

Influence of Polymer–Polymer Interactions on Properties of Ink Jet Coatings

Khizyr Khoultschaev[▲] and Tom Graczyk[▲]

Arkwright, Inc., Guilford, Connecticut

The main properties and a design concept of modern wide format display graphic media are presented. It is stated that the development of ink jet media requires a detailed understanding of the basic interactions within the materials used in the ink jet receptive coatings. Theoretical and practical aspects of the consequences of polymer–polymer interactions in ink jet receiver coating are discussed. It is shown that the charge density on the chain of the macromolecule has an influence on the formation of soluble and insoluble aggregates in the coating mixtures. Several examples are presented how the type of modification and charges of polyvinyl alcohol will have an effect on print quality and waterfastness. The effect of the ink jet formulation components' ratio on prints quality, image gloss and waterfastness is discussed.

Journal of Imaging Science and Technology 45: 16–23 (2001)

Introduction

Small format color ink jet printing is well-established technology in the office environment. The newer, and potentially broader, application for the ink jet technology is that of wide format printing. Large format ink jet printing is used by service bureaus and quick printers where the most important factors are delivery time and limited amount of copies. The prints are used in applications such as posters, billboards, mural and floor graphics, points of purchase, and service.

Small size enterprises such as service bureaus use at least a dozen different media. The largest volume of media type is photo-based stock followed by coated woodfree papers. The last one is growing rapidly at the expense of photo base. Coated woodfree stocks and cast-coated papers are less expensive than a photo base stock, but when laminated, achieve nearly the same results. This is what is driving the growth in the coated woodfree market. There are many types of films, including white opaque and transparency films. Back lit films are the most growing segment. Polyvinyl chloride film is used for outdoor applications in conjunction with pigmented inks providing weatherability of printed images. Canvas and art papers are very popular for art reproductions.

Wide format display graphic media should give excellent image quality and at the same time have capability to absorb a high amount of ink. Additionally, color brilliance and fidelity, freedom from surface dusting and color rub-off, instant drying and more consistent quality should characterize images over the wide range of humidity normally encountered during the printing. As often happens, one set of qualities can be obtained only at the expense of another, thereby making it difficult to obtain all of the required qualities.

Commercially available ink jet recording media are used frequently for outdoor applications. The improvement in light fastness is achieved by application of pigmented inks. In recent years, significant progress has been made in expanding the color gamut of pigmented inks to be similar to dye-based inks. However, due to the nature of pigmented inks and method of water dispersion preparation, they behave differently on an ink jet receiving substrate.^{1–3} The challenge is to develop media with significant ink immobilization and good lamination properties, both economically and with ease of manufacture. Ultimately, ink jet products are sought to work equally well on a broad range of printers, using both pigmented and dye-based inks. Customers exposed to different printing systems and types of inks would favor universal media compatible with all ink jet printing devices and inks.

The design of ink jet receiving layers requires a detailed understanding of basic interactions between ingredients 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.⁴ Unfortunately, it is not always

Original manuscript received March 15, 2000

▲ IS&T Member

Supplemental materials—Figure 2 can be found in color on the IS&T website (www.imaging.org) for a period of no less than 2 years from the date of publication.

©2001, IS&T—The Society for Imaging Science and Technology

possible to find a commercially available resin with more than two or more desired functions.

Any classical water and light fade resistant ink jet formulation, described in the patent literature consists of silica type pigment, resin binder(s) and dye mordant. An ink receiving layer must have a pigment and a dye mordant to accommodate dyes in such a way that they will not be washed out from the printed areas when the imaged product is exposed to excess water. In general, the presence of a pigment in the formula also increases the UV resistance of the coating.⁵⁻⁸ Polymeric resins bind pigment particles together and facilitate molecular diffusion of ink vehicle (water and organic solvents) into the coated media. The ink receiving layer may contain one or more water-soluble and water dispersible polymers. Suitable examples of water soluble binders include regular and modified polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid, polyacrylamide and their copolymers, methylcellulose, cellulose derivatives, and gelatin.⁹⁻¹² Water dispersible resins include polyacrylates, polymethacrylates, polyurethanes, and polyvinyl acetate.

Different polymer binders have different water absorption power. Water absorptivity is dependent on their structure, hydrophilicity of the functional groups and molecular weight. Because the ink-medium interaction is the main driving force for molecular diffusion of ink vehicle into the coated media, the selection of polymer binders in the design of receptive coating is very important.

Development of water, light fade and scratch resistant media requires coatings utilizing several ingredients frequently not miscible. In the following sections, we will discuss how the interactions between different chemicals in the ink jet formulation would influence the coating process and final properties of the media.

Experimental

Materials

The 4 mil gauge Mellinex clear polyester film from ICI was used as the base for model coatings. Both sides of the film were previously primed with a water receptive primer to accept the aqueous solutions. Other films used were 7 mil gauge polyethylene extrusion coated photobases with and without subbing from Felix Schoeller Technical Papers Inc. Subbing is a thin layer of resin(s) on the surface of photobase for promoting the application of waterborne formulations on this substrate. Both grades have a certain amount of polyethylene on the backside to compensate the possible curl after the ink jet coating application.

Two types of papers were used as a coating base: 105 g/m² matte paper from International Paper and 168 g/m² cast coated paper from Champion International. Matte bond paper is an alkaline sheet with HST of about 180 sec at 85% reflectance and Sheffield smoothness of 60 cc/min. Cast coated paper's Sheffield smoothness was 32 cc/min.

Formula Preparation

Batches of about 250 g size were prepared for each formulation. The ingredients were added slowly one by one, and blended using a high torque laboratory mixer with RPM display. The blend was gently mixed subsequently by magnetic bar to prevent settling.

For example, System 1 mix was prepared as follows: 60 g of a 10% solution of anionic modified polyvinyl alcohol¹³⁻¹⁴ was mixed with 2.72 g of polyvinyl pyrrolidone (K-90, supplied by ISP). To prevent polymer complex formation and precipitation, 2.0 g of cationic polyurethane was added drop-wise during the intense mixing. Water

was added to adjust concentration and viscosity. The mixture was stirred for an additional 20 min. The desired pH of the formulations was maintained by addition of hydrochloric acid (36% conc.) or ammonia and measured using a combination pH electrode. Low shear viscosity of each coating formulation was measured at 60 rpm using a Brookfield Synchro-Lectric Viscometer.

Sample Coating

All coating trials were performed on the Laboratory Band Coater. The machine coating speed was set up to match the best drying conditions. Meyer rods of 24 – 65 gauge were used to achieve the desired coat weight. The coated substrate was dried with hot air by passing over the drying head 2–3 times to remove the water and induce cross-linking. In some experiments, IR heating was also applied. Band coatings were done on approximately 10 in. wide by 8 ft. long loops of substrate. The coated web was cut into 8.5 × 11 inch size sheets for printing. The dry coat weight range of the ink jet layer was 8–10 g/m².

Printing Quality Test

Microsoft Power Point™ software was used to develop the pattern of three primary (cyan, magenta, yellow) and three secondary colors (blue, red, green) and black. This pattern was used to evaluate coated media. Large rectangular shaped prints were used to evaluate mottle. Overlapping color strips revealed the intercolor bleed (if any). Secondary color strips along the paper were used to quantitatively evaluate the dry time.

The coated samples were imaged on several wide format printers: EnCad Nova Jet PRO (aqueous dye inks Graphic Standard (GS) and pigmented Graphic Outdoors (GO)) and HP 2000 series (dye and pigment based inks) or their equivalents. All of the printings were done at TAPPI standard conditions of 72°F and 50% RH. Mottle, background and inter-color bleed, feathering, and uniform color fill were evaluated visually using a rating scale of 0–5, where 0 is the best. Degree of cracking of printed images with pigmented ink was rated by resemblance to images in Fig. 3, below. Other parameters such as color density, dry time and water fastness were expressed in actual numbers.

Dry Time Test

The dry time was estimated as follows: images were left to dry after printing for a given time (depending on the experiment), namely 5, 4, 3 or 2 min. After that the strip test was performed. The printed sheet was fixed on the board having 45 degree slope. The 2.5 × 11 inch strip of Oce 3 mil Symmetrical Double Matte Film was placed on top of the color cells reserved for the dry time test. Immediately following, a 1 kg weight was slid over the strip from top to bottom. The times corresponding to the furthest point showing offset on the strip for the red, blue and green colors were recorded. The overall dry time was the sum of the time allotted for drying after printing and the time corresponding to the ink offset on the strip.

Water-Fastness Test

Three primary colors and black ink were evaluated quantitatively in the water-fastness test. Strips of tested media with printed 2 cm × 2.5 cm rectangles of cyan, magenta, yellow and black inks were immersed in deionized water. Samples were not disturbed, and water in the test beaker was not stirred during the test. The optical density before and after the test was measured

TABLE I. The Interaction of Several Cationic Polymers with Anionic Polymers of Different Charge Densities

Name	Cationic Polymer		Polyacrylic Acid		Anionic Polyvinyl Alcohol	
	Relative Charge Density [§]	Molecular Weight	pH of Mixture	State of Mixture	pH of Mixture	State of Mixture
copolymer of DADMAC*	++++	Low	2.5	No precipitation	4.2	No precipitation
Cationic PVA	+	High	2.6	Precipitation	6	No precipitation
copolymer of DADMAC*	+++	Medium	1.8	Precipitation	5	No precipitation
Cationic polyurethane	++	NA	2.6	Precipitation	5	No precipitation
Polyethyleneimine	++++	High	2.8	Precipitation	3	No precipitation
VP-co-DEAMEMA [†]	++	High	2.6	Precipitation	6	No precipitation
VP-co-MAPTAC [‡]	+++	High	2.4	Precipitation	6	Coacervate

* copolymer of diallyldimethyl ammonium chloride (DADMAC)

[†] copolymer of vinyl pyrrolidone (VP) with quaternized diethylaminoethylmethacrylate (DEAMEMA)

[‡] copolymer of vinyl pyrrolidone (VP) with methacrylamidopropyl trimethylammonium chloride (MAPTAC)

[§] relative charge density: "++++" corresponds to highly charged polymers (more than 70% of monomers have charges); "+" is the case when the amount of charged monomers is not more than 5 %

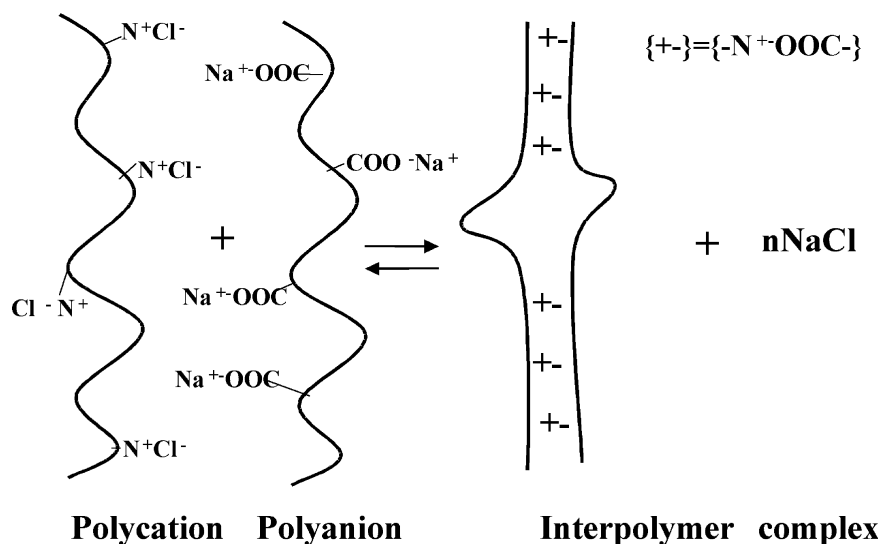


Figure 1. Reaction between oppositely charged linear polymers.

using a Macbeth TR927 densitometer. Water fastness was determined as a percentage of the optical density of inks left on the medium after the test as compared to their initial densities. Samples were tested for 0–5 hours water fastness dependent on the experimental design.

Gloss Measurement

Surface gloss was measured using a portable Micro Tri-Gloss Meter (BYK-Gardner) according to the standard procedure. Readings were taken at 85° along the machine direction for all tested materials. The measured gloss of coated and clear polyester film on unprinted areas was, in most cases, above 100 units due to partial reflection of the light by the internal surface(s) of the film.

Results and Discussion

Polymer–Polymer Interactions

Development of water and light fade resistant coatings frequently requires blending incompatible materials. Attempts to blend these ingredients could create many problems. We will focus only on those associated with possible interactions between components of the coating mixture. The polymer–polymer and polymer–pigment interactions can be divided into two general

categories: ionic interactions and non-ionic interactions.

Ionic interactions involve oppositely charged polymers and pigment particles. Negative charges are due to the presence of acid groups in the resin structure. Positive charges in most cases relate to the presence of groups with quaternized nitrogen. Reaction between oppositely charged polymers would result in the formation of complexes and complex associates.^{15,16}

Reaction between typical countercharged linear polymers is illustrated in Fig. 1. Polyelectrolyte complex, the product of such reactions, is stabilized by salt bonds formed between anionic and cationic groups of these polymers. The equilibrium of this reaction can be effected by several factors like pH and ionic strength of the surrounding media.

In some cases the complex formation could be followed by precipitation of insoluble polymer–polymer associates. Depending on certain individual properties of blended ingredients (charge density, molecular weight) and mixing conditions (concentration, pH, and ionic strength) complex formation might not cause the solid–liquid phase separation of the system. For instance, if the charge densities on polymer chains of both polymers are low there is no chance of the complex formation. If one polymer is highly charged and another has low

TABLE II. Resin Composition of System 1

Polymer	Ratio
Anionic polyvinyl alcohol	10
Cationic polyurethane latex	1
Polyvinyl pyrrolidone	1

charge density, it is possible to form soluble interpolymer complexes.⁹ Another example of soluble complexes includes a system where the low molecular weight, highly charged polymer, is mixed with the excessive amount (more than 100% by mass) of long chained polymer of high charge density.

Table I summarizes the reaction results of pairs of commercially available resins used in the ink jet coatings. Cationic resins such as quaternary amines, polyamines and cationic polyurethane of different charge density were mixed with polyacrylic acid and polyvinyl alcohol bearing a negative charge. Aqueous solutions of two oppositely charged polymers were mixed at 1:1 mass ratio. Drastic change in turbidity of the system was taken as an indication of the interpolymer complex formation. Recorded pH of the surrounding medium was "as is" for each system, and it was not adjusted. High molecular weight polyacrylic acid (PAA) and modified polyvinyl alcohol of slight negative charge were used in this study.

It can be seen that there is a great difference between these two systems based on the charge density of anionic polymers. Almost all the tested PAA involved systems (high charge density) formed precipitates with polycations of different charge density at their natural pH of the mix. In the contrary, reactions of the same polymers with slightly negatively charged PVA did not yield precipitates. It is obvious that combinations of high charge density resins yielding precipitates cannot be used in ink jet formulations. Furthermore, other resins of the same kind but with moderate or low degree of charges on the polymer chain can be incorporated into the coating. Subsequently, the successful design of ink jet coating can be done by regulating the degree of interactions between polymers in the coating formulation.

Non-ionic interaction between two polymers occurs mostly due to the hydrogen bonding. This type of interaction is strongly dependent on pH. For instance, polyacrylic acid (PAA) and polyvinyl pyrrolidone (PVP) form an insoluble complex stabilized through hydrogen bonding below pH 3.9. Above that pH, PAA and PVP coexist in the solution without creating hydrogen bonds. Consequently, PAA and PVP or their copolymers can be incorporated in the coating formulations above certain pH without a problem of precipitation.

Effect of Coating Fluid pH on Print Quality

Two coatings of the same thickness were made of System 1 composed of resins presented in Table II. It was found that even an insignificant shift in the simple parameter of pH of the coating fluid could cause dramatic changes in the performance of the dry coatings.

First coating mixture had pH = 4.2, and pH of the second fluid was adjusted to 3.5. Samples were imaged using Encad Nova Jet Pro with pigmented GO inks. Copies of actual images are presented in Fig. 2. It can be seen that image made on the product derived from the fluid of pH = 4.2 had an unacceptable intercolor bleed. This print imperfection did not exist on the sample coated with the pH = 3.5 fluid.

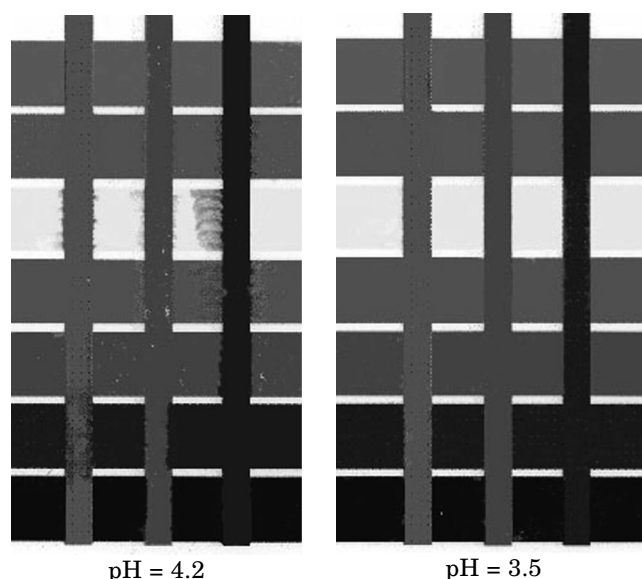


Figure 2. Images made on Encad Nova Jet Pro with GO pigmented inks.

There is a chance of interpolymer reaction between anionic polyvinyl alcohol and cationic polyurethane. Degree of interaction between anionic PVA and cationic polyurethane depends on the pH of the coating fluid. Structure of dry coatings would be different due to the distinct level of PVA-polyurethane interactions. The latter is the reason for significant differences in the performance of the coatings caused by minor pH changes in the original formulation.

Another type of image quality imperfection is so-called "mud cracking": solid color fill areas would have cracks resembling mud cracking. 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) in Fig. 3 are examples of severe crack formation and crack free imaging respectively. Images (B)–(D) correspond to intermediate cases. There is no detailed explanation for the phenomenon of crack formation in images made with pigmented inks. However, it was possible to explore a correlation between crack formation and dry time. Apparent mechanisms for image deterioration are presented in the following section entitled "Cracks versus Dry Time with Pigmented Inks".

Effects of Polymer-Polymer Interactions on Water Fastness

Ratio of polymers and types of functional group charges in their structure can also influence the degree of interactions between polymers. The latter will again affect the performance of the ink jet coatings. Two model systems based on polyvinyl alcohol and cationic polyurethane were studied. System 2 was the same as System 3 except anionic polyvinyl alcohol (PVA) was replaced with cationic PVA. Waterfastness of images made with HP 2000 CP on both coatings was evaluated.

The ability to fix the dyes of the studied systems was strongly dependent on the type of polyvinyl alcohol. Retention of magenta ink was higher in coatings based on anionic PVA in comparison to systems with cationic PVA. The level of waterfastness was high (85% after 1 h, anionic PVA) even without a dye fixative. Samples with PVA had waterfastness of 30% only.

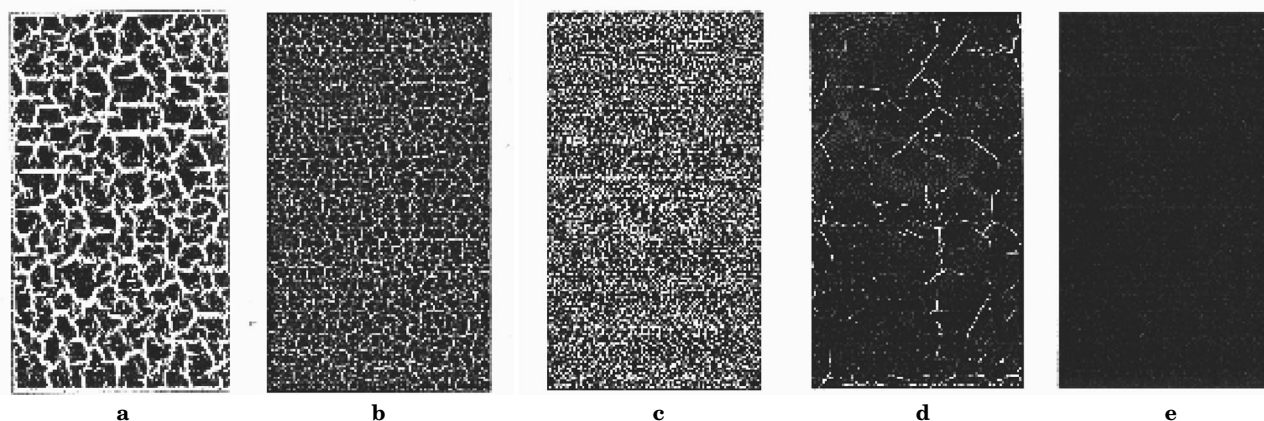


Figure 3. Different types of crack formation patterns encountered for different formulations. Image (E) corresponds to the crack free formulation.

TABLE III. Resin Composition of System 2 and 3

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

Magenta had the lowest waterfastness among the primary colors in most cases and was chosen as an example in the study. The effect of the amount of polyethyleneimine on waterfastness of magenta color is presented in Fig. 4.

The difference in performance between both systems disappeared with the increase in concentration of polyethyleneimine (see Fig. 4). Figure 5 presents magenta ink waterfastness in time for both systems with one percent of polyethyleneimine. The ability to retain inks decreased steadily and reached 50 percent of initial value after 15 min for System 3 with cationic polyvinyl alcohol. There was also some diffusion of inks from the coating with anionic PVA (System 2) in the first minutes after immersion in water. However, the level of the reduction of the ink density on the image was much smaller than in the case of cationic PVA. Waterfastness for both systems levels off after 0.5–1 h.

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 also cationic groups on the PVA chain in the System 3. Some of these cationic sites on the urethane latex and PEI are engaged in the electrostatic bond formation with carboxylic groups of anionic PVA in the System 2. If water fastness presumably is proportional to the concentration of cationic sites in the formulation, System 3 should have a higher level of water fastness than System 2. 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 a network stabilized through electrostatic interactions between anionic groups of PVA and cationic groups of polyurethane. On the contrary, System 3 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 3 is solely due to the binding of anionic dyes by cationic sites.

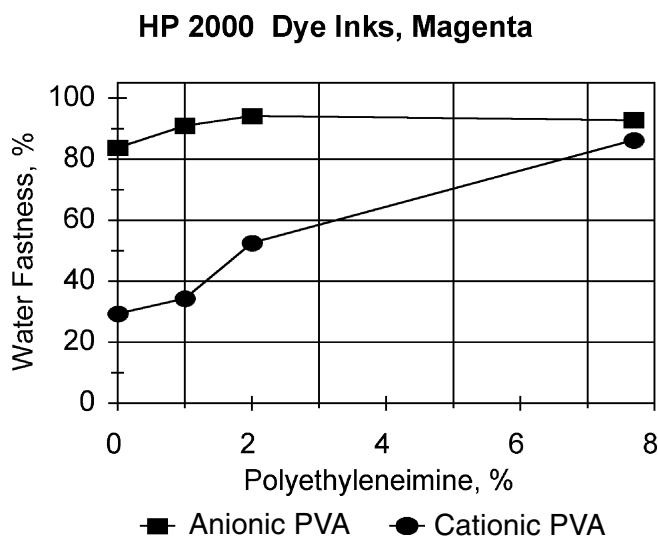


Figure 4. Magenta ink water fastness as a function of polyethyleneimine concentration.

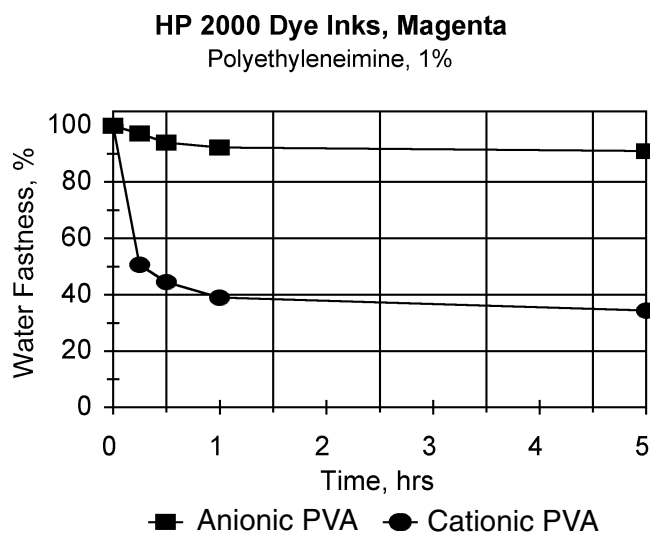


Figure 5. Magenta ink water fastness as a function of time.

TABLE IV. The Effect of PVA/PUR Ratio on Print Quality as Measured by Gloss, Bleed and Cracks; HP 2000 and Encad Nova Jet PRO Printers with Pigmented Inks

Formula	PVA/PUR Ratio	pH	HP 2000 Pigmented Inks					EnCad Pigmented Inks			
			Print Quality			85° Gloss		Print Quality		85° Gloss	
			Bleed	Cracks	Base	Primary Colors	Secondary Colors	Bleed	Cracks	Primary Colors	Secondary Colors
Anionic PVA	10:1	7.2	0*	C†	115	78	39	2	C/E	75	46
	5:1	7.0	1	C	113	74	52	3	C/E	75	70
	2:1	6.6	2	B	115	78	51	5	C	86	82
	1:1	6.6	4	A	108	73	50	5	A	82	75
Cationic PVA	10:1	5.3	0	B/C	111	67	42	1	C	77	77
	5:1	5.2	0	B	114	63	47	0.5	B/C	74	71
	2:1	5.2	0	B	116	56	43	2	E	76	87
	1:1	5.2	0	C	114	53	49	4	E	83	86

* intercolor bleed is rated using 0 to 5 scale where 0 corresponds to "best case, no bleed" and 5 corresponds to "worst case, flooding"

† degree of cracking is rated according to the patterns presented in Fig. 3

HP 2000 Dye Inks, Magenta

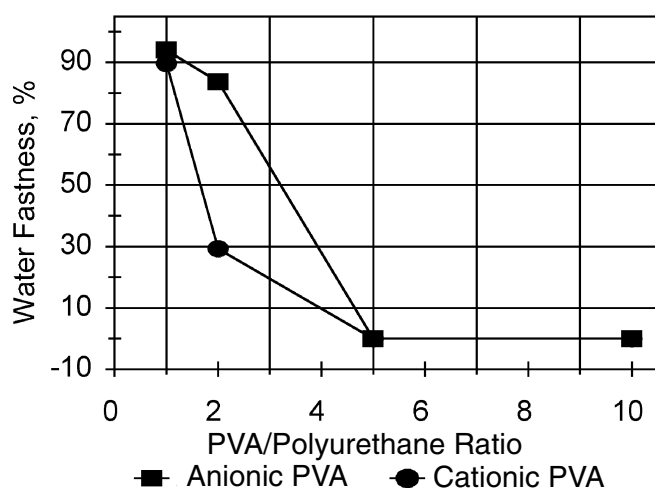


Figure 6. Water fastness of magenta as a function of PVA/polyurethane ratio.

It was important to evaluate the effectiveness of electrostatic interactions in the stabilization of the network. We studied the waterfastness of coatings at different PVA/polyurethane ratio. Waterfastness of magenta ink is plotted against the PVA/polyurethane ratio as shown in Fig. 6.

There was no difference in the waterfastness at 1:1 ratio no matter what type of PVA was used in the formulation. Anionic PVA based coatings had better performance in the range of 1:1 to 5:1. We discussed earlier the case of 2:1 ratio in more detail (Figs. 4 and 5). No difference in ability to fix dyes was found if the PVA/polyurethane ratio was 5:1 or higher. Apparently, electrostatic interactions between components of the ink jet coatings are not the major contributors to the stability of the coating at all the PVA/polyurethane ratios. Stability of the coating is mainly due to the abundant presence of water resistant polyurethane in the formulations (ratio 1:1). In this case, electrostatic interactions do not play the leading role in maintaining the integrity of the coating in water. Electrostatic bonds between the components of the coating became more important when the amount of polyurethane was gradually diminished

(moving from 1:1 to 5:1 ratio in Fig. 6). Finally, coatings would dissolve even in the case of anionic polyvinyl alcohol if PVA was the predominant component in the coatings (ratio 5:1 or higher). The number of electrostatic bonds between anionic PVA and cationic polyurethane are very low and they cannot maintain the integrity of the coating.

Effects of Polyvinyl Alcohol/Polyurethane Ratio on Print Quality

Print quality of studied coatings did not depend on the ratio of resins when dye based inks were used. However, it was found that gloss of images made with pigmented inks was dependent on the type of polyvinyl alcohol and PVA/polyurethane ratio. 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 on print quality such as gloss, bleed and cracks are presented in Table IV. The system pH was measured after the mixing of ingredients and was not adjusted.

Data in Table IV show that gloss of secondary colors was lower than gloss of primary colors for all the tested PVA/PUR ratios. The difference in gloss between primary and secondary colors was diminished with the increase of PUR in the formulation and is the most pronounced for HP 2000 printer. At the ratio of PVA/PUR 1:1 the difference in gloss between secondary and primary colors was 10–15 points only. At the 10:1 ratio 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. For EnCad printer variation between primary and secondary colors is significantly lower and about 5–10 points except for anionic PVA at PVA/PUR ratio 10:1, where the difference was 30 points.

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 not necessarily true that a mixture of resins that yields clear glossy films when coated individually will also give glossy coatings when combined in the formulation. There are a few factors potentially affecting 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

TABLE V. Print Quality of System 4 Coated on Different Substrates. Encad Nova Jet PRO and HP 2000 Printers with Dye and Pigmented Inks

Substrate	Dye GS inks		HP	Pigmented Inks		EnCad GO inks			
	Dry time, sec	Print quality Bleed		Dry time, sec	Print quality Bleed	Cracks	Dry time, sec	Print quality Bleed	Cracks
PET film	567	3	303	0.5*	C*	165	4	E	
Photobase	374	2	259	1	B	170	4.5	E	
Cast paper	237	2	60	0	B	60	1.5	C	
Matte paper base	277	1	46	0	C	60	1	C/E	

* rating scales for intercolor bleed and degree of cracking are the same as in Table IV.

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. Incompatible polymers form their own microphases in the coating and reflect light differently.

Cationic PVA based coatings did not reveal intercolor bleed at any tested PVA/polyurethane ratio when imaged with HP pigmented inks. The level of image cracking was at the same level for different ratio of resins. In the contrary, the higher the polyurethane content in the coatings the worse the intercolor bleed for coatings with anionic PVA. Image cracking also became more pronounced (Table IV) in systems with anionic PVA. The ability to absorb water depends on the hydrophilicity of functional groups of polymers. The water absorbing capacity of the same polymer would be dramatically reduced if the functional groups were engaged in bonding with functional groups of other polymers in the coating. Subsequently, dry time would be longer for systems comprising resins prone to interpolymer bond formation.

For the anionic PVA based system the 1:1 PVA/polyurethane ratio presumably corresponds to the maximum of possible interactions between negatively charged groups of anionic PVA and cationic sites of polyurethane. The maximum interactions could be interpreted as the highest degree of crosslinking in the polymer matrix. Hydrophilic resins absorb less water at higher degree of crosslinking and this explains why, in the case of anionic PVA, containing coatings intercolor bleed was more pronounced at 1:1 ratio. In the case of coatings with cationic PVA, PVA/polyurethane ratio did not have an effect on the intercolor bleed because there were no electrostatic bonds created.

Encad Nova Jet Pro with GO inks applied a significantly higher volume of inks than the HP 2000 CP printer. Intercolor bleed increased with the increase in the polyurethane content in the coatings, even in the case of cationic PVA, when the Encad printer was used for imaging. Ability of coatings to absorb inks was gradually reduced with the increase of hydrophobic polyurethane in the matrix. Cationic PVA based system had the capacity to accommodate inks at any PVA/polyurethane ratio if the imaging was done using HP inks. However, the polymer matrix was no longer able to absorb all the ink when the higher volumes of ink were applied with the Encad printer.

Cracks versus Dry Time with Pigmented Inks

Dry time is one of the major characteristics of ink jet media, usually defined as the time period after printing until there is no ink offset onto another substrate contacting the printed image. There is no concern for cast coated

and coated bond papers because the water absorption power of the base itself significantly reduces the dry time. For other products like photobases, film, drying time is dependent on the chemistry of the coating.

In order to study the effect of dry time on the image quality System 4 (PVA: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. The samples were printed with three sets of inks and print quality results are presented in Table V.

For EnCad GS dye based inks the dry time of the media with the sealed surface was longer than for products with the porous ones. This difference was much more pronounced in the case of pigmented inks. Cast coated and bond paper base products had one order magnitude shorter dry time than coated polyester film and photobase. EnCad pigmented inks GO have 1–2 min 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 significantly the intercolor bleed. For the EnCad printer the bleed rating went down from 4–4.5 to a nearly no bleed situation on matte paper (rating 1). The difference among the coated media was less visible for HP inks that have much lower intercolor bleed. All tested samples printed on HP 2000 printer with pigmented inks cracked. In contrast, prints made using EnCad pigmented inks performed well on the products with substrates such as polyester film and photobase, but there was severe cracking of images on the paper base products.

Pigment mud-cracking on an ink jet receiving layer is a complex phenomenon. It can be dependent on surface roughness, pore distribution, surface chemistry of pigment and ink jet receptive layer. It was found that rate of drying pigmented inks can have an influence on cracks formation

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. Several types of bases having different degree of porosity were coated with the same formula and printed with EnCad GO pigmented inks. Prints made on samples with shorter dry time have cracks in the 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

This article discusses 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. The order of addition of ink jet formulation components is important for coating operations and the performance of the coating itself. Interactions between polymers in the coating could increase water fastness of ink jet coatings and effect print quality. Short dry time can lead to cracks' formation of ink jet receiving media printed with pigmented inks. ▲

Glossary

DEAMEMA	diethylaminoethylmethacrylate
DADMAC	diallyldimethyl ammonium chloride
MAPTAC	methacrylamidopropyl trimethylammonium chloride
PAA	polyacrylic acid
PEI	polyethyleneimine
PVP	polyvinyl pyrrolidone
PVA	polyvinyl alcohol
PUR	polyurethane
VP	vinyl pyrrolidone

Acknowledgment. The authors would like to thank Shailesh Mody and Padma Reddy for their help in the preparation of the experimental data presented in this article.

Reference

1. P. Gregory, Dyes versus pigments: The truth, *Recent Progress in Ink-Jet Technologies*, 276 (1996).
2. R. Work, Color Pigmented Ink Jet Printing for Outdoor Applications, *6th Annual Ink Jet Printing Workshop*, Framingham, MA, Session 22, 1997.
3. S. Sargent, N. D. Behan, D. Atherton, S. Yen, M. Huang, and K. Sun, Polymer Matrix for Ink Jet Media, U.S. Patent 5,700,582 (1997).
4. S. Yuan, S. Sargeant, J. Rundas, N. Jones, and K. Nguyen, The development of receiving coatings for ink jet imaging applications, *Proceedings of 13th Intl. Conference Digital Printing Technologies*, IS&T, Springfield VA, 1997, p. 413.
5. A. Niemöller and A. Becker, Interactions of ink jet inks with ink jet coatings, *Proceedings of 13th Intl. Conference Digital Printing Technologies*, IS&T, Springfield VA, 1997, p. 430.
6. A. Lavery and J. Provost, Color-media interactions in ink jet printing, *Proceedings of 13th Intl. Conference Digital Printing Technologies*, IS&T, Springfield VA, 1997, p. 437.
7. M. Fryberg, R. Hofmann and P. A. Brugger, Permanence of ink jet prints: A multi-aspect affair, *Proceedings of 13th Intl. Conference Digital Printing Technologies*, IS&T, Springfield VA, 1997, p. 595.
8. R. W. Kenyon, Beyond the Black-Novel High Waterfast Dyes for Colour Ink Jet Printing, *Proceedings of 13th Intl. Conference Digital Printing Technologies*, IS&T, Springfield VA, 1997, p. 278.
9. H. Maruyama, K. Kajyani and M. Shiraishi, Paper Coating Agent, U.S. Patent 4,617,239 (1986).
10. T. Sato, N. Fujiwara and A. Kihara, Process for Production Vinyl Alcohol Polymers, U.S. Patent 5,710,211 (1998).
11. S. F. Bedell and M. S. Viola, Ink Jet Transparency, U.S. Patent 4,547,405 (1985).
12. H. Onishi, J. Iida and A. Owatari, Ink Jet Recording Film Comprising Cationic-Modified Polyvinyl Alcohol and Recording Method Using the Same, U.S. Patent 5,662,997 (1997).
13. E. Seno, T. Katayama and H. Miyazaki, Heat-Sensitive Material, U.S. Patent 5,478,792 (1995).
14. K. Haraida and T. Yoshitako, Absorbents with Improved Water Absorbing Power, U.S. Patent 4,251,643 (1981).
15. V. A. Kabanov, A. B. Zevin, M. I. Mustafaev, and B. A. Kasaikin, *Polymeric Salts and Ammonium Salts*, E. J. Goethals, Ed., Pergamon, Oxford, 1980, p. 173.
16. A. B. Zevin and V. A. Kabanov, *Usp. Khim.* **51**, 1447 (1982).