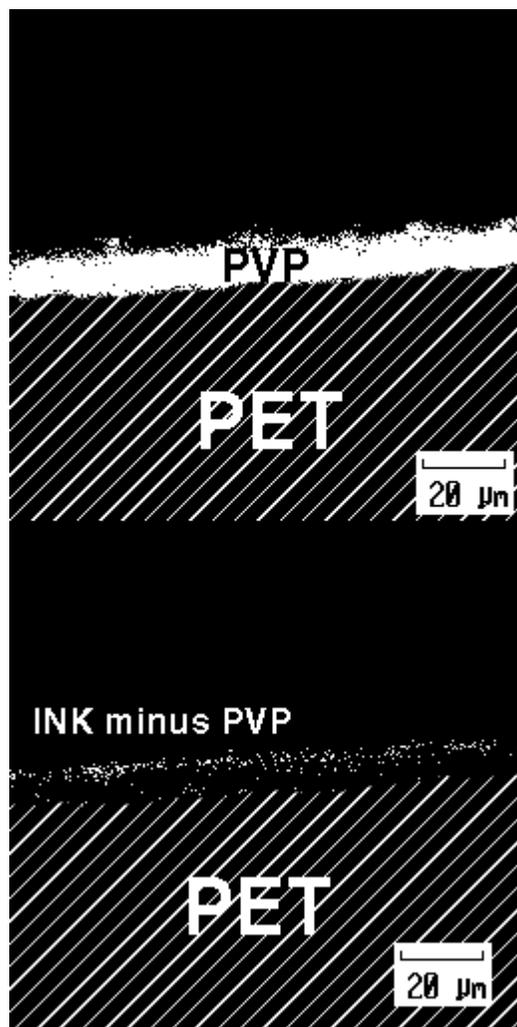


Figure 6. The negative ion mode image of the PVP-characteristic ions at 26, 42, and 84 in a cross-section of HP Premium Glossy film and [SO<sub>3</sub><sup>-</sup> ion image at 80] minus [CNO<sup>-</sup> ion image at 42].

### POLECTRON PS/PVP Latex

Although PVP intrinsically enables the retention of ink in the vicinity of the printed surface, this dye binding property may also be affected by the physical structure of the coating layer. As part of our attempt to examine issues related to morphology, we analyzed a polystyrene latex in which the 0.5 micron particles are stabilized by grafted chains of PVP, in addition to a physically adsorbed anionic surfactant. The emulsion, commercially known as **Polectron**, is produced with a 70/30 styrene/VP monomer ratio. We chose this rather unusual system, in part because the actual latex particles should be quite receptive to dyes, thus providing another ink immobilization mechanism. In this context, we analyzed cross-sections of films generated on the HP 850C. As we have shown, the magenta dyes associated with this particular printer are quite amenable to analysis by TOF-SIMS.

In cross-section, the image associated with the ink-characteristic peaks at 87<sup>+</sup>, 89<sup>+</sup>, and 480<sup>+</sup>-555<sup>+</sup> is essentially identical to the Polectron image generated from the PVP-characteristic ions at 112<sup>+</sup> plus 124<sup>+</sup>, as shown in Figure 7. The negative ion mode images, illustrated in Figure 8, nicely confirm the positive mode results. The image generated from the PVP-characteristic ions at 26<sup>-</sup>, 42<sup>-</sup>, and 84<sup>-</sup> mirrors the corresponding ion image of the positive ions at 112<sup>+</sup> plus 124<sup>+</sup>. The image of the sulfonate ion (SO<sub>3</sub><sup>-</sup>) at 80<sup>-</sup>, though weak and somewhat diffuse, is observed throughout the coating thickness.

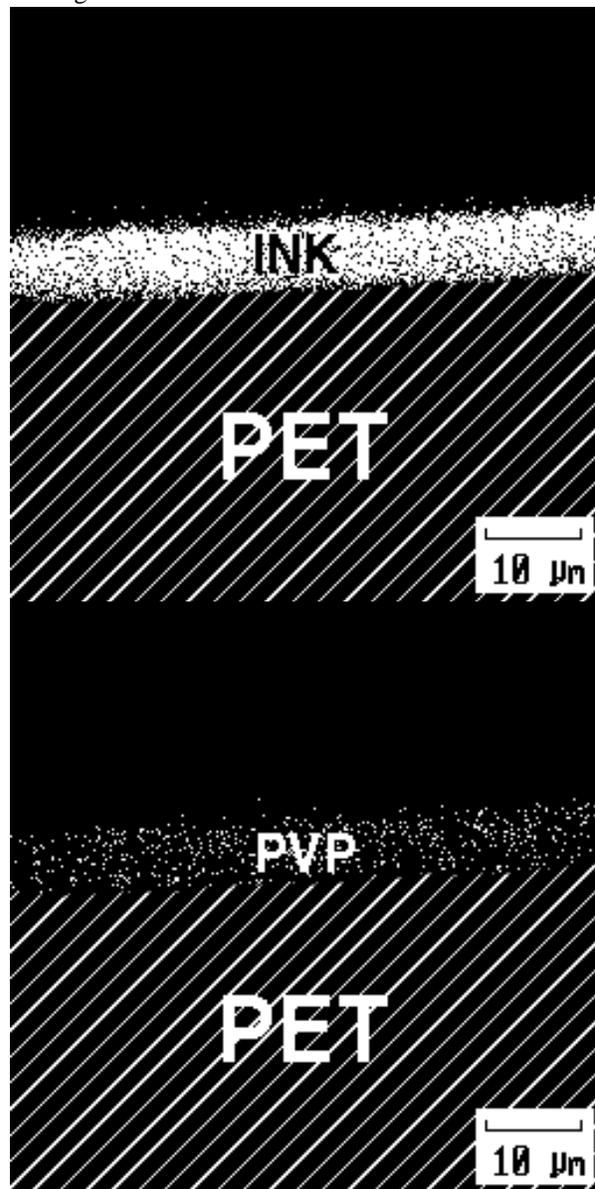


Figure 7. The positive ion mode image of the ink-characteristic ions at 87<sup>+</sup>, 89<sup>+</sup>, and 480<sup>+</sup>-555<sup>+</sup> in a cross-section of the Polectron (PS/PVP) film and the polymer coating image generated from the PVP-characteristic ions at 112<sup>+</sup> + 124<sup>+</sup>.



Figure 8. The negative ion mode image of the PVP-characteristic ions at 26°, 42°, and 84° in a cross-section of the Pollectron (PS/PVP) film and the sulfonate ion ( $\text{SO}_3^-$ ) image at 80° due to the ink.

Because the grafted PVP chains are loosely distributed throughout the PS emulsion, it appears that the resulting solid-state morphology now allows facile ink penetration, despite the presence of two components that would otherwise inherently manifest the ability to restrain the diffusion of dye molecules away from the coating surface. In essence, then, this behavior is not unlike the situation that we have already encountered for PVOH, in which ink diffusion was also unrestricted all the way to the PVOH/PET film interface. In that case, intermolecular hydrogen bonding between individual polymer chains of PVOH results in a *water-swallowable* physical gel. Recognizing the functional equivalence between PVOH and Pollectron, therefore, we surmise that the PVP-stabilized PS latex particles are somehow distributed in a similarly open network, i.e., the colloidal structure of the dispersion determines the morphology, forming some kind of *porous* coating structure. Consequently, despite the presence of PVP, the overriding *physi-*

*cal* structure of the emulsion facilitates unimpeded ink diffusion directly to the substrate interface.

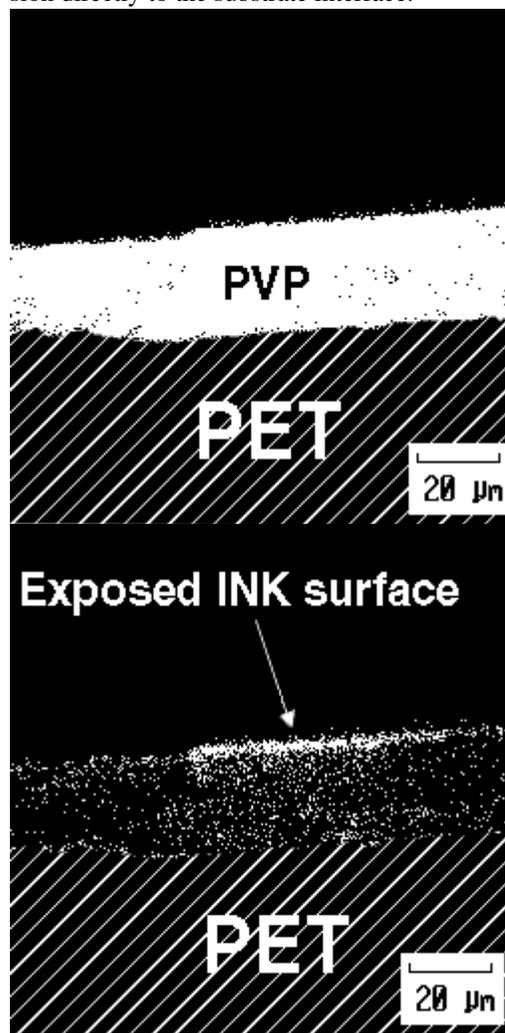


Figure 9. The negative ion mode image of the PVP-characteristic ions at 26°, 42°, and 84° in a cross-section of the Pollectron/PVOH film and the sulfonate ion ( $\text{SO}_3^-$ ) image at 80° due to the ink.

Now consider the effect of blending Pollectron with PVOH. In cross-sectional images (not shown), the *ink-characteristic* peaks at 87°, 89°, and 480°-555° are now at *background* levels, which suggests that essentially *no* penetration of ink into the coating has occurred. The negative ion images confirm the fact that deep ink penetration does *not* occur, as illustrated by the coating profiles in Figure 9. In this mode, while the  $\Sigma$ PVP-characteristic ions at 26°, 42°, and 84° is easily seen, the sulfonate ion ( $\text{SO}_3^-$ ) of the ink is strong *only* in the top ~4 microns and *only* in one section. (During the microtoming procedure, we noticed that the blend was quite *brittle*, making the cross-section somewhat difficult to prepare; hence, the thin 80° line is probably due to a cutting artifact, thereby exposing the (curled-over) ink surface to the ion beam).

These results remind us of the **PVP** case in which the absence of a dye signal was attributed to the fact that **PVP** must immobilize the dye molecules in an extremely thin sub-micron region at the coating surface. Our interpretation of the **Polectron/PVOH** data retains the notion of a thin dye layer but now we ascribe the effect to a *coalesced PS latex barrier*, induced by some sort of *phase separation* phenomena between the **PS** particles and the attached **PVP** chains that quite naturally results from the ability of **PVP** and **PVOH** to engage in intermolecular hydrogen bonding interactions. However, we do not exclude the possibility that (*surface-adsorbed*) **PVP** may still play a role, perhaps even a critical role, in dye fixation at the newly-formed **PS** phase boundary.

Finally, we present some ancillary performance data that supports the model of a phase-separated barrier. Visually, the *pigmented black* image of the blend is actually improved compared to **Polectron** by itself, which nicely supports the idea of latex coalescence. Because intermolecular hydrogen bonding between **PVP** and **PVOH** would actually open the fully hydrolyzed **PVOH** gel structure, the shorter dry time that is observed for the blend is thus easily accounted for. Hence, we are starting to appreciate that the physical structure of the film, in conjunction with the intrinsic dye binding ability of the polymer, may actually be quite significant with respect to the *overall* performance.

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5. Because PET yields background signals for many of the ions considered in this paper, we have shaded the PET in order to emphasize the signals emanating from the coating, per se.
6. We transformed the original gray-scale images to 2-color B&W, which occasionally enhances the background noise.