

# Influence of Polymer-Polymer Interactions on Properties of Ink Jet Coatings

*Khizyr Khoultaev and Tom Graczyk  
Arkwright, Inc.  
385 Long Hill Road, Guilford, CT 06437*

## Abstract

Theoretical and practical aspects of the consequences of polymer-polymer interactions in ink jet receiver coating are discussed. Several examples are presented pertaining to type of modification and charges of polyvinyl alcohol will have an effect on print quality with dye and pigmented inks. It is shown that the introduction of a dye fixative to the coating improves the water fastness but has negative effect on print quality. It was found that the pH adjustments in the ink receiving layers increase the gloss of the media.

## Introduction

The design of ink jet receiving layers requires a detailed understanding of basic interactions between components of the coatings. In the simplest case a single polymer could fulfill the assigned task in the coating due to its chemical nature. However, it could be complicated, or even impossible, in the presence of another chemical, which is brought into the formula to accomplish another important task. Properties like water and UV fade resistance require special polymers with different functional groups (1). Unfortunately, often it is not possible to find a commercially available resin with more than two desired functions.

Many classic water and light resistant ink jet formulations described in the patent literature consist of a silica type pigment, resin binder(s) and dye mordant. An ink receiving layer must have a pigment and dye mordant to accommodate dyes in a way that they will not be washed out from the printed areas when coating is exposed to an excess of water. In general, the presence of pigment in the formula increases the UV resistance of the coating (2-4). The polymeric resins are also essential to bind pigment particles together, to facilitate molecular diffusion of ink vehicle into the coating media and to absorb ink liquid containing water and organic solvent such as glycols. The ink absorbing polymer matrix can contain various binders for improving the film forming properties of the coating, prints quality and the drying properties of different inks. The ink receiving layer may contain one or more water-soluble and water dispersible polymers.

The development of water and light resistant coatings frequently requires blending incompatible materials. In the

following sections we will discuss how the interactions between different chemicals in the ink jet-receiving layer would influence the coating process and final properties of the media.

## Experimental

4-mil clear polyester film (PET) was used as the base for model coatings. This grade of ICI film has been primed from both sides allowing to coat aqueous solutions. The 7-mil gauge polyethylene extrusion coated photobases was corona treated to achieve the surface tension about 42 dynes/cm before the ink jet receptive coating was applied.

Two types of papers were used as a coating base: 105 g/sq.m. matte paper from International Paper and 168 g/sq.m. cast coated paper from Champion International.

## Results and Discussion

### pH of Coating Fluid

The effect of coating pH on print quality with dye-based and pigmented inks was studied on two model systems. To simplify the model no pigments were introduced to the polymeric mixes. Both compositions had the same ratio of polyvinyl alcohol to cationic polyurethane to polyvinyl pyrrolidone. System 1 contained anionic modified polyvinyl alcohol while System 2 contained cationic modified polyvinyl alcohol.

Polymer	System 1	System 2
Anionic polyvinyl alcohol	10	
Cationic polyvinyl alcohol		10
Cationic polyurethane latex	1	1
Polyvinyl pyrrolidone	1	1

The gloss readings of the base coated with both systems were in the narrow range of 110-115. The readout above 100 units was due to internal reflections of the clear film. There was no difference in the gloss between dye based inks for Systems 1 and 2. Generally, they were 5-10 points below the gloss of the base. The gloss of printed areas with pigmented inks was significantly lower than unprinted ones.

The reduction in gloss was higher for secondary than for primary colors. For example for System 1 the numbers were as follow: 115, 78 and 42. It can be seen that gloss readings for the primary colors in System 1 was higher than in System 2 for both types of pigmented inks. It could be related to the crack formation in System 2.

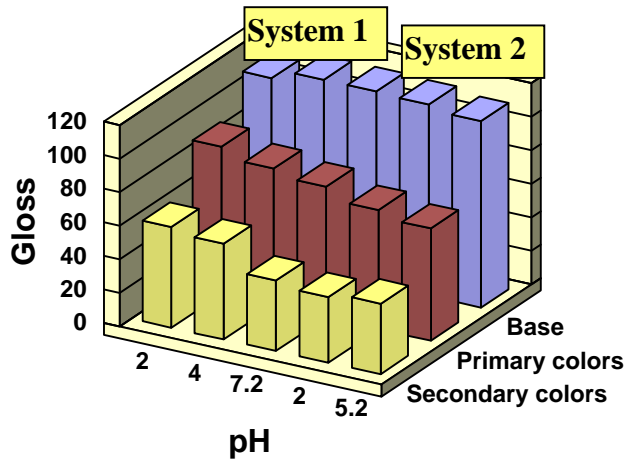


Figure 1. Gloss of systems 1 and 2 coated on PET film as a function of pH for HP 2000 printer with pigmented inks.

The gloss of secondary colors was always lower than gloss for primary colors in System 1 with EnCad and HP pigmented inks. System 2 followed the same trend with HP inks but the case of EnCad inks there was no difference in gloss readings between secondary and primary colors that were at the level of 75.

The change of coating fluid pH did not have an effect of the base gloss. System 1 responded to the gradual reduction of pH by increased gloss readings for both primary and secondary colors on EnCad and HP pigmented inks (Figure 1 & 2). In the contrary, there were no changes in gloss for System 2. The interpretation of this set of data is presented in the next section.

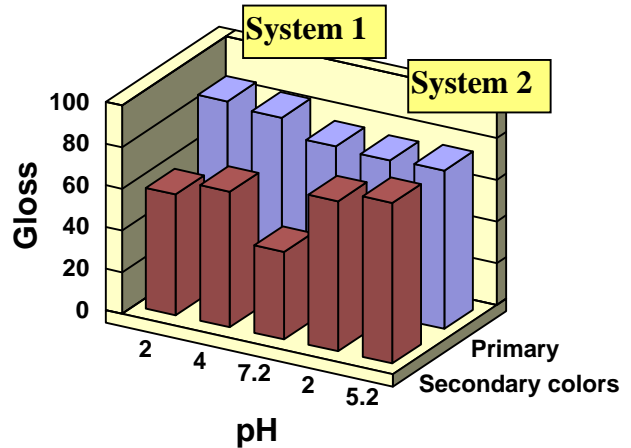


Figure 2. Gloss of Systems 1 and 2 coated on PET film as a function of pH. EnCad printer with pigmented inks.

Table 1. Print quality of Systems 1 and 2 coated on PET film as a function of pH for HP 2000 and EnCad printers with pigmented inks.

Printer		HP		EnCad	
System	pH	Bleed	Cracks	Bleed	Cracks
1	2	0	C	3.5	E
	4	0	C	2.5	E
	7.2	0	C	2	C/E
2	2	0	B	1	C
	5.2	0	B	1	C

<sup>1</sup>-intercolor bleed is rated using 0 to 5 scale where 0 corresponds to "best case, no bleed" and 5 corresponds to "worst case, flooding"

<sup>2</sup>-degree of cracking is rated according to the patterns presented in Figure 3

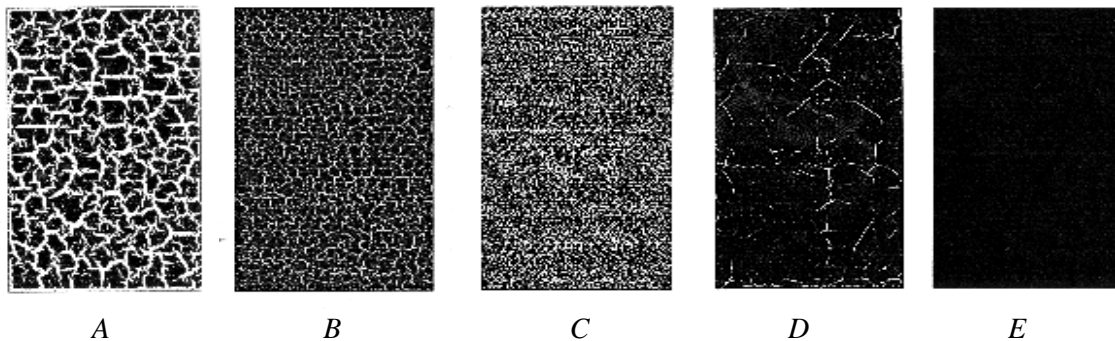


Figure 3. Different types of crack formation patterns encountered for different formulations. Image (E) corresponds to the crack free formulation.

Different types of image cracking are encountered when printing with pigmented inks. We differentiate this phenomenon by type of cracks and degree of cracking. The images (A) and (E) on Figure 3 are examples of severe crack formation and crack free imaging respectively. Images (B)-(D) correspond to intermediate cases. There is no detailed explanation to the phenomenon of crack formation on images made with pigmented inks. However, it was possible to explore a correlation between crack formation and dry time. Apparent mechanisms for the image deterioration are presented in the section below entitled "Cracks versus Dry Time with Pigmented Inks".

### Water Fastness

The effect of coating composition on print quality with dye and pigmented inks was studied on two other model systems in an aqueous medium. To simplify the model no pigments were introduced to the polymeric mixes. Both compositions had the same ratio of polyvinyl alcohol to cationic polyurethane. System 3 was the same as System 4 except anionic polyvinyl alcohol (PVA) was replaced with cationic PVA. In comparison to System 1 and 2 the ratio of polyvinyl alcohol to polyurethane latex was reduced from 10:1 to 2:1.

Polymer	System 3	System 4
Anionic polyvinyl alcohol	2	
Cationic polyvinyl alcohol		2
Cationic polyurethane latex	1	1
Polyethyleneimine	varies	varies

Magenta had the lowest water fastness among primary colors in most tested systems and was chosen as an example in the study. The effect of the amount of polyethyleneimine on water fastness of magenta color is presented in Figure 4. Water fastness of the studied systems was strongly dependent on the type of polyvinyl alcohol. Water fastness of the magenta ink with anionic polyvinyl alcohol is higher than with the cationic one, and nearly independent of the amount of polyethyleneimine. The level of water fastness is still high (85% after one hour) even without a dye fixative. The system with cationic polyvinyl alcohol had water fastness of 30% only. It is noted that the topcoat slips from the substrate and measured value has approximate meaning only. The difference between both systems disappeared with the increase in concentration of polyethyleneimine. However, at 7.5 percent of dye fixative water fastness of the anionic system was still about 6 percent higher.

The Magenta water fastness of System 4 with cationic polyvinyl alcohol and one percent of polyethylene-imine decreased steadily and reached 50 percent of initial value after 15 minutes. There was also some diffusion of inks from the coating with anionic PVOH in the first minutes after immersion in water (Water fastness above 90 percent). However, the level of the reduction of the ink density on the

image was much smaller than in the case of cationic PVOH. Water fastness for both systems levels off after 0.5 -1 hours.

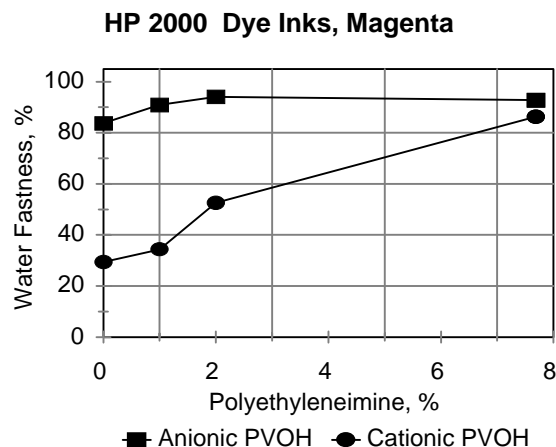


Figure 4. Magenta ink water fastness of as a function of polyethyleneimine concentration.

Both systems have two types of cationic sites able to bind anionic dyes: cationic groups on the surface of urethane latex particles and protonated amine groups on the chain of polyethyleneimine. In addition, there are some cationic groups on the PVOH chain in the System 4. Some of these cationic sites on the urethane latex and PEI are engaged in the electrostatic bond formation with carboxylic groups of anionic PVOH in the System 3. If water fastness presumably is proportional to the concentration of cationic sites in the formulation, System 4 should have higher level of water fastness than System 3. Apparently the coating itself should be water-resistant in order to maintain the integrity of the image receiving layer immersed in water. Coating containing anionic material resembles an interpenetrating network stabilized through electrostatic interactions between anionic groups of PVOH and cationic groups of polyurethane. Subsequently, this combination of resins performs as one unique compound. In the contrary, System 4 composed of cationic resins is less water-resistant because it cannot have this type of interactions to increase the integrity of the coating. Water fastness of System 4 is solely due to the binding of anionic dyes by cationic sites.

### Polyvinyl Alcohol/Polyurethane Ratio

The dependence of gloss on printed areas with pigmented inks, and water fastness with dye inks on the type of polyvinyl alcohol, lead to two new sets of experiments. The ratio of polyvinyl alcohol to cationic polyurethane was studied in broad range from 10:1 to 1:1. Anionic and cationic polyvinyl alcohol were used again in the study.

The data presented in Figures 5 & 6 show that for all tested ratios of secondary colors was lower than primary colors. The difference between primary and secondary colors was reduced with the change in the ratio of

PVOH/PUR from 10:1 to 1:1 for both polyvinyl alcohols. At the ratio of PVOH/PUR 1:1 the difference in gloss between secondary and primary colors was 10-15 points only, while at the ratio 10:1 the difference was nearly 30-40 points. Systems with anionic polyvinyl alcohol gave higher gloss with pigmented inks than cationic polyvinyl alcohol especially in the case of primary colors. It is worth mentioning that there were no differences in the gloss readings between dye based inks for Systems 1 and 2. Interactions between dye based inks with the resins of the coatings are not as pronounced as in the case of pigmented inks.

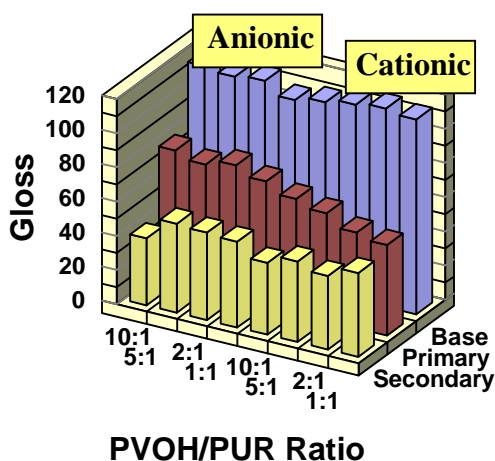


Figure 5. The effect of PVOH/PUR ratio on gloss for HP 2000 printer with pigmented inks

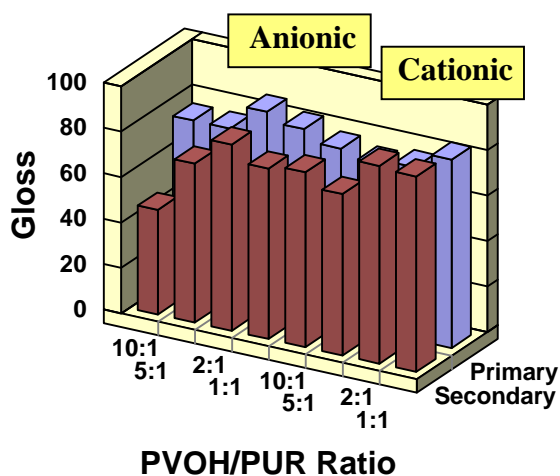


Figure 6. The effect of PVOH/PUR ratio on gloss for EnCad Nova Jet PRO printer with pigmented inks

The gloss readings of the final product generally depend on the gloss of the base substrate and the coating. In the case of the printed area, the change in coating morphology due to interaction with ink will have an effect

on the gloss. It is also not necessarily true that a mixture of resins which yield clear glossy films if coated individually will also give glossy coatings when combined in a coating formulation. There are a few factors which might decrease the gloss of the ink jet coating. First, the most obvious is the interaction between resins leading to the formation of insoluble polymer associates. The combination of these associates with other non-reacting resins of the mix results in a coating with uneven optical density and reduced gloss. The second factor is the phase separation of resins in the coating during the solidifying process. Non-compatible polymers form their own microphases in the coating and reflect light differently.

The differences between the performance of dye-based inks and pigmented inks on the same medium are due to the complexity of the composition of the pigmented inks. Pigmented inks are dispersed and remain as a stable suspension in water through the variety of polymers employed. Apparently, the interaction of polymers in the pigmented inks with the resins of the ink jet coating changes locally the structure and surface of the coating which results in the different light scattering properties of the printed area as noted previously.

This effect is more pronounced in the case of secondary colors because that area takes at least a double amount of inks in comparison to the area of primary colors. Subsequently, the fact of the ink-coating interaction can be monitored by changes in gloss.

It is important to note that the degree of interaction (e.g. gloss reduction) is dependent on the chemistry of both coatings and inks. For instance, the gloss of secondary colors was always lower than gloss for primary colors in System 1 with EnCad and HP pigmented inks. System 2 followed the same trend with HP inks but in the case of EnCad inks there was no difference in gloss readings between secondary and primary colors.

Results supporting the hypothesis of ink-coating interactions were obtained in studies of gloss changes at different pH of the coating fluids. The change of pH did not have an effect of the base gloss. System 1 responded to the gradual reduction of pH by increased gloss readings for both primary and secondary colors for both EnCad and HP pigmented inks. On the contrary, there were no changes in gloss for System 2. The increase in proton concentration would not change any functional group in System 2 where PVOH is cationic. On the other hand, the PVOH in System 1 is anionic and the amount of negative charges is dependent on pH. A decrease in pH reduces the amount of negative charges in the system, subsequently, increasing the possibility of (ink polymer/coating resins) interaction.

#### Cracks versus Dry Time with Pigmented Inks

If the ink-receiving layer consists of polymers with high water absorption capacity like polyacrylic acid, polyvinyl pyrrolidone, polyvinyl alcohol, and cellulose derivatives, the printed images will dry fast (1). The ability to absorb water depends on the hydrophilicity of the functional groups of these polymers. Water molecules from

the ink would be readily accommodated if those functional groups were available to them. The water absorbing capacity of the same polymer would be dramatically reduced if the functional groups were engaged in bonding with other functional groups. Subsequently, coating consisting of resins capable of forming too many bonds with each other would have long dry time characteristics in comparison with the coating where polymers do not react.

**Table 2 Print quality of System 5 coated on different substrates. EnCad Nova Jet PRO and HP 2000 printers with pigmented inks.**

Substrate	HP UV inks			EnCad GO inks		
	Dry time, sec	Print quality		Dry time, sec	Print quality	
		Bleed	Cracks		Bleed	Cracks
PET film	303	0.5	C	165	4	E
Photobase	259	1	B	170	4.5	E
Cast paper	60	0	B	60	1.5	C
Matte paper	46	0	C	60	1	C/E

<sup>1</sup>-rating scales for intercolor bleed and degree of cracking are the same as in Table 1.

In order to study the effect of dry time on the image quality with different type of inks System 5 (PVOH:PUR:PVP was 2:1:0.3) was coated on four substrates having different smoothness and porosity: PET film, polyethylene coated paper, glossy cast coated paper and matte paper. They were printed with two sets of pigmented inks and print quality results are presented in Table 2

The drying time of media with the sealed surface was longer than for products with the porous ones. Cast coated and matte coated paper base products had one order magnitude shorter dry time than polyester film and photobase. EnCad pigmented inks GO have 1-2 minutes shorter dry time than HP pigmented inks on impermeable substrates. Fast absorption of the ink's fluid by porous substrates did not allow them to spread on the surface. It reduced greatly intercolor bleed. For the EnCad printer the bleed rating went down from 4-4.5 to nearly no bleed situation on matte paper (rating 1). The difference among media was less visible for HP inks that have much lower intercolor bleed.

All coated samples printed on HP 2000 printer with pigmented inks cracked. No significant difference on degree of cracking was observed in the case of HP pigmented inks as in the case of intercolor bleed. In contrast, prints made using EnCad pigmented inks performed well on the products with substrates as polyester film and photobase but there was severe cracking of images on the paper base products.

The rule "the shorter the dry time the better" apparently is not true all the time. It should be pointed out what types of inks are used in the printing device. As it is illustrated the same formulation coated on several types of bases having different degree of porosity exhibits different print quality with EnCad GO pigmented inks. Prints made on samples with shorter dry time have cracks in the solid ink fill areas. In this case the rate of water/solvent absorption was so fast that the pigments were separated from their carrier and flocculated with each other. The latter resulted in uneven distribution of inks on the coating, which caused the cracking effect. This points to a clear indication that there is a certain limit for reducing drying time in the efforts to develop a universal medium for all types of inks and printing devices.

## Conclusions

The paper discussed several factors influencing the design of ink jet media. The type and charge density of ionic polymers in the coating has to be tightly controlled in order to prevent phase separation. Interactions between polymers in the coating could increase water fastness of ink jet coatings. Short dry time can lead to cracks' formation of ink jet receiving media printed with pigmented inks. The gloss of media can be affected by pH of the coating.

## Reference

1. Yuan S., Sargeant S., Rundas J., Jones N., Nguyen K., The development of receiving coatings for ink jet imaging applications, *13<sup>th</sup> Intl. Conference Digital Printing Technologies*, Seattle, WA, pp. 413-417 (1997)
2. Niemöller A. and Becker A., Interactions of ink jet inks with ink jet coatings, *13<sup>th</sup> Intl. Conference Digital Printing Technologies*, Seattle, WA, pp. 430-436 (1997)
3. Lavery A. and Provost J., Color-media interactions in ink jet printing, *13<sup>th</sup> Intl. Conference Digital Printing Technologies*, Seattle, WA, pp. 437-442 (1997)
4. Fryberg M., Hofmann R., Brugger P.A., Permanence of ink jet prints: A multi-aspect affair, *13<sup>th</sup> Intl. Conference Digital Printing Technologies*, Seattle, WA, pp. 595-599 (1997)

## Biography

Khizyr Khoultaev is a research chemist with Arkwright, Inc. since 1997. He holds BS (1987) and PhD (1991) degrees in polymer chemistry from Moscow State University. Khoultaev conducted a research on papermaking chemistry being a post doctoral fellow at the University of British Columbia (1995-1997). Fields of interest include interpolymer complexes, polymer - colloidal dispersion interactions, papermaking chemistry, specialty coatings.