Adhesion in LEP and its Correlation to Paper Surface Chemical Makeup

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Abstract

In digital printing, adhesion of marking materials, such as ink, to a substrate, such as paper or plastic, is of paramount importance. In Liquid Electrophotographic Printing (LEP), the adhesion is even more critical as the typical LEP process does not involve any post-printing fixing step. In an earlier publication, we have shown that acid-base and van-der Waals interactions at the ink-paper interface determine the adhesion in LEP. In this paper, we attempt to correlate such interactions to paper surface components which contribute to both good and bad adhesional characteristics. We have selected four representative commercially available papers and isolated their coating materials. These coating materials were dissolved in non-polar and polar solvents, such as chloroform, toluene and water, and then analyzed using FTIR spectroscopic measurements, proton NMR and LCMS analyses. Our results indicate presence of styrene butadiene rubber in most coated papers with different amounts of butadiene to styrene (B toS) ratios. We found that generally 1:1 to 1:1.2 B to S ratios were better performers while B to S of 1:2 to 1:2.5 were poorer performers. We also found that papers with some amounts of poly vinyl alcohol or starch as co-binders of the media coating showed good adhesion. Uncoated papers with carboxylic acid also showed good adhesion.

Introduction

Excellent ink-paper adhesion can provide important print and pages attributes - visually pleasant image quality, high print durability for rub resistance, water fastness and smear fastness, and overall throughput of a printing process, and reduce wastage of materials. LEP is an excellent digital printing technology that uses electrostatically chargeable liquid toners (aka. ElectroInks) to print high resolution images on a variety of paper or non-paper substrates. Figure 1 shows a simplified schematic of an HP-Indigo LEP digital press. Simplistically, this press can be considered a hybrid of the dry electrophotographic laser printer and high volume commercial offset press. The latent image formation portion of the LEP press looks somewhat similar to a laser printer with photoconductor, a uniform charging unit, laser writing unit and various developer or ink transfer units. The other portion of the press has similarities to an offset press, where the developed image is offset to an intermediate transfer medium before transferring to paper.

In LEP the ElectroInks comprise mainly, copolymers of ethylene and acrylic/methacrylic acids. When such inks are printed on paper surfaces (or other substrates), the carboxylic groups may form acid-base interaction and hydrogen bonding with hydroxyl, amine, amide or other carboxylic groups of paper surfaces. If such bond formation can occur, a high adhesive strength (characterized by work of adhesion) [1] results. Figure 2 shows such a case where a carboxylic group of ink particle forms hydrogen bonding with a hydroxyl group of paper. Ink-paper adhesion, in LEP and several other print technologies, is a surface phenomenon. Understanding the critical factors that promote ink-paper adhesion can lead to good interfacial adhesion as well as provide an understanding of paper strength and appearance [2].

In this paper, we report chemical extraction and identification of paper surfaces and correlate the extracted materials to measured adhesion properties.

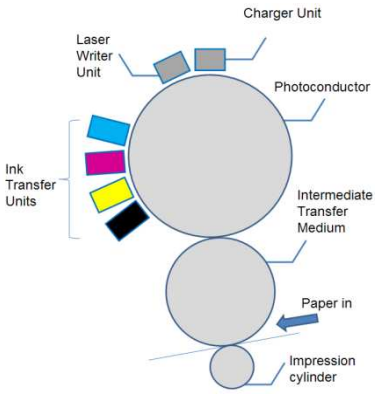

Figure 1. A schematic diagram of HP-Indigo LEP press.

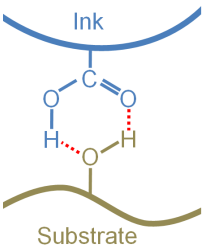

Figure 2. Hydrogen bonding between ink-paper is shown.

Experimental Methodology

As mentioned in the previous section, in LEP ink-paper adhesion is a surface phenomenon. As shown in Figure 3, the paper is composed of cellulose and fillers in the core, but generally, has a coating on the top and bottom surfaces. When a layer of ink is printed on such a coated paper, the ink layer *rests* on the coating layer of the paper as shown in the SEM cross-section of

a printed paper in Figure 4. As mentioned previously, no appreciable penetration of the ink into the paper occurs in LEP.

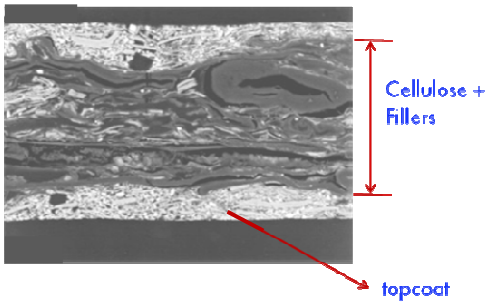

Figure 3. A simplified coated paper structure.

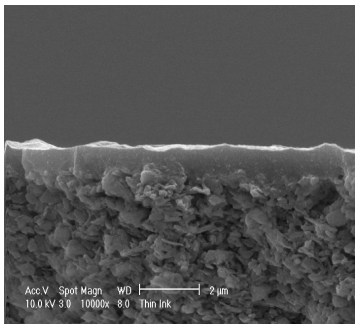

Figure 4. An ink layer is printed on a coated paper using LEP.

For the present study, four commercially available papers, named A, B, C and D, are chosen. Two of the papers (A and D) show excellent ink-media adhesion while the other two show poor and unacceptable adhesion. By careful analyses of these papers, one can draw conclusion about desirability of paper surfaces. First, solid 100% black was printed on these papers using HP-Indigo 5500 digital press. Second, adhesion characteristics were measured using simple "tape peel test" using a common 1" drafting tape 3M-230. The four papers' adhesion characteristics is shown in Figure 5 and listed in Table 1. The peel numbers shown in Table 1 is the percent amount of ink left after the tape pull exactly 10 minutes past the printing.

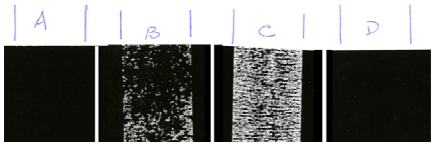

Figure 5. Four papers chosen for this study and their adhesion characteristics.

It needs to be emphasized that good ink adhesion is highly dependent on the paper coating. For example, Figure 6 shows a case where the top coating of paper A was scraped off using a sharp knife. Subsequent tape-peel measurement shows the degradation of LEP ink-adhesion in this original excellent paper.

Since the adhesion of ink is highly dependent on the surface composition, one has to analyze the surface of the top coating. The method presented in the paper involves removal of such a coating and analyzing the scrapped material.

Paper id	Paper Description	Peel Number*
A	Coated	95
B	Coated	77
C	Coated	55
D	Coated	99

*Table 1. The four papers chosen for this study and their peel characteristics. *The peel number is the percentage of ink left in the tape peel area versus non-peel area.*

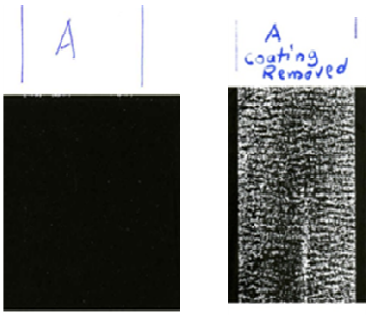

Figure 6. Ink adhesion worsens when the top coating surface of paper A was removed.

Figure 7 shows the different steps taken for preparation of the study. The extracted materials were sequentially extracted by boiling in chloroform and water.

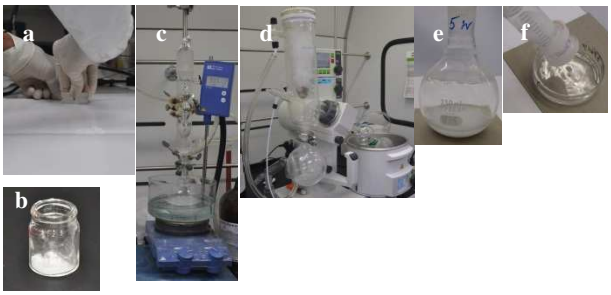

Figure 7. The steps using in preparing the sample.(a)the coating is scrapped off using a razor, (b)collected coating, (c)the sample is sequentially boiled, (d)the sample is concentrated, (e)concentrated sample and (f)the decanted liquid is filtered using a syringe filter.

The collected samples were analyzed using FTIR, LCMS, differential scanning microscopy (DSC) and ^{1}H NMR to provide a rough estimate of the top coating constituents. Report of pigments such as CaCO3 and Kaolin clay are omitted here as they are not expected to be the determining factor of ink-paper adhesion.

Results and Discussion

From Figure 8, one can conclude that while SBR is present in paper D, some forms of acrylates are also present in this paper as a strong band is seen at 1735 cm^{-1}. In Figure 8, we have also compared the chloroform extract with polymethyl methacrylate. Of

course, one can easily see that PMMA is not the material present in paper D.

To further elucidate the chemical structures, we have performed proton NMR. Figure 9 shows proton NMR of the same SBR used in Figure 8. It is possible to identify the regions where styrene (around 7.2 ppm) and butadiene (around 5.3 ppm) signals are seen. The aliphatic regions of the NMR profile (1 -3 ppm) also show important information. It is important to remember that when a pure polystyrene is measured in proton NMR, two distinctly differentiated signals are seen in the region of 6-7 ppm [4], while in styrene-butadiene copolymer these two bands often merge resulting in a single peak around 7.2 ppm for styrene and another signal for butadiene near 5.2 ppm. Pure aromatic benzene, as a reference, shows a very narrow signal at 7.25 ppm [5]. In styrene acrylate, two separated signals are again seen around 6.5-7.5 ppm as has been shown by Brar and coworkers [6].

Figure 10 shows the actual ^{1}H NMR measurement of CHCl3 extract of paper D. From the discussion above, it is easy to identify styrene and butadiene in paper D, as well as the presence of styrene acrylate in the coating. Similar structural elucidation methods are adopted for the other papers.

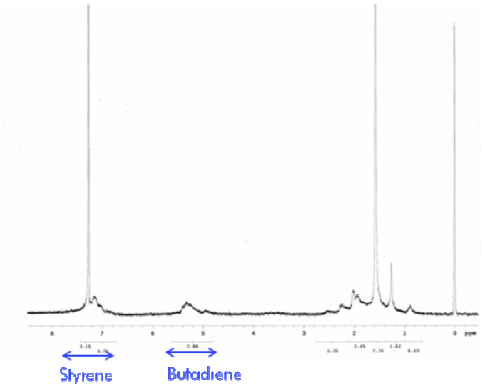

Figure 9. Proton NMR measurement of Rvene-4151 (SBR) in $CDCl_3$.

Figure 11 shows the FTIR spectra of the water extract of paper D. The water extract of this paper produces a well-formed continuous film. A high quality FTIR spectrum was obtained when the dried water extract was dissolved in water and measured on a PTFE film. The measured spectrum was then compared with polyvinyl alcohol and soluble starch for identification.

With the agreement as seen in Figure 11 between the water extract of paper D and polyvinyl alcohol, one can possibly conclude that PVOH appears to be the co-binder in this paper. A complementary measurement LCMS of the water extract of paper D was performed. Figure 12 shows the LCMS measurement of water extract and strong possibility of PVOH is seen also.

Adopting the processes similar to the above, the binders and co-binders were identified for all the four papers and are listed in Table 2. In this table, we have also listed the scraping-recovery yields (amount of coating removed from the two sides of a paper), texture feel, total polar content, T_g of the extracted coating, butadiene/styrene ratio, main binder and co-binder in the papers.

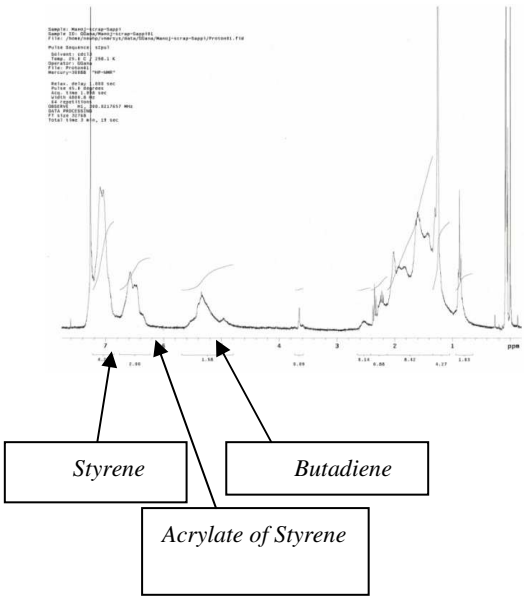

Figure 10. ^{1}H NMR of CHCl3 extract of paper D. In this paper, in addition to styrene and butadiene, some forms of styrene acrylates are also seen.

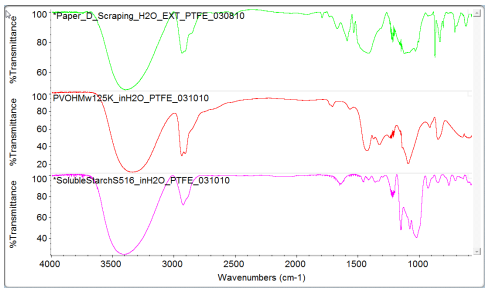

Figure 11. FTIR measurement of water extracts of paper D and comparison with polyvinyl alcohol and starch.

From Table 2 it is seen that the total polar content of the surface may be the single determining factor in adhesion properties of papers. All the coated papers analyzed in the present study have SBR as the main binder and starch seems to be a common co-binder also. Even though PVOH is not very common, the improvement in ink-paper adhesion with this co-binder is noticeable.

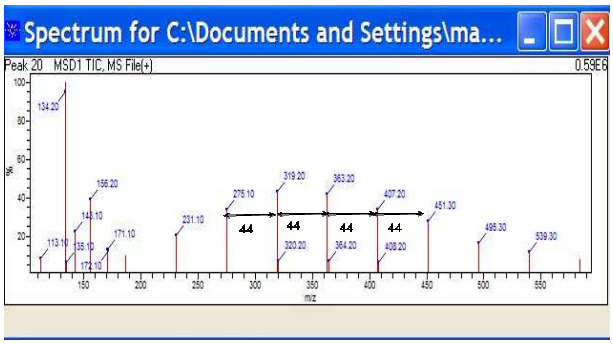

Figure 12. LCMS measurement of water extract of paper D. A difference of 44 is seen in m/z lines, once again suggesting presence of PVOH in the coating.

Paper #	Peel #	Scraping per Sheet			Coating		Coating Co-binder[2]	Comment
		Yield (mg) /Comment	T_g of coating material (°C)	Polar Content (mg)*	Binder[1]	B/S*		
A	95	400/ Hard	59.3	10	SBR	1:0.69	Starch	Just Right
B	77	103/ Hard	64.8	2	SBR	1:0.5	Starch	Not Enough Polar
C	55	453/ SOFT	35	4.9	SBR, Acrylic Resin	1:1.86	PEG, Starch	Too Soft and Not Enough Polar
D	99	146/ Hard	48.5	10	SBR, Styrene-Acrylate	1:1.34	PVOH	Best Paper

*Table 2. Summary of all the measurements. The glass transition temperature, T_g, is measured in a DSC instrument. Total polar content is measured by boiling the coating scraping in water and then drying the extract.*B/S is butadiene to styrene ratio and is obtained from NMR measurements.*

Summary

In this paper a correlation of ink-paper adhesion in LEP printing and paper surface active components is made. It is shown that in LEP, surface interaction between ink and paper is very crucial and a careful understanding is necessary for an improved ink-paper adhesion. In general, right polar group in the right amount appeared to promote good adhesion.

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Authors Biographies

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