

# Elucidating PVP Dye-Binding Mechanisms in Ink Jet Media

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## Abstract

The extensive use of polyvinyl pyrrolidone (PVP) as an ink acceptor material derives from two concurrent attributes: the propensity to bind anionic dyes and the ability to rapidly absorb the liquid vehicle.<sup>1</sup> Recognizing that polymer microstructure and morphology regulates ink permeability, we utilize a diverse array of PVP copolymers in order to systematically investigate the simultaneous impact of comonomer composition on ink penetration and dye immobilization. On the basis of the offset (dry time) protocol and corresponding optical density measurements, we elucidate the fundamental mechanisms underlying the chromatographic separation of ink jet dyes from aqueous solvents during the diffusion of picoliter ink drops into hygroscopic films of various PVP copolymers.

## Introduction

The panoply of complex phenomena inherent in ink jet ink-media interactions complicates an understanding of the implicit *structure-property-performance relationships* governing the phenomenology of ink jet printing. The management of the intricately related processes of dye binding, dye aggregation, and solvent imbibition necessitates the identification of competing and overlapping mechanisms controlling the dynamic physical interactions that occur between dissolved aqueous dyes and the polymer matrix during the process of ink absorption. In this paper, we determine the extent of ink penetration and the effectiveness of dye binding in model PVP copolymer coatings in an effort to correlate the effect of solid-state film microstructure on printing performance. We reconcile a number of observations through simple and easily appreciated correlations, using fundamental property data in conjunction with phenomenological performance measurements. All of our results are presented as a function of ink viscosity. This has allowed us to establish an empirical basis of the underlying mechanisms involved in the physics of ink-media interactions. Our endeavors are part of a larger coordinated effort directed towards the establishment of physical models of ink jet media and the design of appropriate polymers specifically for ink jet applications.

## Experimental Protocol

Laboratory films were coated out of water or isopropanol onto ICI white opaque polyester. These films

were printed with an HP 850C, using a standard imaging test pattern which allowed each color to be separately analyzed. We have employed a drying protocol which is widely used in the analysis of ink jet prints. Each of the *three process colors* (cyan; magenta; yellow) in addition to the *composite dye black* (C+M+Y) was printed in the form of a test strip along one edge of the film. Because the top edge is drying or absorbing the ink *even* as the rest of the image is *still* being printed, the four test strips for each color embody information about the *rate* of drying as a function of distance along the edge. Therefore, once the entire imaging test pattern is printed, the amount of ink offset to another (special) receptor material<sup>2</sup> will vary (for each color) as a function of *distance* along the edge. Defining the offset time as the point where the (offset) optical density is less than or equal to 0.1, we utilize this variable as some (kinetic) measure of the process of ink absorption. Observations based upon the offset protocol are purely operational and they need to be interpreted according to the exact nature of the particular system, which includes such attributes as the bulk morphology and the surface structure. Finally, we measured the optical density of solid color patches for the cyan, magenta, and yellow *dye-based* inks as well as the *pigment-based black* ink. All of the PVP copolymers illustrated in Figure 1 are from the International Specialty Products (ISP) portfolio.

## Results & Discussion

### Vinyl Pyrrolidone/Dimethylaminoethylmethacrylate (VP/DMAEMA) Copolymers

Utilizing PVP K90 as our reference system, the data for CP 845 in Figure 2 shows that the incorporation of only a few mole % DMAEMA *uniformly* reduces *all* of the ink offset times. And yet, the corresponding optical densities are only marginally lower in comparison to that for PVP K90, as shown by the data in Figure 3. At low DMAEMA levels, the additional free volume enables the diffusion rate of water and other cosolvents in the ink to *increase*. However, the negligible change in the optical density indicates that the propensity of PVP to bind anionic dyes is basically unaffected. At much higher DMAEMA levels, however, the optical density is noticeably lower, as shown by the data for CP 937 in Figure 3. The corresponding reduction in the yellow and cyan offset times suggests that the simultaneous depletion of VP moieties and the concomitant increase in free volume may conspire to entrain dye molecules away from the film surface. While these two

factors appear to act in concert for the yellow and cyan inks, some other mechanism must be occurring in the case of the magenta ink, since the magenta optical density is anomalously low while the corresponding offset time is surprisingly high. Despite a measurable increase in film free volume and the associated dilution of **VP** moieties, these related observations suggest that a unique dye-binding mechanism is operative that somehow promotes dye aggregation within the vicinity of the film surface.

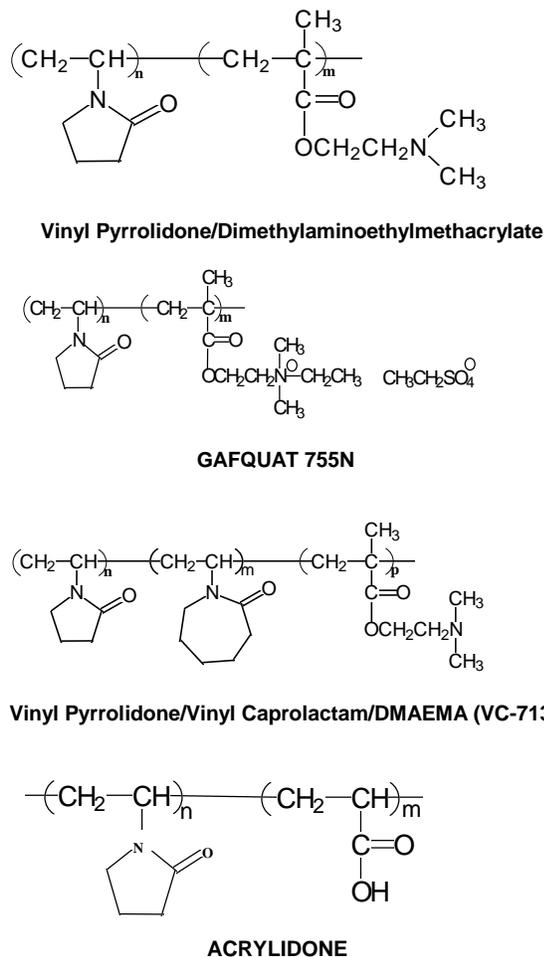


Figure 1. Structures of PVP Copolymers.

In the **VP/DMAEMA** system, hydrolysis of the ester functionality necessarily creates residual methacrylic acid moieties, which may enable the formation of a *polyelectrolyte gel* complex, occurring through electrostatic interactions between the amine groups on **DMAEMA** and the residual carboxylic acid groups.<sup>3</sup> The absence of free charges would therefore preclude the use of *protonated* amino groups in dye-fixation. However, dye binding experiments have shown that the hydrophobic character of the free, uncharged **DMAEMA** moiety may actually *enhance* the affinity of certain dyes for **PVP**.<sup>4</sup> Hence, we attribute the relatively high magenta offset time of **CP 937** to dye immobilization *within* hydrophobic microdomains of phase-separated *unprotonated* **DMAEMA** moieties.

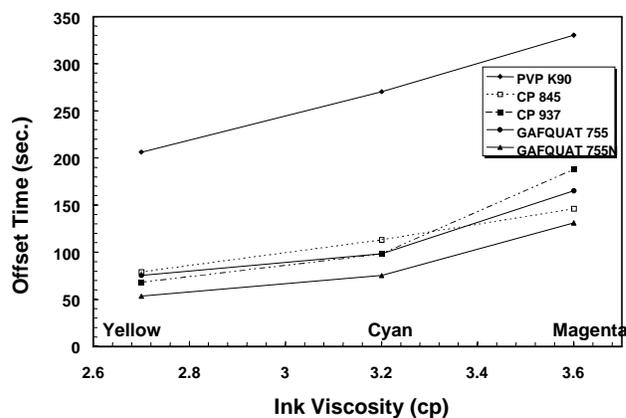


Figure 2. Offset time vs. ink viscosity for the VP/DMAEMA copolymers, including GAFQUAT 755/N (quaternized CP 937).

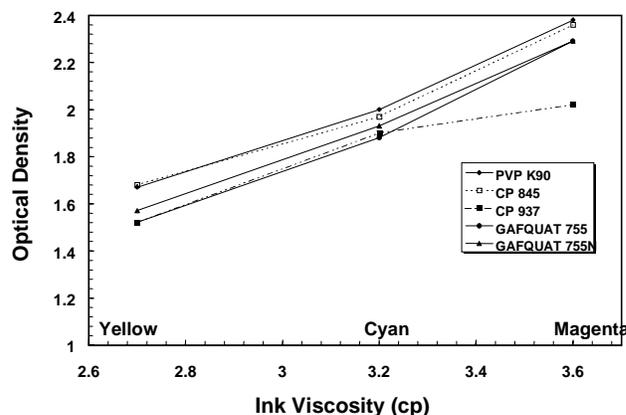


Figure 3. Optical density vs. ink viscosity for the VP/DMAEMA copolymers, including GAFQUAT 755/N (quaternized CP 937).

Upon quaternizing *half* of the **DMAEMA** moieties, as shown by the curves for **GAFQUAT 755** in Figures 2-3, even as the yellow and cyan data are essentially unaffected, the magenta response is unique. The *decrease* in the offset time is easily rationalized by the fact that now *only 50%* of the original unprotonated **DMAEMA** groups remain, which is nicely illustrated in the way the point for **755** is *equidistant* from the values for **CP 937** (above) and **CP 845** (below). Consistent with this proposition, the sizable *increase* in the magenta optical density suggests that the depletion of either the *number* or the *size* of hydrophobic microdomains mitigates against the agglomeration of the magenta chromophores. Neutralizing the remaining unquaternized **DMAEMA** groups now lowers *all* of the offset times, as shown by the curve for **GAFQUAT 755N** in Figure 2. The elimination of phase-separated hydrophobic regions correlates with the uniformly lower offset times for *each* ink. Conversely, the *increase* in the yellow and cyan optical densities and the fact that the magenta optical density is unchanged implies that, of the two cationic moieties embodied by the protonated and quaternized polymer, it is the *protonated* amino group that actually, or at least more effectively, engages in electrostatic dye-binding interactions.

### Vinyl Pyrrolidone/Vinyl Caprolactam (VP/VCAP)

The VP/VCAP data is presented in Figures 4-5, in which we also include the curve for VC-713, a terpolymer of VP, VCAP, and dimethylaminoethylmethacrylate (DMAEMA).

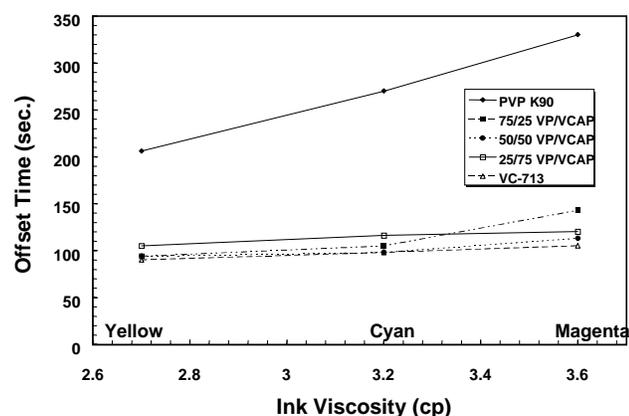


Figure 4. Offset time vs. ink viscosity for VP/VCAP copolymers, including VC-713, a terpolymer of VP, VCAP, and DMAEMA.

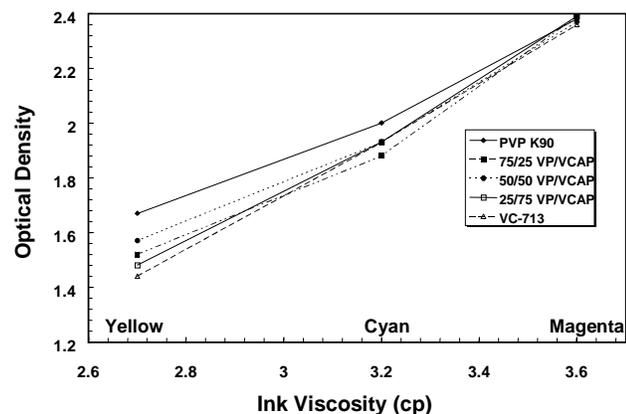


Figure 5. Optical density vs. ink viscosity for VP/VCAP copolymers, plus VC-713, a terpolymer of VP, VCAP, and DMAEMA.

The copolymerization of VP and VCAP proceeds through the incorporation of extended sequences of each monomer.<sup>5</sup> The relatively flat offset response is indicative of preferential surface segregation of the hydrophobic VCAP blocks, in addition to the fact that VCAP reduces the overall bulk hygroscopicity of the film. Moreover, as the VP/VCAP film becomes less hygroscopic, the expected slower rate of ink diffusion is confirmed by the uniformly higher offset times for the 25/75 composition.

Although the offset response is somewhat masked by the retarding effect of the hydrophobic VCAP barrier, the offset curves nevertheless exhibit a measurable viscosity dependence, which is reflected by the loss in optical density for the yellow and cyan inks for each of the VP/VCAP copolymers. These observations contrast rather dramatically with the results for the magenta ink. Assuming that the hydrophobic VCAP barrier at the surface reduces the diffusion rate of all the inks equally (the solvent content is nominally identical) which therefore, allows sufficient time

for dye adsorption to occur at the pyrrolidone (and caprolactam) moieties along the polymer chain, the singular retention of the magenta optical density must be a manifestation of the intrinsically high (solution-state) binding constant between PVP and the particular dyes in this ink.

Superimposed on the intrinsic dye-binding potential of the respective polymers, however, are other factors, such as the overall bulk morphology, which may also play an important role in the dynamics of ink immobilization, potentially augmenting any apparent decrease in the offset times or the optical densities with respect to the reference curves for PVP K90. Indeed, a closer examination of the offset data reveals subtle effects arising from changes in polymer conformation that provides a basis for resolving the intricate interplay between the intrinsic dye-binding capacity of PVP and the opposing process of solvent imbibition.

Because VCAP is significantly more hydrophobic than VP, microphase separation induces the transformation of the polymer chain from a random or extended coil to a more compact coil,<sup>6</sup> as shown in Figure 6 by the minimum in the solution-state viscosity<sup>7</sup> at the 50/50 composition. The retention of the solution-state microstructure in the solid-state film is manifested by the analogous offset response. The phase-separated morphology of the 50/50 composition reduces all of the ink offset times, as shown in Figure 4. Despite the greater bulk hygroscopicity of the 75/25 composition, the deviation of the magenta offset at this point is another manifestation of the specific interactions inherent between PVP and the dyes in this ink, resulting in this chromatographic effect. The sharp upward inflection contrasts with the nominally similar offset times of the 50/50, 25/75, and 0/100 copolymers. The deviation of the 75/25 point is reminiscent of the inflection in the VP/VCAP cloud point curve, suggesting that the accessibility of the polymer by individual dye molecules depends on the exposure of the microphase-separated domains.<sup>8</sup>

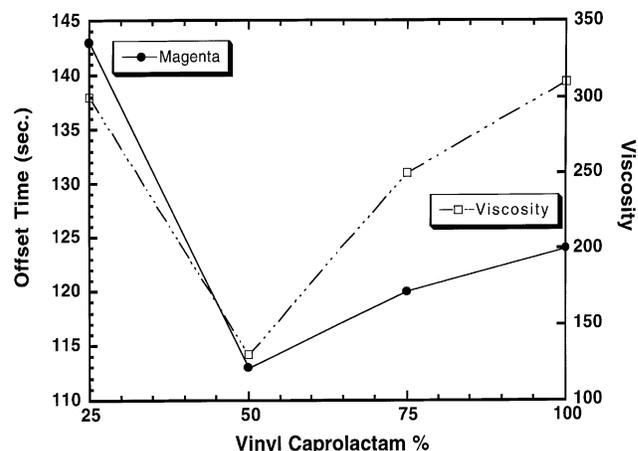


Figure 6. Offset time for the magenta dye-based ink vs. vinyl caprolactam wt. % for the VP/VCAP copolymer; the solution-state Brookfield viscosity is also shown.

The addition of a small percentage of the DMAEMA monomer to an otherwise nominal 25/75 VP/VCAP copolymer uniformly lowers the offset curve even further, as

shown by the data for **VC-713** in Figure 4. The terpolymer has a cloud point temperature of 37C,<sup>8</sup> which is somewhat lower than the corresponding cloud point for 25/75 **VP/VCAP**, again revealing the hydrophobic character of the **DMAEMA** moiety. Moreover, the glass transition temperature of **VC-713** is 157C, which is almost 20 degrees lower than that of 25/75 **VP/VCAP**. Clearly, the incorporation of only a few mole % **DMAEMA** significantly changes the morphology of the **VP/VCAP** system, in which the **DMAEMA** group, quite probably relegated to the **VCAP** phase, imparts more free volume into the glass phase of the polymer coating. In fact, the downward shift of the entire offset curve is paralleled by a subtle decrease in the magenta optical density.

### Vinyl Pyrrolidone/Acrylic Acid (VP/AA) Copolymers

**VP/AA (ACRYLIDONE)** films manifest substantial water-resistance<sup>9</sup> due to the network of hydrogen bonds that are formed between the **VP** and **AA** groups, which thereby inhibits the penetration of water into the film. The detrimental effect on the ink diffusion rate results in relatively high offset times, as shown by the data in Figure 7, in which the extreme water-resistance of the 25/75 composition is manifested by the highest offset times. Notwithstanding the rate-controlling impact of the water-resistant barrier on the shape of the offset curves, the offset times still exhibit a measurable dependence on the ink viscosity. While the realization of ink diffusion is reflected by the loss in optical density for the yellow and cyan inks, the increase in the magenta optical density is clearly indicative of the intrinsic affinity between the magenta dyes and **PVP**, the manifestation made possible by the inhibition of ink penetration and the concomitant increase in the time for dye adsorption.

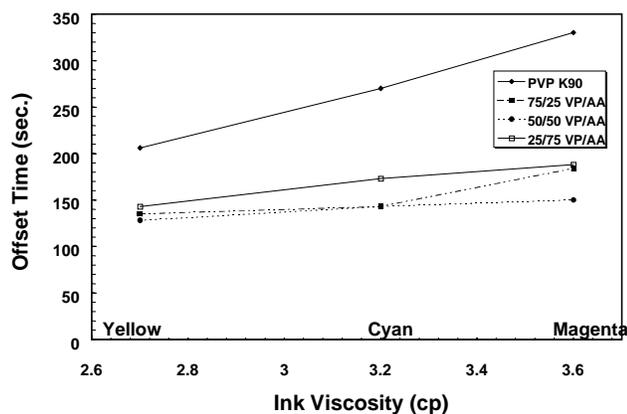


Figure 7. Offset time vs. ink viscosity for the **VP/AA** copolymers.

The extent of hydrogen bonding varies with the comonomer composition. Indeed, the minimum in the solution-state viscosity at the 50/50 composition is indicative of the contraction of the polymer chain to a compact coil.<sup>9</sup> This microstructural effect is manifested by the fact that all of the ink offset times display a minimum at the 50/50 composition, thus implying that the conformational state in solution is essentially maintained in the final

film. The enhanced rate of diffusion at the 50/50 composition is reflected by an analogous decrease in the optical density for the yellow and cyan inks. Conversely, the retention of the magenta optical density is indicative of the particular affinity of the magenta chromophore(s) for **PVP**. The deviation of the magenta offset at 75/25 **VP/AA** is further proof of this specific dye-binding interaction.

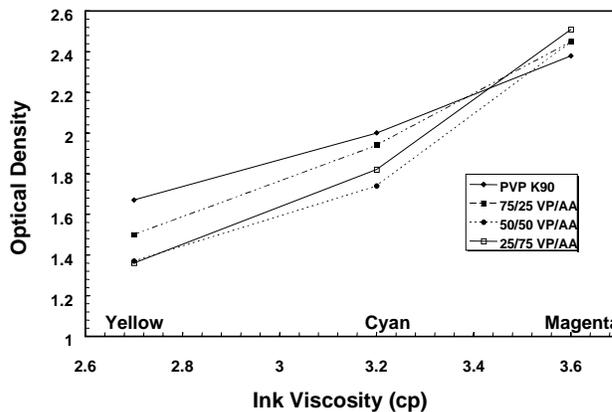


Figure 8. Optical density vs. ink viscosity for the **VP/AA** system.

## Summary

We have examined the dynamics of ink immobilization at the surface of three different **PVP** copolymer systems. In accordance with intuitive expectations, and utilizing **PVP K90** as a reference, the opposing and intricately related processes of dye-binding and solvent imbibition generally preclude the retention of dye molecules at the surface of any system characterized by a measurable amount of film free volume. However, at sufficiently hydrophobic or water-resistant surfaces, the intrinsic affinity between the magenta dyes and **PVP** allows the optical density to remain unchanged or to even increase with respect to that for **PVP K90**. Indeed, the distinctive behavior of the magenta ink emerged as the basic theme of this study, underscoring our attempts to identify the various fundamental mechanisms underlying the physics of ink jet ink-media interactions.

Because our research objectives are tantamount to redefining the entire family of **PVP** copolymers as an ink jet media enabling technology, the results that we have presented in this paper are only a preliminary account of our research strategy. The stimulating diversity of these polymer products promise fascinating media design options for formulators, specialty coaters, and others involved in the manufacture of film and paper products for ink jet printing. We are currently exploring a range of issues regarding ink-media interactions and we have already discovered some extremely interesting, occasionally unexpected, and sometimes even counterintuitive behavior of ink diffusion as a consequence of various **PVP** copolymers. At this point, a comprehensive series of experiments directed at a more fundamental understanding of ink diffusion and dye aggregation is in progress as we continue to complement and refine our empirical studies. As new product introductions

and continuous refinements necessitate more advanced technology, we shall seek to expand the range of products within the **ISP** portfolio, even as we continue to explore and understand the behavior of our current polymers.

### Acknowledgments

The actual data in this study was generated by Mr. Ken Bosland. We acknowledge the careful and conscientious measurements he performed using the offset protocol, which he also implemented and refined. Dr. Phil Wolf, Director of Process Chemistry & Industrial Applications at **ISP**, provided the resources for this research. His enlightened approach to industrial research management, in addition to his promotion and support of our broader technical research programs is greatly appreciated. Funding was made possible by the generous support of Dr. Robert Mininni, VP of R&D. The viscometric and thermodynamic data on the **VP/VCAP** copolymers is due to Dr. B. Srinivas of **ISP**. A deeper understanding of the **VP/DMAEMA** system emerged from a number of engaging conversations with Dr. Michael Tallon, Dr. K.-C. Liu, and Mr. Frank Fusiak. Finally, we recognize

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