LAMINATION STUDY OF INK JET MEDIA

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ABSTRACT

The lamination of modern wide-format ink jet media is a challenge today. Many commercially available ink jet media have excellent print qualities but are difficult to laminate. The development of ink jet media requires a detailed understanding of the interactions of the laminating film and its adhesive layer, the ink-receiving layer, and the inks absorbed by the printing media. Generally, unprinted areas have better adhesion to laminating films than printed areas. The lamination of secondary colors is often more difficult than that of primary colors. Images printed with pigmented inks are often much harder to laminate compared to images printed with dye-based inks.

We show that depending on the composition of the coating, unprinted areas can have lower adhesion than printed ones. We found that the type of polyvinyl alcohol in the ink jet receiving layer could have a significant influence on the adhesion of the laminating film. Partially hydrolyzed polyvinyl alcohol has better adhesion to unprinted areas than that which is fully hydrolyzed. On the other hand, fully hydrolyzed polyvinyl alcohol provides better adhesion with primary and secondary colors.

INTRODUCTION

Digital imaging and ink jet printing are two important factors influencing revolutionary changes in the graphic art industry. Wide-format ink jet printing (24-in. wide and greater) is used by service bureaus, design studios, photo shops, and quick printers, where the most important factor is delivery time per copy produced. The ink jet prints are used in applications such as posters, billboards, murals, and floor graphics *(1)*.

The print-for-pay industry uses at least a dozen different media. The largest-volume media type is photo-based stock followed by coated bond. The latter is growing rapidly at the expense of photo base. Coated bond stocks and photo-like papers are less expensive than a photo base stock but, when laminated, achieve nearly the same results as more expensive materials. This is one of the features driving the growth in the coated bond market. There are many types of films, including white opaque and transparency film. Backlit film is a fast-growing segment. Vinyl film is used for outdoor applications in conjunction with pigmented inks, which provide weatherability. Canvas and art papers are very popular for artists' prints.

Wide-format display graphic media should be designed to provide excellent quality of images and, at the same time, have the capability to absorb a high amount of ink. Additionally, color brilliance and fidelity, freedom from surface dusting and color ruboff, instant dry time, and consistent quality should characterize images over the wide range of humidities commonly encountered during 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 requisite qualities *(2–4)*.

The typical water- and light-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 dye mordant to accommodate dyes in a way that they will not be washed out from the printed areas when the coating is exposed to an excess of water *(5)*. In general, the presence of pigment in the formulation increases the ultraviolet (UV) resistance of the coating *(6)*. Pigment must also be included in the formulation for bond paper coatings to smooth the uneven structure of the paper surface. The polymeric resins are also essential to bind pigment particles, facilitate molecular diffusion of the ink vehicle into the coating media, and absorb ink, which contains 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, the quality of prints, and the drying properties of inks. This ink-receiving layer may contain one or more water-soluble and water-dispersible polymers.

Polymer binders have a different water absorption power. Water absorptivity depends on polymer structure, hydrophilicity of the functional groups, and molecular weight. Furthermore, water hydrates various binders and influences the interaction of polymer binders with both liquid and vaporous water. Additionally, the choice of the binder will be governed by the degree of ink flux from the printing device *(7).* Since the interaction of inks with medium is the main driving force for molecular diffusion of an ink vehicle into the coated media described here, the selection of polymer binders in the design of the receptive coating is very important.

Laminating of the printed image is employed in most ink jet printing applications. At least 80% of ink jet prints are laminated *(8).* Most media printed with dye-based inks are not water resistant and have a tendency toward fading in the presence of light. Laminating, especially encapsulating of prints, is necessary to protect against spillage, rain, and UV light. Laminating also provides abrasion protection and allows achieving the desired gloss level and visual effects *(9, 10).*

Generally, there are two types of laminates: thermal and pressure-sensitive. Pressure-sensitive laminating films used in cold lamination are much more expensive than thermal laminating films. These types of laminating films are usually applied for mounting to boards and laminating specialty finishes. Thermal laminating films are more commonly employed in the wide-format ink jet industry due to the significant cost advantage. The hot laminating films are 4–5 times less expensive than cold laminating ones. However, the hot laminating application to ink jet media is a great challenge because few available ink jet photo papers can be laminated by thermal film or hot lamination.

The development of media for outdoor applications requires understanding the interaction between the ink jet receiving layer and laminating film adhesives. In the following sections, we compare five commercially available laminating films and their adhesion to photo paper, imaged with several dye and pigmented inks. Four commercial photo papers were also printed with different inks and subsequently laminated with two types of films. The strength of the lamination adhesion was studied for single layers of polyvinyl alcohol having different degrees of hydrolysis and with other common polymers used in ink jet technology to define the parameters governing laminating properties. The effect of the pigment/binder ratio and coating weight of the ink jet receptive layer on the final properties of the media and thermal lamination was also investigated.

EXPERIMENTAL

Materials

Substrates: The 7-mil-gauge polyethylene extrusion-coated photo base was used as a base for model coatings. The base had a certain amount of polyethylene on the back side to compensate for the possible curl after ink jet coating application. The photo base was corona treated to achieve a surface tension of about 42 dynes/cm before the ink jet receptive coating was applied. Matte paper (105 g/m^2) was also used as a coating base. It is an alkaline sheet with an HST of about 180 seconds at 85% reflectance and a Sheffield smoothness of 60 cm^3/min.

Laminating films: Five different 3-mil-thick, glossy films recommended for lamination of wide-format ink jet media were tested in the study. DigiSeal UVI and Opti Clear were purchased from USI, Quality DigiGuard from QUALITY Mounting & Laminating Systems, and Jet Guard and Thermashield from Seal.

Formulation preparation

Batches of about 250 g were prepared for each formulation. The ingredients were added slowly one at a time and blended using a high-torque laboratory mixer. Most polymers were premixed with water to prevent precipitation or coacervation. Subsequently, the blend was gently mixed with a magnetic bar to prevent changes in the sample.

Printing Quality Test

An 8.5x11-in. imaging pattern was developed to evaluate the printing quality of the ink jet media. In the pattern, two sets of primary color squares were designed to test water-fastness of the printing media. Large rectangular areas of three primary colors (cyan, magenta, and yellow), three secondary colors (blue, red, and green), and black were used to check banding and mottle of the printing media. Overlapping narrow color strips revealed any intercolor bleed.

The ink jet media were imaged on several wide-format printers: ENCAD Croma24® with dye-based inks (GS), Nova Jet PRO® [aqueous dye inks (GA) and pigmented inks (GO)], and HP 2000® series (dye- and pigment-based inks) or their equivalents. All prints were done at TAPPI standard conditions of 72°F and 50% RH. Print quality was evaluated visually (subjectively) for mottle, background and intercolor bleed, feathering, and uniform color fill using a rating scale of 0 to 5, where 0 is the best rating. Other parameters, such as color density and water-fastness, were expressed in actual numbers.

Prints for lamination test
A 9x12-in. imaging pattern was used for testing the laminating properties of the ink jet media. Three primary and three secondary color strips (1 x 10 in.) plus a nonprinted strip (1 x 10 in.) were designed and paralleled to determine the peel strength of each color strip and the nonprinted area printed parallel to each other.

Water-fastness determination
Three primary colors and black ink were evaluated quantitatively in the water-fastness test. Strips of tested media printed with 2x2.5-cm rectangles of cyan, magenta, yellow, and black inks were immersed in deionized water. The optical density of the printed area before and after the test was measured using a Macbeth TR927 densitometer. Water-fastness was determined as a percentage of the optical density of the inks left on the medium after the test compared to their initial densities.

Dry and wet rub
Dry rub was measured by using 1x3-in. samples of white laser copy paper. The strip of paper was rubbed three times along 2x3-in. rectangles of the secondary colors blue, red, and primary black. The degree of ink transfer to the rubbing paper was then evaluated. The average of the secondary colors was reported. A similar 0–5 rating system was used.

Wet rub was measured in a similar way, but before the test, a drop of water was placed on Whitman filter paper for better water absorption. The color rectangles were rubbed five times, and the degree of coating degradation was reported.

Lamination
Before lamination, a 1x8.5-in. strip of paper was placed on top of the printed test pattern to cover all colors. This procedure allowed us to initiate the peel test later. Lamination of all samples was performed on commercially available laminators: MRL42 from USI or Falcon 36 from GBC Pro-Tech. The optimum lamination temperature was selected experimentally for each laminating film. Lamination was run at 0.48 m/min.

Peel Strength Determination
Specimen preparation: Eight 1x10-in. strips were cut from each laminating test sample using a specimen cutter.

Machine Testing: A TLMI Release and Adhesion Tester from Testing Machines Inc. was used to determine the peel strength of all specimens. The peel strength test was performed at a 180° angle and a rate of 12 in./min *(11)*. Average peel strength was reported in g/in. At least two specimens of each color from the same media were tested. The tester can detect peel strength from 0 to 2000 g/in. If the peel strength value was greater than 2000 g/in., the specimen cannot be delaminated, and coating layer failure occurs. Values greater than 2000 g/in. were simplified and taken as 2000 g/in. in calculating average peel strength for the primary and secondary colors. For simplicity, adhesion values for only the primary and secondary colors were reported. The comparative laminate adhesion strengths of ink jet media were evaluated by this method.

The laminating ratings were defined as follows and are similar to TAPPI Test Method T 539 *(12)*, but the best laminating rating was considered to be 0 instead of 5. See **Fig. 1.**

- **Excellent** means that lamination cannot be separated by a very strong peel (greater than 2000 g/in.); otherwise the peel will damage the coating layer.
- **Very good** indicates that lamination can be separated by a very strong peel (at 1500–2000 g/in.), and the coating will remain acceptable.
- **Good** means that lamination can be separated by a strong peel (at 1000–1500 g/in.).
- **Fair** indicates that lamination has a considerable resistance to peel, and the peel strength is 500–1000 g/in.

- **Poor** means that lamination has a slight resistance to peel, and the peel strength falls to 0–500 g/in.
- **Unacceptable** indicates that lamination has no resistance to peel, and the peel strength is about 0 g/in.

The rating does not indicate the difference between primary and secondary colors. We estimate that peel strength for secondary colors needs to be about 1000 g/in. to achieve long-lasting adhesion to the printed substrate. The adhesion to unprinted areas, which are on the edges of printed area, should be higher due to direct exposure to delaminating forces. The peel strength should be above 1500 g/in. to have very good adhesion.

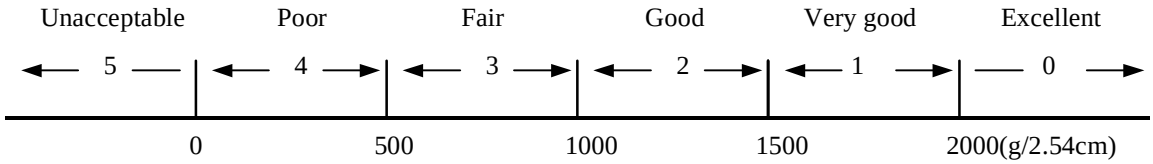

Figure 1. Relationship between peel strength and adhesion ratings.

RESULTS AND DISCUSSION

Bond Strength and Interfacial Adhesion

The bond strength of a laminate essentially depends on both the adhesive and the cohesive strength of the laminating system *(13–15).* Peel strength of the laminate is typically determined by debonding the laminate using a T-peel test *(12, 16).*

Figure 2 presents several possible modes of failure:

- Debonding of the ink jet underlayer from the substrate
- Debonding of the ink jet top layer from the underlayer
- Debonding of the adhesive from the ink jet layer
- Debonding of the adhesive from the laminating film
- Substrate or film failure (tear).

The failure of the laminate will occur at its weakest link. It is generally desirable to have high bond strength to the substrate, with failure occurring as the adhesive debonds from the ink jet layer.

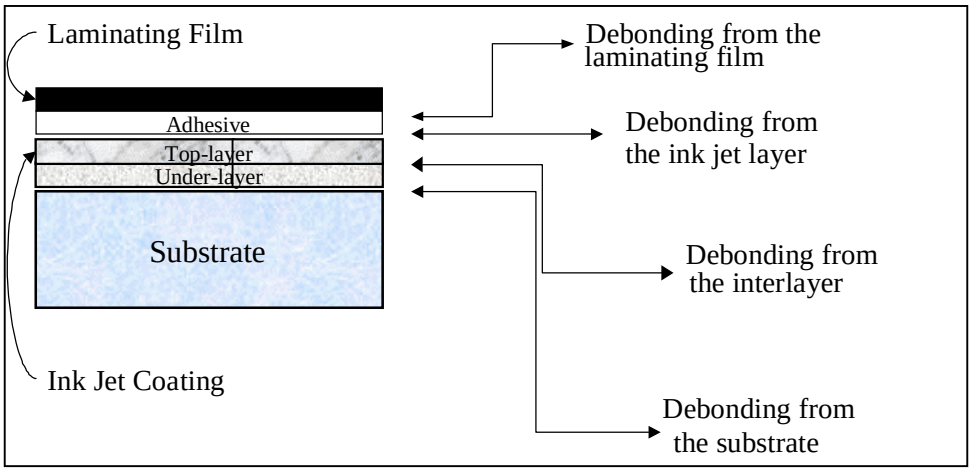

Figure 2. Possible delaminating failures of ink jet–laminated prints.

Peel strength of the laminate system depends on several parameters:

- Viscoelastic properties of the adhesive
- Rate of peel
- Temperature
- Angle of the peel
- Substrate stiffness
- Coat weight of the ink jet layers
- Thickness of the adhesive.

It is desirable to have a strong interaction between the adhesive, the ink jet receiving layer, and the substrate to form stable bonds. The different types of possible interactions include:

- Polar interaction
- Electrostatic interaction
- van der Waals forces
- Chemical bonding.

In ink jet photo paper, the most widely used substrates are quite inert, are nonpolar, and have a low surface energy. The adhesion to the substrate is achieved by applying corona treatment of the base prior to ink jet layer coating *(16)*. The additional use of a primer coat is also common.

Ink jet layers are usually made hydrophilic to absorb aqueous inks. The adhesives of laminating films are hydrophobic with some degree of polarity. The high bond strength of the laminate can be achieved if we understand the parameters governing the adhesion of the laminating film and the ink jet layer. It is important to define the optimum matching of adhesives and the ink jet receiving layer in terms of compatibility. The compatibility of ink jet layers depends on variables such as the polymer composition of the ink jet matrix, the hydrophilicity of the matrix, the pigments, and the surfactant system. In this study, the first three parameters are investigated.

Lamination Temperature

There is some confusion regarding a lamination temperature, although each laminating film has a manufacturer-suggested temperature. Some lamination shops apply a higher temperature than that recommended by the manufacturers for faster lamination. Several commercially available ink jet photo papers printed on the HP 2000CP printer with dye-based inks were laminated with five different films from three manufacturers. The lamination was started at the manufacturer-suggested temperature and then increased in increments of 10°F. Generally, better laminate adhesion was achieved at 20°F above the manufacturer-suggested temperature.

Laminating Films

Three commercial photo papers were printed with HP dye and pigmented inks and EnCad GS dye inks. These were subsequently laminated with five commercially available films from three suppliers. The applied temperature selected according to the previous experiment was expected to result in the best adhesion value for each film. The actual laminating temperature used was about 20°F higher than the manufacturer-suggested temperature, except for film B, which was applied at 185°F.

The results of the lamination study of photo paper I are presented in **Table I.** The films in Table I are placed in the order of manufacturer-suggested sealing temperatures. There is a significant difference between adhesion results, depending on the applied laminating films, printers used, and inks used. Ratings of adhesion to the unprinted areas of the photo papers varied from excellent (0) to poor (4).

Table I. The comparison of adhesion ratings of different commercial laminating films. Commercial photo paper I printed on HP 2000 printer (dye and pigmented inks) and EnCad Nova Jet PRO with GS dye inks and laminated with 3-mil glossy films.

Name		Laminating Film				
		A	B	C	D	E
Suggested Temp	^{o}F	185	185	205	205	220

Real Temp	°F	205	185	220	220	240
Unprinted		0	3	4	0	0
Primary Colors	HP Dye	2	2	2	2	2
Secondary colors		2.5	4.5	4.5	4	4
Primary Colors	GS inks	4	4.5	3	0	1
Secondary colors		5	5	5	5	4.5
Primary Colors	HP UV ink	3	3	4	4.5	2.5
Secondary colors		4	5	5	5	5

All laminating films tested had relatively good adhesion to HP dye primary colors (rating 2), while the ratings for the EnCad inks varied from excellent (D) to very poor (B). Film A provides acceptable lamination to only HP secondary colors (rating 2.5). Delaminating was observed for all other films in graphic-intensive prints in areas where the secondary colors were applied.

Both the HP and EnCad GS dye inks demonstrated better adhesion for primary colors than for secondary colors. Secondary colors are a mixture of two primary colors, and twice the amount of ink is deposited on the photo paper surface. In most cases, the absorption capacity of the coating is insufficient for secondary colors. We assumed that the ink solvents stay on the surface of the ink-receiving layer and reduce adhesion to the laminate. For some ink jet media, yellow inks do not penetrate well and stick to the surface of the media. Yellow ink demonstrated very low peel strength. Consequently, this results in low adhesion for green and red inks, which are comprised of cyan with yellow and magenta with yellow, respectively.

Pigmented inks were the most difficult to laminate. Generally, areas printed with HP pigmented inks showed poorer adhesion than areas printed with dye inks. All tested laminating films have ratings of 2.5–4.5 for primary colors and 5 for secondary colors. The more comprehensive internal study showed that other commercial pigmented inks also performed poorly. Pigment particles in the pigmented inks migrate poorly into the ink jet receiving layer, and they tend to stay on the surface of the media. This results in poor adhesion to the laminate film.

An evaluation of other commercially available photo papers showed that the adhesion rating depends on both the laminating film and the ink jet receiving layer. The order of films from best to worst was different for each photo paper tested. None of the films tested can be considered universal for all inks and media.

Lamination of Commercial Photo Papers

Four different commercially available photo papers were printed on an HP 2000 and an EnCad Nova Jet PRO printer with both dye and pigmented inks. They were subsequently laminated with 3-mil glossy film E at the previously determined optimum laminating conditions.

Table II. The comparison of adhesion properties measured as a peel strength for different commercial photo papers printed on HP 2000 and Nova Jet PRO printers (dye and pigmented inks) and laminated with film E.

Photobase	Printer	Inks	Peel Strength, g/2.54 cm		
			Unprinted	Primary	Secondary
1	HP 2000	Dye	2000	1500	686
		Pigmented		909	0
	Nova Jet PRO	Dye		2000	0
		Pigmented		1535	11
2	HP 2000	Dye	2000	2000	2000

		Pigmented		951	186
	Nova Jet PRO	Dye		2000	72
		Pigmented		549	4
3	HP 2000	Dye	2000	1500	1192
		Pigmented		1863	1540
	Nova Jet PRO	Dye		2000	2000
		Pigmented		1361	1785
4	HP 2000	Dye	18	1413	1477
		Pigmented		573	496
	Nova Jet PRO	Dye		157	1
		Pigmented		1337	1014

Three of the four photo papers tested had excellent adhesion to the laminating film in unprinted areas, with peel strengths exceeding 2000 g/in., as shown in **Table II.** The adhesion to secondary colors was lower than that to primary colors for the first two photo papers. Peel strength ratings for primary and secondary colors cover a broad range—1 to 5. For both printers with pigmented inks, secondary colors had very poor adhesion to the laminate film.

The first photo paper had very good adhesion to most primary colors on both printers. Adhesion to the secondary colors of HP dye inks was marginal, about 680 g/in. The laminating film debonded (i.e., had zero peel strength) from EnCad (dye and pigmented) inks and HP pigmented inks.

The second photo paper showed excellent adhesion to HP dye inks, both primary and secondary, but poor adhesion to HP pigmented inks. This paper also had very good adhesion to primary colors with EnCad dye inks, but secondary colors could be easily delaminated. The use of EnCad pigmented inks resulted in even lower adhesion than HP pigmented inks.

The third photo paper had very good adhesion to both dye and pigmented inks on HP and EnCad printers. The peel strength on the Nova Jet PRO with pigmented inks was in contradiction to the statement that primary colors have better adhesion than secondary colors. For this photo paper, laminate adhesion to secondary colors is higher than to that to primary colors. The discrepancy arose from the limitations of the peel strength tester and the way that the data were treated; this is described in "Experimental." This phenomenon also occurred in the fourth photo paper with HP dye inks.

The fourth photo paper had very unusual properties. This photo paper had no adhesion to the laminating film in unprinted areas. The printed areas had excellent adhesion to the laminate on the HP 2000 printer with dye inks. The adhesion was worse for HP pigmented inks and EnCad dye inks. We assumed that the solvents present in the inks interacted with the ink-receiving layer, softening its surface and making it more compatible with the laminating film. Note that adhesion to EnCad pigmented inks is surprisingly good. This shows that the interaction of inks with the laminating adhesive is still poorly understood.

In general, each ink jet photo paper demonstrated a particular lamination characteristic with different inks. This characteristic essentially resulted from the chemistry and design of the ink jet coating. In most cases, the ink jet media could be well laminated on unprinted areas. Lamination adhesion would be reduced to some extent once the ink jet media were printed with inks. The ink jet media with dye inks demonstrated better lamination adhesion than with pigmented inks because the dye-based inks more easily penetrated the ink jet receiving layer than did the pigmented inks. In light of the ink jet coating design, the ink jet receiving layers absorbed the dye inks and pigmented inks very well. Dye-based or pigmented inks must penetrate the layer to achieve good lamination. Additionally, the ink jet receiving layers must possess a strong bonding ability to the substrate. It is a challenge to design this type of ink jet receiving layer.

Lamination of Primary and Secondary Colors

Ink jet technology uses the CMYK color system, i.e., a system consisting of the four primary colors—cyan, magenta, yellow, and black. The secondary colors—blue, green, and red—are compositions of the primary colors.

Compared to the primary-color inks, twice the amount of secondary-color ink is deposited on the ink-receiving surface. This large amount of ink is not completely absorbed into the ink-receiving layer as is the case with primary colors. With secondary colors, more of the ink stays on the surface of the ink-receiving layer. Consequently, for most of tested ink jet papers, laminate adhesion to primary colors is better than that to secondary colors. **Table III** presents peel strength values of primary and secondary colors for the ink jet receiving layer, optimized for lamination purposes.

In the optimized ink-receiving layer, the laminate adhesion of all primary colors is virtually identical. For photo paper formulations at a coat weight of 5 g/m^2, peel strength is about 1000 g/in. The peel strength of the secondary colors is about 1.55 times lower than that of the primary colors. The adhesion increases with coat weight, and the difference between primary and secondary colors diminishes.

For most commercial products, there is a significant difference in adhesion between primary colors. **Table IV** presents peel strength values for commercial ink jet photo paper I used in several printers. One set of prints was laminated, and another was tested for water-fastness. The prints prepared on the HP printers had the lowest laminate adhesion to yellow. For example, for the HP 2000 printer, the peel strength of black, cyan, and magenta is greater than 2000 g/in., but that for yellow is zero. The black color of the HP 750 printer also has marginal adhesion to the laminate. The adhesion of the primary colors on photo paper I printed with the EnCad Nova Jet PRO printer with GS and GA inks was independent of the type of color and is above 2000 g/in.

Table III. Peel strength (g/2.54 cm) of formulation I at coat weight 5 g/m^2, printed on HP 2000 with dye inks and laminated with film E.

Primary Colors	Peel Strength, g/2.54 cm	Secondary Colors	Peel Strength, g/2.54 cm
Black	1004		
Cyan	1035	Blue	689
Magenta	980	Green	519
Yellow	1107	Red	786
Average	1031	Average	665
Ratio Primary/Secondary	1.55		

The second part of Table IV presents water-fastness data. For this set of experiments, peel strength values of images printed on HP printers correlated well with water-fastness data. That is, primary colors with the lowest water-fastness also had the poorest adhesion to the laminate. For example, the HP 2000 printer water-fastness of black, cyan, and magenta for photo paper I was greater than 70% after 5 hours, while that of yellow was only 11%. The print had no adhesion to this color. Yellow inks were particularly hard to fix in the ink-receiving layer. This color migrates with the glycols to the surface and reduces or prevents lamination.

Table IV. Laminate peel strength (g/2.54 cm) and water-fastness of photo paper I printed on different wide-format printers. The prints were laminated with film E.

Laminate Peel Strength, g/2.54 cm				
Printer	Black	Cyan	Magenta	Yellow
HP 2000	2000	2000	2000	0
HP 750	33	1094	1600	954
Nova Jet PRO GS inks	2000	2000	2000	2000
Nova Jet PRO GA inks	2000	2000	2000	2000
Water Fastness, 5 hrs				
HP 2000	77	70	82	11
HP 750	40	94	88	68
Nova Jet PRO GS inks	53	73	52	23

Nova Jet PRO GA inks	48	62	16	53

The water-fastness of photo paper printed on the Nova Jet PRO printer depended on the type of ink. Graphic art (GA) inks had the lowest water-fastness for magenta, while graphic standard (GS) inks had the lowest values for yellow. For this set of experiments, laminate peel strength was greater than 2000 g/in. More experiments are required to clarify the issues of lamination and water-fastness. We assume that a good laminating film will minimize any difference between primary colors, particularly when peel strength is greater than 2000 g/in.

Laminating Characteristics of Polyvinyl Alcohol

In the previous sections, we discussed the laminating performance of five commercially available films and four photo papers. We showed that lamination of ink jet photo papers could be achieved with only limited success. In the following sections, we discuss the lamination adhesion of several polymers used in ink jet technology to define the parameters governing laminating properties.

Six different grades of polyvinyl alcohol (PVOH) commonly used as the surface coating for ink jet paper were tested in this study. They were coated on a paper with a polyethylene layer that was previously corona treated to provide good adhesion to the base. Polyvinyl alcohol Airvol 125 is fully hydrolyzed (above 99.3%), while Airvol 523S is 87–89% hydrolyzed. Cationic-modified polyvinyl alcohols A and B are 99% and 88% hydrolyzed, respectively. Anionic-modified polyvinyl alcohols C and D are 97% and 93% hydrolyzed, respectively. The sheets with different polyvinyl alcohol layers were printed on HP 2000 printers with dye and pigmented inks and subsequently laminated with films A and E.

Table V presents the adhesion results for film E only. Data for film A follow the same trend as for film E, with one exception that is discussed later. The films of vinyl alcohol polymers printed with pigmented inks have no adhesion to the laminate; these data are eliminated from the table for clarity. Film E has excellent adhesion to the unprinted areas for the four tested polyvinyl alcohols that are above 2000 g/in. Adhesion to the unprinted areas is lower for the fully hydrolyzed Airvol 125 and cationic-modified highly hydrolyzed PVOH A (1443 and 1051 g/in., respectively). Film A has excellent adhesion to unprinted areas for all PVOH samples, except for anionic-modified PVOH D, which has a peel strength 653 g/in.

Table V. The comparison of laminate adhesion measured as a peel strength for different types of polyvinyl alcohol used in ink jet receiving layers printed on HP 2000 printer with dye inks and laminated with film E.

Polymer	Degree of Hydrolysis	Peel Strength, g/2.54 cm		
		Unprinted areas	Primary colors	Secondary colors
Airvol 125	>99.3	1443	1482	872
Airvol 523S	88	2000	882	317
PVOH A	99	1051	1829	1766
PVOH B	88	2000	1266	144
PVOH C	97	2000	1475	1487
PVOH D	93	2000	1183	118

The degree of polyvinyl alcohol hydrolysis has an effect on the laminating properties of the dye inks. For film E, a polyvinyl alcohol surface with a high degree of hydrolysis provides a higher peel strength for primary and secondary colors than a surface with a partly hydrolyzed PVOH. The difference is observed for both unmodified and modified partly hydrolyzed polyvinyl alcohol. For example, fully hydrolyzed polyvinyl alcohol (Airvol 125) had a peel strength to the primary and secondary colors of 1482 and 872 g/in., respectively, while for the unmodified Airvol 523S, the peel strength was 882 and 317 g/in., respectively. A similar significant difference was seen for the cationic-modified polyvinyl alcohols A and B (1829 vs. 1266 and 1766 vs. 144 g/in., respectively).

The interaction between the laminating adhesive and the ink-receiving layer is a very complex phenomenon. The ink-receiving layer of fully hydrolyzed polyvinyl alcohol provided medium adhesion in unprinted areas but good

adhesion in printed areas. Partly hydrolyzed PVOH had excellent adhesion in unprinted areas but much lower values in printed areas, especially for the secondary colors. Most laminating films are based on ethylene vinylacetate copolymers and blends as an adhesive. Acetate groups of copolymers interact with acetate groups of partly hydrolyzed PVOH and provide adhesion. This explains the good adhesion to the unprinted areas for the partly hydrolyzed polyvinyl alcohol. On the other hand, hydroxy groups from fully hydrolyzed polyvinyl alcohols do not have the same ability to interact with acetate groups, and therefore laminate adhesion to unprinted areas is significantly lower.

The interaction between laminating film and ink jet receiving layer can change dramatically after printing. Ink jet ink solvents such as glycols are probably incompatible with acetate groups, because adhesion decreases with a decreasing degree of PVOH hydrolysis. On the other hand, fully hydrolyzed PVOH improves adhesion due to the interaction of hydroxy groups of polyvinyl alcohol with hydroxy groups of glycols. It apparently prevents polyvinyl alcohol crystallization and provides better laminate adhesion.

The use of anionic-modified polyvinyl alcohol results in significantly different adhesion strengths, depending on the type of laminating films tested, as shown in **Table VI.** For the first film, the peel strength is the lowest for unprinted areas and the highest for secondary colors. The second film provides the best lamination to unprinted areas, and the adhesion decreases in the following order: unprinted > primary colors > secondary colors. The peel strength to secondary colors is about 100 g/in. The poor laminate adhesion to the secondary colors is similar to the delamination problem encountered in a typical field environment. The data are hard to explain without knowing the composition of the adhesives of the laminating films. The impurities of this polyvinyl alcohol can also play a role.

Table VI. The comparison of laminate adhesion measured as a peel strength of anionic modified polyvinyl alcohol D (93% of hydrolysis) used in ink jet receiving layers printed on HP 2000 printer with dye inks and laminated with films A and E.

Laminating Film	PVOH Degree of Hydrolysis	Peel Strength, g/2.54 cm		
		Unprinted areas	Primary colors	Secondary colors
A	93	653	896	1508
E	93	2000	1183	118

Lamination Time After Printing

Most ink jet media printed in small shops are laminated immediately, despite the manufacturers' recommendation to wait at least 24 hours before laminating. The media that provide good laminating properties immediately after printing have a competitive edge in the marketplace. The effect of time after printing prior to lamination on adhesion was studied for three different commercial photo papers designated I, II, and IV.

Figure 3 shows that the strength of the lamination adhesion for photo paper I is independent of the time period between printing and subsequent lamination. Peel strength of the primary colors was higher than that of the secondary colors and was unchanged in the 3-week testing period. The lamination to unprinted areas was the highest and exceeded 2000 g/in.

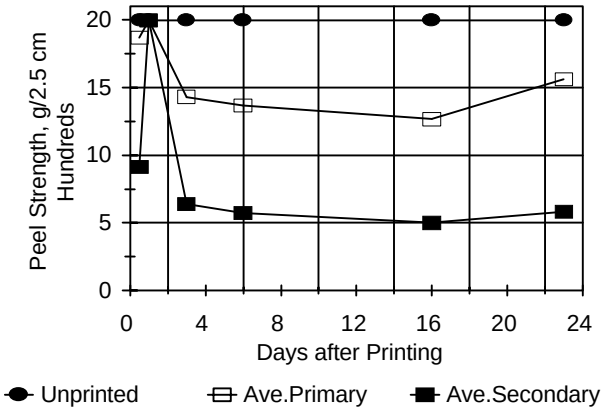

Figure 3. Peel strengths of photo paper I as a function of number of days after printing.

Glossy photo paper II had excellent laminate adhesion to unprinted areas (see **Fig. 4**). Again, the adhesion to primary colors was higher than that to secondary colors. The peel strength of primary colors decreased from 1700 g/in. after 12 hours to 1300 g/in. after 6 days. After this period, adhesion increased slightly. A much larger difference was observed for secondary colors. Peel strength increased from 900 g/in. after 12 hours to 2000 g/in. the next day and subsequently dropped to 500 g/in. after 6 days. The peel strength numbers increased slightly with increasing time between printing and laminating but never approached the peel strength achieved 1 day after printing.

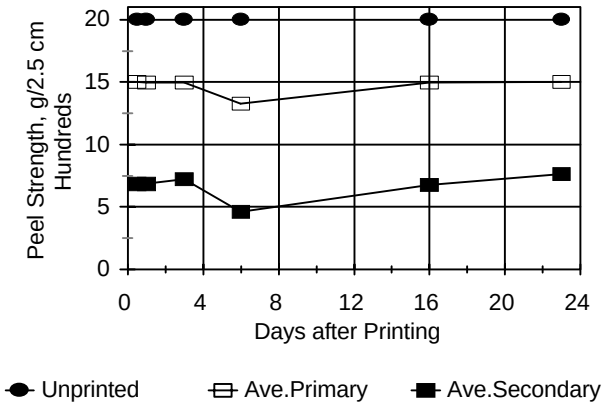

Figure 4. Peel strength of photo paper II as a function of the number of days after printing.

There is a significant difference between photo paper IV and the other grades tested (see **Fig. 5**). This paper had limited adhesion to unprinted areas, and peel strength decreased steadily with an increase in time between printing and lamination. Sixteen days after printing, the paper had no adhesion to the laminating film. Adhesion of the primary colors was lower than that for the secondary colors (this phenomenon was explained previously). The peel strength of the primary colors was at a constant level of 1500 g/in. for about a week and decreased to 450 g/in. after 16 days. The peel strength of the secondary colors increased from an initial value of 1500 g/in. to the maximum 2000 g/in. and subsequently dropped to the initial value.

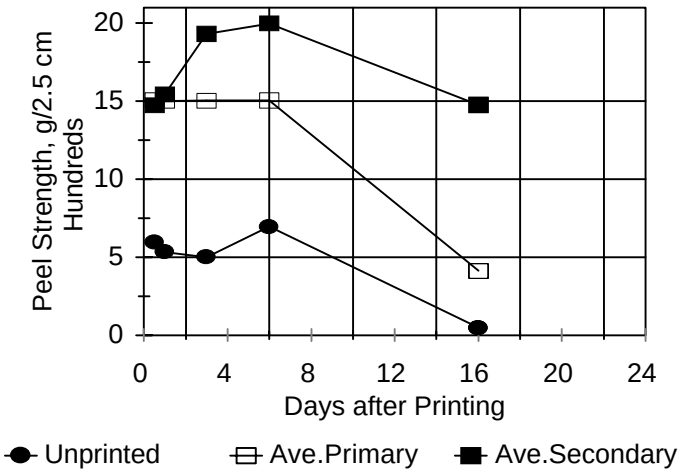

Figure 5. Peel strength of photo paper IV as a function of lamination time after printing.

The consistent and strong adhesion between the laminating film and ink jet–printed areas several weeks or even months after lamination is very important in the graphic arts industry. Several commercial photo bases were tested in the lab at different intervals after lamination. We found that, for up to 1 month, peel strength to unprinted areas and primary and secondary colors did not change. However, it can be assumed, based on the lamination study in which the time between printing and laminating was varied, that in a longer period of time (such as 6 months or a year), lamination quality can deteriorate. This is especially true if the prints are kept in a broad range of temperatures causing deterioration of the adhesive properties.

Ink Jet Receiving Layer Coat Weight

Print quality strongly depends on ink jet receiving layer coat weight, but the relationship is not straightforward. At high coat weight, color density becomes low, and print defects, such as banding, are observed due to insufficient ink spread between two consecutive head passes.

The effect of coat weight of the photo paper formulation applied to an impermeable substrate, such as photo base, on the laminating properties of the primary and secondary colors is presented in **Fig. 6.** Note that adhesion, expressed as peel strength, increases with coat weight. This relationship is slightly different for the primary and secondary colors. Peel strength of the primary colors reaches a plateau at 1900–2000 g/in. at 8 g/m^2. For secondary colors, adhesion increases constantly with coat weight and is at a level of 1700 g/in. at 20 g/m^2, still below the value for primary colors. For the typical ink jet coat weight in the range of 8–12 g/m^2, there is twice the difference in peel strength between the primary and secondary colors.

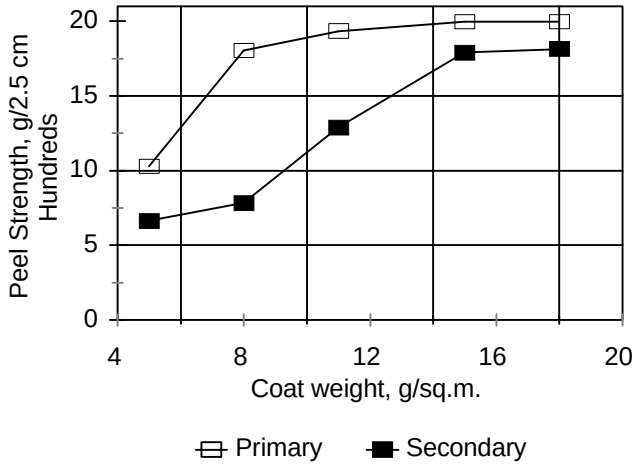

Figure 6. Peel strength as a function of ink receiving layer coat weight.

It was previously shown that ink solvents cause a deterioration in laminate adhesion in most cases. With an increase in ink receiving layer coat weight, more ink penetrates deeper into the polymeric matrix, and less stays on the surface. Since inks become entirely absorbed by the layer, the peel strength improves with coat weight. Several independent experiments carried out by the authors showed that coat weights above 12–16 g/m^2 are needed to provide sufficient laminate adhesion in areas printed with secondary colors. An increase in coat weight can allow lamination in a shorter period of time after printing; this can have a significant effect on small print office performance and profitability.

Adhesion of laminate films to porous ink jet paper is significantly different from photo paper or film. Generally, for an optimized formulation without separation of the pigment from the binder in the coating process, laminate adhesion is independent of coat weight, and is about 2000 g/in. The ink jet inks pass through the ink-receiving layer and are absorbed by the fibrous substrate. This type of base absorbs excessive amount of inks when the coat weight is insufficient and prevents their accumulation on top of the ink-receiving layer. The concentration of inks on the surface (mostly secondary colors) is a reason for insufficient adhesion at low coat weight for nonporous substrates.

Pigments in Ink Jet Receiving Coating

Most ink jet media have a semi-matte or matte finish. These papers contain pigments such as precipitated silica, colloidal silica, and alumina, which provide a matte surface. The pigments also absorb ink fluids. Commercial ink jet paper bonds contain a high pigment/binder ratio to accelerate ink drying and reduce the cost of the media. However, excessive pigment can create several problems. Most ink jet papers have a low resistance to dry rub, and some of them dust due to an insufficient amount of binder.

Paper formulations containing silica pigment, polyvinyl acetate copolymer, PVP, and an additive of dye fixative were used in this study. The ratio of pigment to binder was studied in the range of 0.5 to 2. This is equal to an increase in the amount of pigment in the formulation from 32.8 to 65.2 wt. %. The results presented in **Fig. 7** show that laminating adhesion is excellent and is about 2000 g/in. up to a pigment/binder ratio of 1. Above this point, peel strength declines steadily to 600–700 g/in. for a pigment/binder ratio of 2. Adhesion to unprinted areas drops even faster, and at a ratio of 2, the peel strength is only 400 g/in. At low pigment/binder ratios (near 0.5), adhesion to primary colors is better than that to secondary colors. At a ratio of 0.75, peel strength values are equal for both types of colors, and from this point, adhesion to secondary colors becomes higher.

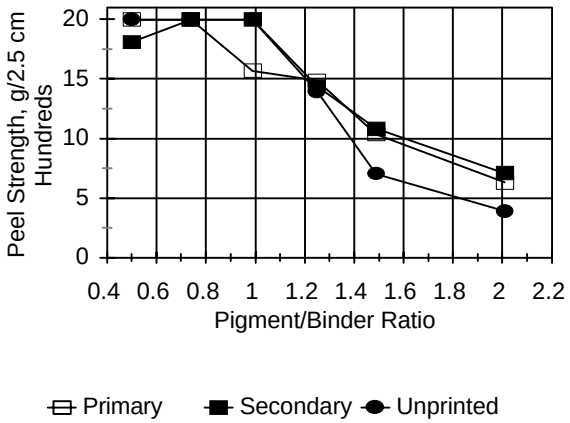

Figure 7. Peel strength as a function of pigment/binder ratio.

Print qualities, such as ink density, intercolor and background bleed, and mottle, strongly depend on the pigment/binder ratio. **Figure 8** presents dry rub and intercolor bleed expressed as ratings, where a rating of 5 is the best and 0 is the worst. With an increase in the pigment/binder ratio, the dry rub and intercolor bleed ratings deteriorate. With an increase in the amount of pigment in the formulas, silica is less associated with the binder, and more can be removed from the paper surface in the dry rub test. Pigment in the ink jet layer absorbs inks but, on the other hand, spreads them, creating intercolor bleed. Both print quality features deteriorate as the pigment/binder ratio increases.

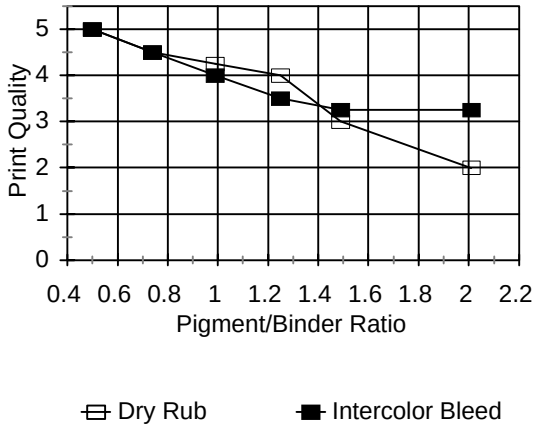

Figure 8. Dry rub and intercolor bleed as a function of pigment to binder ratio.

Figure 9 presents the density of black and the three primary colors for the formulations studied. The density of black and cyan increases for a pigment/binder ratio up to 1 and thereafter steadily decreases. The density of black increases 15 points, giving an intense, deep color that is important in graphic arts. An initial increase in density with increasing pigment is a result of excessive ink spread. However, with additional pigment percentage growth, most of the ink is absorbed by the pigment, and the density of the color decreases. The density of magenta and yellow decreases steadily with an increase in the pigment/binder ratio. The drop is the most pronounced for yellow (25 points).

The effect of pigment/binder ratio on lamination and print quality is a complex issue that depends on polymeric matrix, pigments used, and laminating films. In our study, some photo papers were found to have the same lamination characteristic (exceeding 2000 g/in.) for glossy, semi-glossy, and matte photo papers. However, in these formulations, the amount of pigment is relatively low; the pigment is used only to modify the degree of gloss. Ink jet

paper bonds use significantly higher amounts of pigment. The pigment/binder ratio can be as high as 4:1. Of course, these papers cannot be laminated.

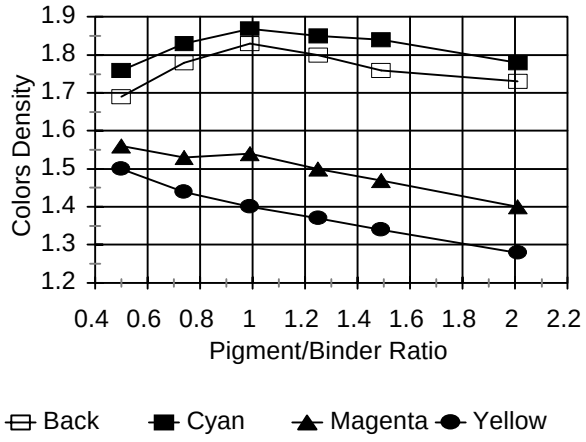

Figure 9. Ink density as a function of pigment-to-binder ratio.

Most of the ink jet media was developed to maximize color gamut, reduce dry time, eliminate intercolor bleed, and reduce tack at high relative humidity. Some of the media have acceptable lamination properties, especially on dye inks. Generally, it is possible to develop media with excellent lamination properties but inferior density of colors and color gamut. Close collaboration is needed between the chemists developing the ink jet receiving coatings for the media and the adhesive chemists designing the laminating films to understand all the interactions between the ink-receiving and lamination layers.

CONCLUSIONS

This paper discussed several factors influencing the design of ink jet media in respect to lamination. The adhesion of five commercially available laminating films to a single photo paper imaged with several dyes and pigmented inks was compared. Four commercial photo papers were also printed with different inks and subsequently laminated with two types of films. We showed that lamination of ink jet photo papers can be done with only limited success.

The lamination adhesion was studied for single layers of several grades of polyvinyl alcohols having different degrees of hydrolysis and other common polymers used in ink jet technology to define the parameters governing laminating properties. The effect of pigment/binder ratio and coating weight of the ink jet receiving layer on the imaging properties of the media and thermal lamination was also investigated.

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