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Applicability of FTIR and Raman Spectroscopic Methods to the Study of Ink Jet and Electrophotographic Prints

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Abstract

Vibrational spectroscopic methods are nowadays widely used in the analysis of materials both in xy- and z-directions. Needs to understand durability, especially light fastness, mechanisms in ink jet and toner adhesion mechanisms in electrophotography call for analytical techniques.

Sample sets to study applicability of various FTIR and Raman techniques to ink-paper interaction analysis included ink jet prints exposed to different amounts of light energy, and electrophotographic prints fixed in different conditions. FTIR-ATR and Raman measurements in xy- and z-directions were found to be the most promising techniques, since the differences between the samples were revealed most distinctly. The confocal Raman technique proved to be applicable to depth profiling of colorant and toner. Step-scan PAS can be used for depth profiling of electrophotographic prints.

Introduction

The general objective of this work is to evaluate the applicability of vibrational spectroscopy to ink-paper interaction studies in ink jet and electrophotography. In ink jet, the main interest is to evaluate light fastness of printed image. In electrophotography, toner adhesion is of primary interest.

Ink Jet - Light Fastness

In many of the present ink jet applications, the prints are expected to be light fast for many years, even when exposed to moisture etc. Factors that affect the light fastness of ink jet prints include e.g. the inherent photo stability of the colorant, its physical location on the media, the environmental factors and the light source. In desktop printing, image quality is generally acceptable if special ink jet papers or other coated media are used, since coatings are able to fix the colorant rapidly and also to protect it from the environment. On uncoated media however, optimal print quality may not always be achieved, since the colorant is vulnerable to the environment. With coated media, the most common interaction mechanism between dye and coating components is believed to be the strong ionic interactions, whereas, with plain papers, relatively weak hydrogen bonding is said to be the most common interaction mechanism.[1,2,3]

The role of interactions between ink and paper in determining light fastness of an ink jet print is still unclear. For this reason the optimization of inks and media to achieve excellent light fastness in all situations is complicated. Studies indicate that the photo degradation of printed ink jet dyes cannot be explained by any single, well-defined mechanism.[4] In the case of ink jet colorants, the photo degradation of the chromophore usually occurs either by oxidation or by reduction, the former being more common in the presence of light, moisture and oxygen. Photo degradation reactions result from the excitation of the dye from ground state to a higher singlet state, due to photon absorption. Since the dye has excess energy at the excited state, it is prone to photo degradation reactions, provided that the excited state is long lasting. The dye may also transfer its excess energy to another dye at a lower excited state level, this is known as catalytic fading.[5,2]

Electrophotography - Adhesion

Toner adhesion to paper is believed to occur both mechanically and chemically. In mechanical adhesion, as the toner penetrates to the voids in paper structure, the polymeric molecules interlock within themselves and with the surface. The mechanical forces are relatively weak but with small polymer molecules the bond strengths can be enhanced. Mechanical bonding is believed to be strongest with porous and rough structures because of the better chance of intermingling between the polymer particles and a greater potential bonding area. Shear tests have however shown that the smoothest surfaces give the strongest bonds. This gives evidence that chemical adhesion is also involved. There are several theories of the origin of chemical adhesion: chemical reaction, adsorption, electrostatic and diffusion theory. The most accepted theory is that of adsorption where wettability and surface energy of the substrate and viscosity of the colorant are important.[6,7]

The existence of both mechanical and chemical interactions signifies that both the physical and the chemical structure of paper are important. The role of surface chemistry is more critical to toner adhesion than to image quality. Paper surface energy, which effects the wetting, can be influenced with organic compounds added as internal or surface sizing. Of physical properties of the paper, porosity and roughness have the most pronounced influence on the mechanical adhesion.[8,9]

Analytical Methods in Interaction Studies

Traditional print quality measurement methods do not yield enough information for deduction of interfacial mechanisms between ink or toner, and paper, hence other methods are needed. Many analytical methods have been used in the field of paper and printing technology.

The physical state of prints, characterized by aggregation and penetration of ink and toner, has been studied with different microscopic methods, often combined with thin-cuts of paper. These include optical microscopy,[10] atomic force microscopy (AFM),[11] and transmission (TEM) and reflection (REM) electron microscopy.[12] These methods do not give direct information on the chemical structure of the interface. Also, the use of resin in conventional microtoming methods may be problematic if electrophotographic toners are studied, since resin is also their main component.

The chemical state of prints has been studied using various methods. Paper[13] and thin layer chromatography[14] have been used in ink jet printing area in particular. The downside of these methods is that there is much more ink solvent present than in actual ink jet printing situation and real prints cannot be studied. The use of thermal analysis[15] and absorbance and zeta potential measurements[16] on interaction studies in ink jet printing has also been reported. Electron spectroscopy for chemical analysis (ESCA) has been used in studying both the chemical structure of the paper surface and the print properties, including toner adhesion. It gives information on the chemical structure of material, such as the electronic structure and bonding of single atoms, but is unable to detect certain chemical groups essential in ink/paper-interactions, like OH. In some cases, especially in ink jet printing, its extreme surface sensitivity may complicate interaction studies.[17]

Vibrational spectroscopy, or IR and Raman spectroscopy, enables the studies of prints "as is", and thus provides information on the actual ink-paper interactions. So far these methods, especially Raman spectroscopy, have been relatively seldom used in paper and print analysis, mainly due to the fluorescence phenomenon in Raman. Novel excitation sources and FT-devices have largely solved this problem[18]. Although IR- and Raman spectroscopy are both based on molecular vibrations, they are complementary methods, due to the different transfer mechanism of energy from photons to exposed molecules. IR spectroscopy gives information on chemical groups containing highly polar bonds, or bonds whose dipole moment changes during vibration, as, for instance, in the case of water. Conversely, Raman activity results if polarizability of a molecule changes during vibration. This is true e.g. for symmetric covalent bonds, such as N=N.[19]

Both FTIR and Raman spectroscopy have found use in the studies of archeological findings, i.e. properties of historical papers have been examined using the attenuated total reflectance method (FTIR-ATR).[20] Raman spectroscopy has also been applied to analysis of pigment structures and degradation of manuscripts.[21,22] Also, photoacoustic FTIR-spectroscopy (FTIR-PAS) has been utilized in colorant identification and in light absorption measurements of very thin ink layers,[23,24] although Raman spectroscopy is likely to be more applicable to ink studies than IR-spectroscopy, due to its sensitivity to aromatic structures.[25] Discrimination, for example, between blue textile dyes and monitoring the synthesis of azo dye has been accomplished by Raman spectroscopy.[21,22] Different vibrational spectroscopic methods have been widely used in polymer research both in surface studies[26,27] and in depth profiling,[28] which backs their use up in electrophotographic print studies. Raman spectroscopy is particularly suitable for polymer studies, due to its capability of probing C-C and C-H bonds. In addition, the use of 2D correlation spectroscopic methods in interaction has been reported.[29]

Methods

Test Set-ups for Light Fastness and Adhesion Studies

To explore the applicability of FTIR and Raman techniques sets of printed samples were prepared using light exposure time in ink jet and fixing temperature in electrophotography as controlled variables. The ink jet samples consisted of solid yellow areas printed on uncoated paper of 80 g/m^2 containing PCC filler (precipitated calcium carbonate) with an Epson SC 900 ink jet printer. The prints were exposed to artificial sunlight for 6, 12, 24, 48, 72 and 100 hours with Suntest CPS+ xenon arc lamp. Test chamber settings were 615 W/m^2 for irradiance and 40°C for black standard temperature. Relative humidity RH of the measurement room was set to 35% and temperature to 24°C. L*a*b*-values and Raman- and FTIR-spectra were measured from prints before and after light exposure. Color difference $\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ is used as a measure for light fastness. The electrophotographic samples were solid yellow areas printed on 80 g/m^2 uncoated and 100 g/m^2 pigmented papers with a Lexmark Optra C printer. Unfused samples were fixed with a separate Optra C hot roller fuser. The fusing temperatures were varied from 140 to 200°C. Raman and FTIR spectra were measured from toners, unprinted papers and printed samples. Toner adhesion was measured with the tape test.

Selection of Spectroscopic Measurement Techniques

The Bio-Rad FTS 6000 research grade FTIR spectrometer has rapid- and step-scan operation capabilities, and is equipped with an ATR-bench, germanium micro-ATR crystal and photoacoustic cell (MTEC300). The UMA-500 microscope, equipped with MCT detector and

CCD video camera, is used in microscopic analyses and computer controlled IR-mapping. In the FTIR-measurements of this study, a sampling resolution of 8 cm^{-1} was used. The dispersive Raman spectrometer Kaiser Raman Hololab series 5000 is equipped with 785 nm laser and Olympus-microscope. This enables microscopic analyses, Raman-mapping and confocal measurements[30] (depth profiling). The sampling resolution in the Raman studies was 1 cm^{-1}. The measurement schemes are summarized in Table 1.

Table 1. The measurement schemes.

Method	x,y-direction	z-direction
FTIR	Micro-ATR, ATR	Step-scan PAS
	Rapid-scan PAS	
	DTGS	
Raman	Microscope	Confocal measurement

The FTIR-spectrum of the aqueous ink jet ink was measured with a DTGS-detector from a sample dried onto silicon wafer, since water peaks interfere with the interpretation of IR-spectrum badly. Since water is not a Raman-active compound, Raman spectrum could be measured from liquid ink jet ink instead, using a microscope and 100x-magnification. Toner was measured as powder with rapid scan FTIR-PAS and with microscopic Raman with 100x magnification. Fluorescence was found to complicate Raman-measurements and interpretation of the spectra of some colorants and papers, since it lowers significantly the S/N-ratio. In addition to this, too high power of the laser light source may cause problems, since darker colors absorb more energy and may be burned down, due to overheating. Thus, in practice, the same measurement conditions cannot be used for all primary colors (CMYK).

Unprinted papers and printed samples were measured with the micro-ATR-technique, since it is suitable for flexible and reflective surfaces like paper, and its small size enables good contact with the sample. To improve reproducibility, several parallel measurements were made from each sample and the spectra were averaged. The penetration depth of the IR beam may differ between samples due to variability in surface structure and thus variation of the pressure of the crystal against the sample surface. The downside of ATR in paper and print studies is poor spectral resolution from strongly absorbing surfaces. This holds true, e.g., for silica pigment whose bands may dominate the spectra overlapping other peaks. However, spectral subtraction can be used in data analysis to compensate for this. Paper and print samples containing materials with high absorptivity can be measured better with PAS.

Depth profiling can be accomplished in IR spectroscopy with step scan PAS. With this method, the best spectra were obtained when ink had been set as a distinct layer on top of paper, like in electrophotographic prints. With most of the ink jet samples, however, the problem was the extensive penetration of the dye into the paper structure. In addition to this, another downside of depth profiling with PAS is that the exact measurement depth is not known. The position in z-direction can be estimated only if the thermal diffusivities of the components are known. On the other hand, with confocal Raman measurement, depth profiling can be accomplished at controlled steps, which in this set-up range from 0.1 to 10 µm.

Results and Discussion

Light Fastness Studies

Figure 1 presents the Raman spectra of unprinted paper, yellow ink and printed samples exposed to different amounts of light energy. In the spectra of printed samples, there are bands originating from both ink and paper. Generally, prolonging the exposure time results in a decrease of the intensities of ink-originating Raman bands. Based on published data on vibrational frequencies,[31] the yellow ink is an azo dye, which is known to be susceptible to light originating decomposition.[2] Table 2 indicates that as exposure time prolongs, ΔE increases, mainly due to an increase in Δb*. Thus "yellowness" of the print decreases during long exposures, which suggests the decomposition of the azo colorant.

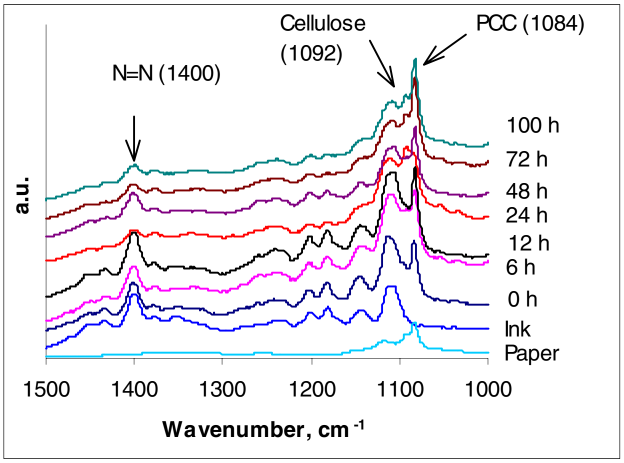

Figure 1. *Effect of exposure time on Raman spectra of yellow ink jet prints. The curves are vertically shifted for clarity.*

Table 2. Effect of light exposure time on color co-ordinates and color difference ΔE for solid yellow print.

Exp. time, h	ΔL*	Δa*	Δb*	ΔE
6	0,78	0,98	4,03	4,22
12	0,94	0,90	6,65	6,78
24	0,85	1,31	11,91	12,01
48	0,04	0,66	14,31	14,33
72	0,17	2,68	23,87	24,02
100	-0,64	3,89	27,17	27,46

Raman intensity ratios for the most intense bands of yellow ink were calculated relative to a band at 1082 cm^{-1}, which originates from the PCC filler. Figure 2 presents these as a function of Δb*. An increase in Δb*, or a decrease in yellowness, results in the decrease in band ratios. Also, various bonds of the colorant molecule seem to be quite equally affected by the exposure. However, there is some variation in the results, which is due to the variation of RH and temperature of test room during the tests. This can be seen from the lower band intensities of the 24 h-spectrum and also as deviation in band intensity ratios.

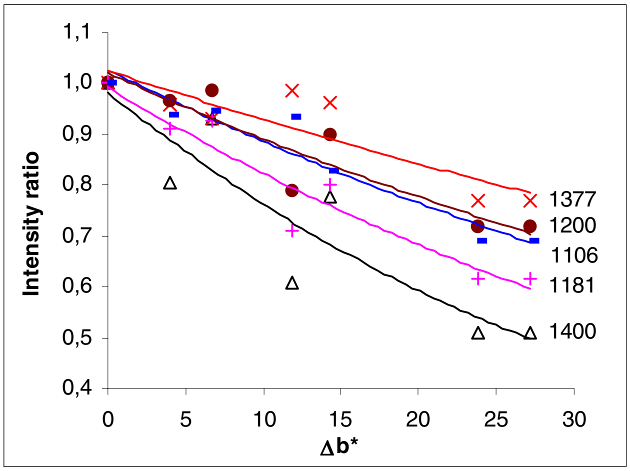

Figure 2. Raman band intensity ratios for yellow ink as a function of exposure time. Reference band 1082 cm^{-1} (PCC filler).

FTIR-ATR-spectra of unprinted paper, yellow ink and printed surfaces are presented in Figure 3. Yellow ink, as measured from paper surface, was poorly detected with FTIR, in spite of the fact that plain yellow ink gave a clear FTIR-spectrum. The likely reason for this is the behavior of dye-based ink jet inks on the surface of uncoated papers. They do generally not form a separate layer on the paper surface, unless paper is extremely strongly sized. Rather, colorant penetrates into the paper bulk with the carrier phase. However, in the ATR-method, the penetration depth of the IR-beam is usually only within a few micrometers, thus the detection of somewhat penetrated colorant is difficult. The Raman depth profiling results presented in Figure 4 affirm that ink has penetrated extensively into the bulk of uncoated paper.

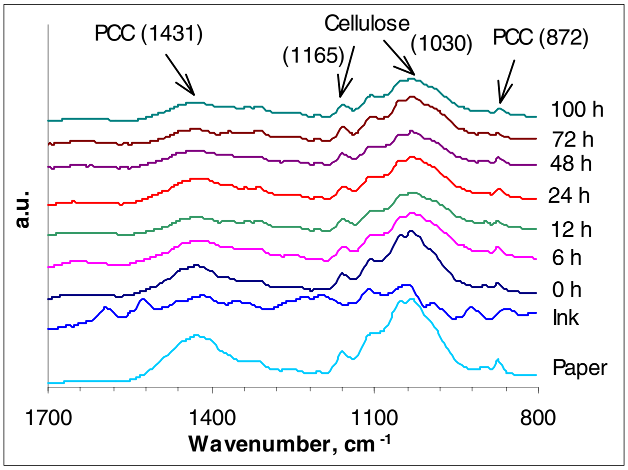

Figure 3. Effect of exposure time on FTIR spectra of yellow prints. The curves are vertically shifted for clarity.

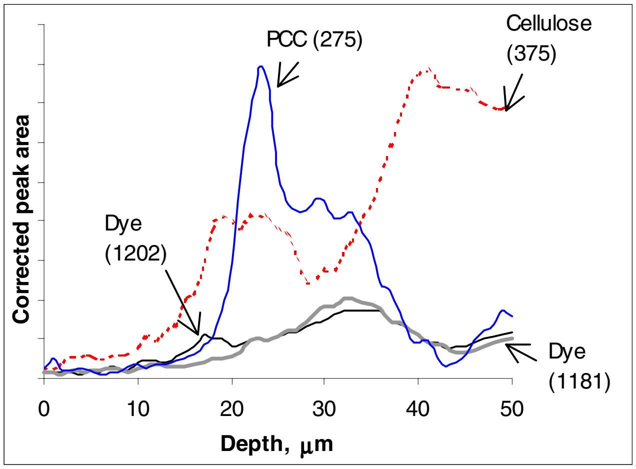

***Figure 4.** Depth profile of unexposed yellow ink jet print. Measurement step is 1 μm.*

Adhesion Studies

Confocal Raman measurements were made from solid yellow electrophotographic prints fixed at different temperatures. A transition phase from maximum concentration of toner to the maximum intensity region of paper components can be defined by comparing the spectra at different depths. It is clear that while going deeper into the sample, bands characteristic of the paper components emerge, while bands from the toner diminish. Figure 5 represents the peak heights of given assigned bands at different depths in the sample. It can clearly be seen that the toner at this fixing temperature (200°C) is as a fairly compact layer which starts to intermingle with the paper filler at around 14 μm. The cellulose band at 1090 cm^{-1} reaches the maximum after the PCC filler. At this depth there is fractionally toner left. Interfacial region is approximately 10 μm wide.

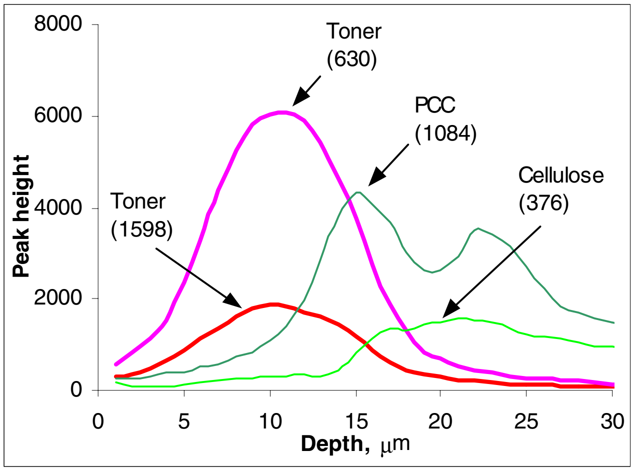

***Figure 5.** Depth profile of a yellow print (200°).*

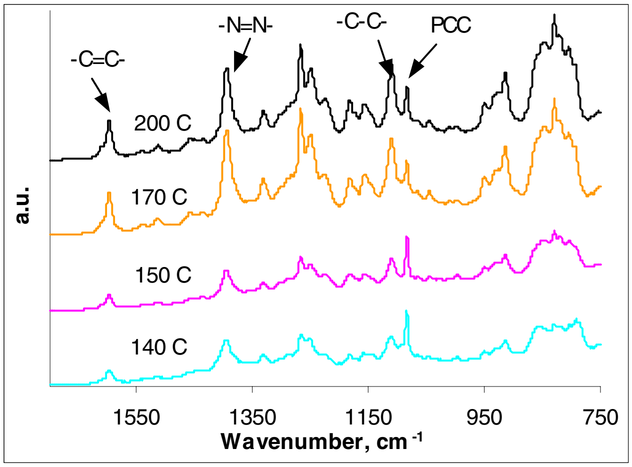

***Figure 6.** Part of confocal Raman spectra at the toner maximum at fixing temperatures 140, 150, 160 and 170°C. Spectra are vertically shifted to improve comparison.*

Figure 6 presents a part of the spectra at toner concentration maximum at different fixing temperatures. It can be noted that toner bands, mostly from the yellow azo pigment, strengthen in relation to the PCC band (1084 cm^{-1}) as the fixing temperature increases.

Given toner bands, like -N=N- bond in yellow azo pigment at 1395 cm^{-1} and -C-C- bond in aromatic structures at 1598 cm^{-1}, were scaled to the cellulose band at 376 cm^{-1}. This band was chosen as a reference because there is no overlapping. The obtained intensity ratios were compared with measured toner adhesion. The results are in Fig. 7. It is explicit that as the toner adhesion is improved by additional fixing energy, the intensity ratios increase linearly.

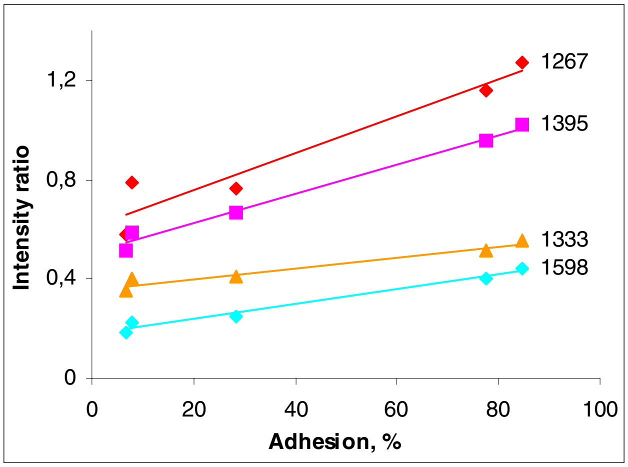

***Figure 7.** Toner band intensities as a function of toner adhesion. Reference band 376 cm^{-1} (cellulose).*

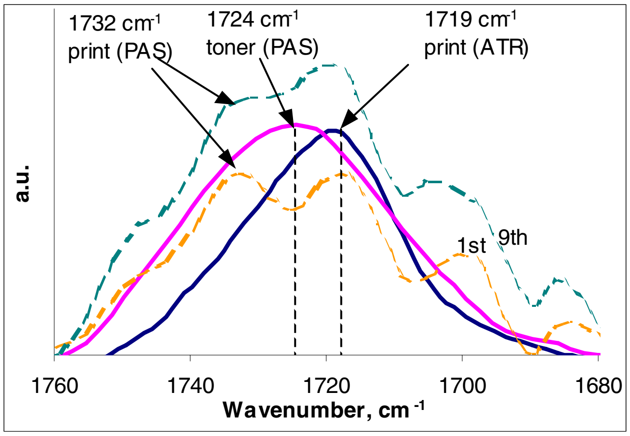

***Figure 8.** Carbonyl band shift in FTIR measurements. Reference band 2965 cm^{-1}. Fixing temperature 160°C.*

Raman measurements from the prints show distinct bands for the toner pigment, whereas with micro-ATR, bands for the toner resin are detected. When comparing the FTIR measurements from the toner (rapid-scan PAS) and prints (micro-ATR and step-scan PAS), it can be seen that there is a clear shift in the position of the carbonyl band of the toner resin from 1724 to 1719 cm-1 (Fig. 8). It is worth noting that in ATR the measurement depth does not reach the paper as in step-scan PAS. Two harmonics of the step-scan PAS shown in Fig. 8 represent the measurements from the surface (9th) and the deepest location (1st).

The unbonded carbonyl band at 1732 cm^{-1} intensifies deeper into the sample and can be assigned to paper. The changes in the carbonyl stretching area show that some molecular changes occur in the toner structure in fixing. Changes in carbonyl bands usually mean the presence of hydrogen bonding[28,32]. Wavenumber shifts were also detected at 1666, 1512, 1246 and 1103 cm^{-1}. A new band in prints appears as a shoulder at 1010 cm^{-1} and toner bands 1543 and 954 cm^{-1} diminish.

Conclusions

The goal of this study was to evaluate the applicability of vibrational spectroscopic methods to the study of non-impact prints. The variables of the light fading experiments in ink jet and fixing experiments in electrophotography led to systematic spectral changes in FTIR and Raman spectra.

In the case of ink jet prints on uncoated paper, Raman spectroscopy appears to be highly applicable to ink/paper interaction studies, due to its sensitivity to colorants. The available FTIR-methods proved to be helpful in studies of plain ink and unprinted paper, but differences between the printed samples related to interfacial interactions could not be discerned.

In the case of electrophotographic print studies, Raman and FTIR spectroscopic methods proved to give complementary information. Raman is sensitive to the toner pigments whereas different FTIR detection methods are sensitive to the toner resin. The two depth profiling methods seem especially promising when toner/paper interactions are considered.

The next step is to study the interactions further with controlled paper and ink samples. This enables more specific examination of the chemical bonds. Also, coated papers will be of interest. In the future, FTIR-ATR-mapping in xy-direction and the use of UV-Raman in print studies will also be examined.

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Biography

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