IS&Ts NIP 14: 1998 International Conference on Digital Printing Technologies

Elucidating PVP Dye-Binding Mechanisms in Ink Jet Media

Jerry R. Pinto and John C. Hornby
International Specialty Products
Wayne, New Jersey

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.[1] 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.

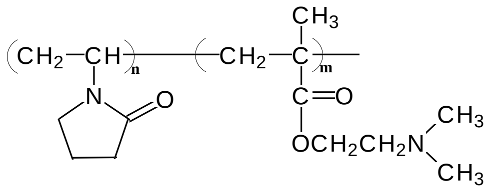
Experimental Protocol

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[2] 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.

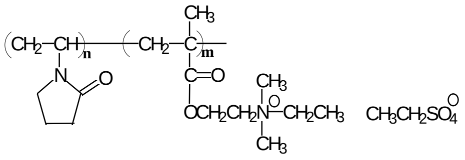
Results & Discussion

Vinyl Pyrrolidone/Dimethylaminoethylmethacrylate (VP/DMAEMA) Copolymers

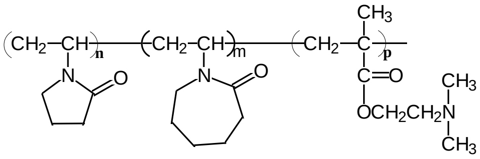
Utilizing **PVP K90** as our reference system, the data for **CP 845** in Figure 2 shows that the incorporation of only a few mole % **DMAEMA** *uniformly* reduces *all* of the ink offset times. And yet, the corresponding optical densities are only marginally lower in comparison to that for **PVP K90**, 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 noticably 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 occuring 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.



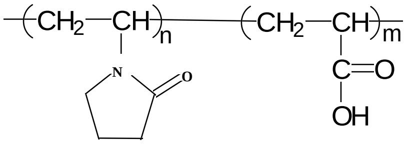
Vinyl Pyrrolidone/Dimethylaminoethylmethacrylate



GAFQUAT 755N



Vinyl Pyrrolidone/Vinyl Caprolactam/DMAEMA (VC-713)



ACRYLIDONE

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, occuring through electrostatic interactions between the amine groups on **DMAEMA** and the residual carboxylic acid groups.[3] 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**.[4] Hence, we attribute the relatively high magenta offset time of **CP 937** to dye immobilization *within* hydrophobic microdomains of phase-separated *unprotonated* **DMAEMA** moieties.

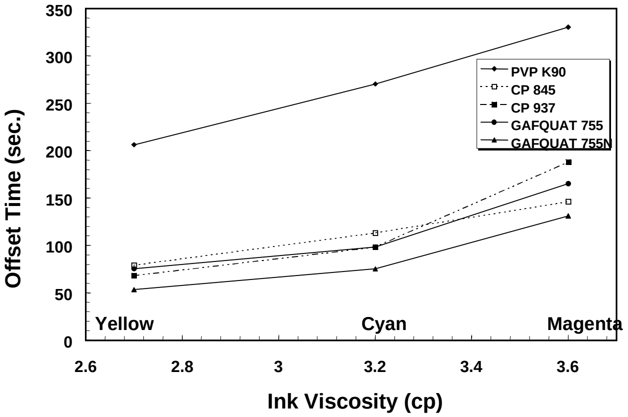


Figure 2. Offset time vs. ink viscosity for the VP/DMAEMA copolymers, including GAFQUAT 755/N (quaternized CP 937).

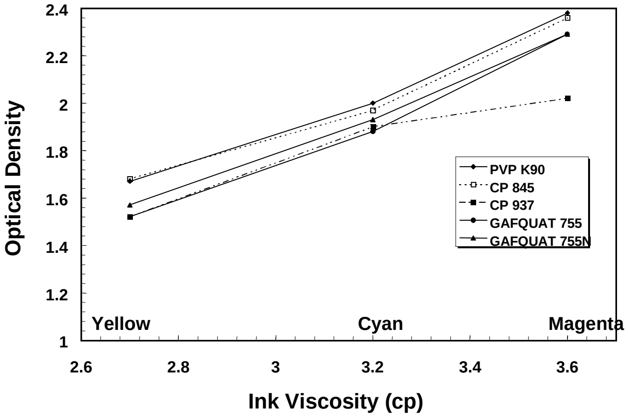


Figure 3. Optical density vs. ink viscosity for the VP/DMAEMA copolymers, including GAFQUAT 755/N (quaternized CP 937).

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**).

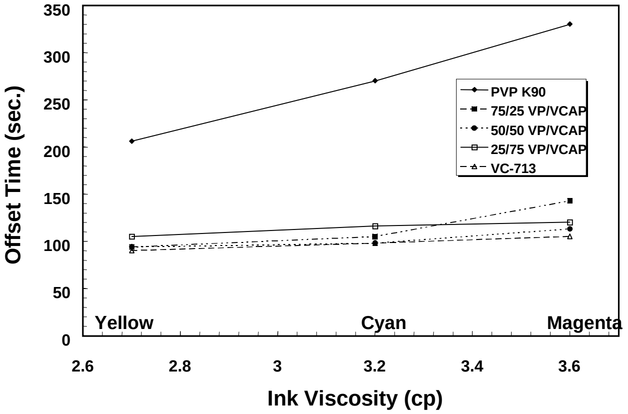


*Figure 4. Offset time vs. ink viscosity for **VP/VCAP** copolymers, including VC-713, a terpolymer of **VP**, **VCAP**, and **DMAEMA**.*

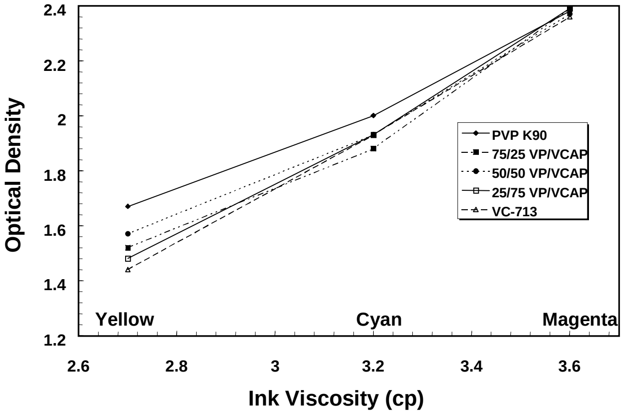


*Figure 5. Optical density vs. ink viscosity for **VP/VCAP** copolymers, plus **VC-713**, a terpolymer of **VP**, **VCAP**, and **DMAEMA**.*

The copolymerization of **VP** and **VCAP** proceeds through the incorporation of extended sequences of each monomer.[5] 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,[6] as shown in Figure 6 by the minimum in the solution-state viscosity[7] 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.[8]

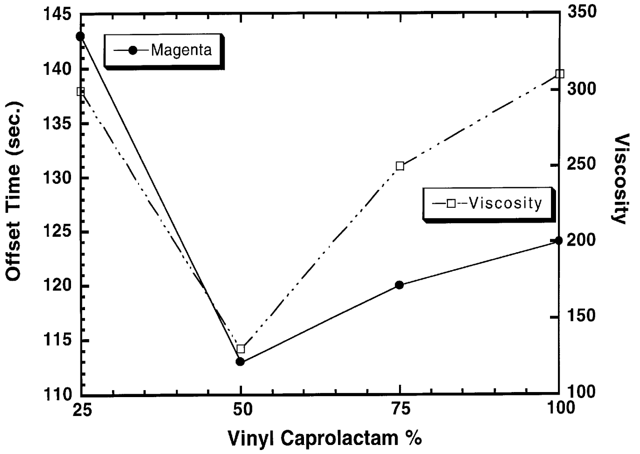


*Figure 6. Offset time for the magenta dye-based ink vs. vinyl caprolactam wt. % for the **VP/VCAP** copolymer; the solution-state Brookfield viscosity is also shown.*

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,[8] 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[9] 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.

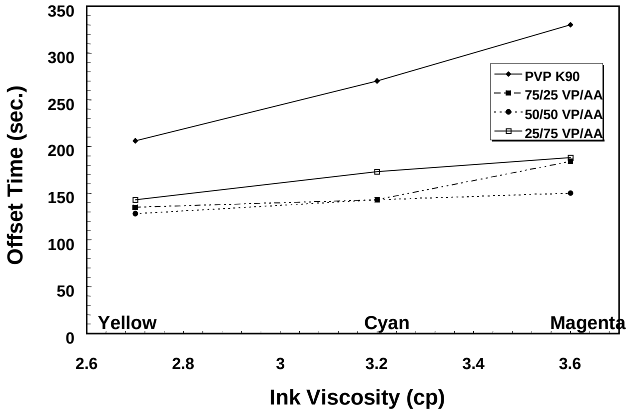


Figure 7. Offset time vs. ink viscosity for the ***VP/AA*** *copolymers.*

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.[9] 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.

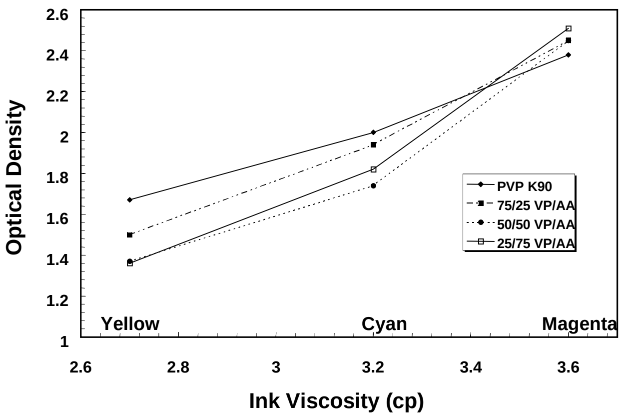


Figure 8. Optical density vs. ink viscosity for the ***VP/AA*** *system.*

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 Mr. Ira Naznitsky and his staff for their critical and expert assistance in the conduct of a variety of literature reviews.

References

1. F. Runge, et al. Ber Buns. *Phys. Chem*. **100**, 661 (1996).
2. Courtesy of T. Graczyk, Oce-Imaging Supplies, Conn.
3. E. F. Panarin, I. I. Gavrilova, and A. I. Lelyukh, *Russian J. App. Chem*. **67**, 608 (1994).
4. T. Takagishi, T. Hosokawa, and Y. Hatanaka, *J. Poly. Sci.: Part A: Poly. Chem.* **27**, 1 (1989).
5. Allaev, M. A. Askarov, B. L. Gafurov, and A. Akbarov, *Dokl. Akad. Nauk UzSSR* **1**, 30 (1991)
6. A. A. Tager, A. P. Safronov, E. A. Berezyk, and I. Yu. Galaev, *Colloid & Polymer Science* **272**, 1234 (1994).
7. ISP intrinsic viscosity of copolymer solutions in water. ISP cloud point data: 2% aqueous copolymer solutions; E. Ranucci, P. Ferruti, M. Nicolai, V. Ferrari, D. Mario-li, A. Taroni, *La Chimica & L'Industria* **74**, 667 (1992).
8. J. C. Hornby, J. D. Pelesko, and D. Jon, Soap/Cosmetics/Chemical Specialties June (1993).

Biography

Dr. Jerry R. Pinto received B.S. and M.S. degrees in Chemical Engineering and a Ph.D. in Physical Chemistry from Columbia University. The interdisciplinary nature of his experience is reflected in the diverse range of research and product development activities that have punctuated his career, from polymerization reaction engineering work with Mobil Chemical to technology development and basic research with DuPont Imaging Systems. Subsequently, Dr. Pinto formed Pinto Research & Consulting, providing clients with a physical understanding of polymer thin film technologies through surface and interfacial analyses. Currently, Dr. Pinto serves as a staff consultant for International Specialty Products, a leading supplier of ink jet polymers.