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Differentiating Digital Printing Through Physical and Chemical Analyses

Ana C. Sousa Ribeiro†, Jon J. Kellar†, Grant A. Crawford †, Steven J. Simske††, Jacob B. Petersen†, South Dakota School of Mines and Technology; Rapid City, South Dakota †; Colorado State University; Fort Collins, Colorado, USA††

Abstract

Over the past decade, the trade of counterfeit goods has increased. This has been enabled by advancements in low-cost digital printing methods (e.g., inkjet and laserjet) that are an asset for counterfeit production methods. However, each printing method produces characteristic printed features that can be used to identify not only the printing method, but in many cases, uniquely identify the specific make and model of printer used to produce a printed document, label, or package. This knowledge can be used for identification and determination of whether or not the analyzed document and/or goods are counterfeit, in addition to the method of production. This is the main goal of the present study.

During the first phase of this research, chemical and physical analyses were performed on printed documents and ink samples for two types of digital printing: inkjet and laserjet. The results showed that it is possible to identify the digital method used to print a document by its unique features. Physical analysis revealed that laserjet prints have a higher image quality characterized by sharper feature edge quality and brighter image areas (when viewed at multiple angles under white light). In addition, the deposited ink layer in the laserjet printed documents was more prominent (10 μm average thickness) than in inkjet documents.

Chemical analysis showed that the inkjet and laserjet inks could easily be distinguished by identifying the various ink components. Ink jet inks included (among others) water, ethylene glycol and dyes and/or pigments while laserjet inks contained components not present in the inkjet inks including styrene, methacrylate, and sulfide compounds.

Introduction

According to the Organization for Economic Cooperation and Development, the trade in counterfeit goods has increased in recent years [1]. This growth is partially due to the development of digital printing techniques that are both affordable and easily accessible [2]. Therefore, the ability to uniquely identify printing methods has drawn considerable interest as a means to detect counterfeit items. This is possible because most industries employ standard printing methods for various substrates, product use cases, and expected run length, all of which can be used to provide a high quality and efficient product [3]. On the other hand, counterfeit products are often made with cheaper printing methods and are used in small to medium runs, thus allowing the possibility for discernment between counterfeit and original products.

In this study two widely used digital printing techniques were analyzed with the aim of identifying key characteristics and unique *'fingerprints'* that arise from different printer brands and various substrates, since its known that these characteristics depend on same factors such as printing technology, ink, substrate, reader and settings [4,5]. It was expected that each printing method will produce unique features, and inks that have been adapted for each printing method will provide similarly unique characteristics [6]. Hence, chemical and physical analyses were performed to identify these signature characteristics for each method, since it is becoming more complicated to distinguish the printing methods just using imaging-based approaches. This is due to the higher quality of the final product owed the continuous improvement of the printing techniques, and also by the increased use of combined printing methods in the same product [3]. The obtained data will ultimately be used to build an automated system that can identify counterfeit goods and documents, since the number of documents authenticated by humans is decreasing [7].

Inkjet Printing Process

During inkjet printing, a print head moves back and forth while the substrate moves through the print system [2]. The print head comprises multiple nozzles that contain small orifices in which ink, contained within the nozzle, is released and sprayed onto the substrate.

When the ink is released, it forms a main droplet and it is accompanied by a tail due to its velocity, resistance of the environment, ink viscosity, and surface tension. This tail is further separated from the main droplet, forming smaller satellites droplets. The satellites droplets will often reach the substrate in a different area than the main drop because they are lighter and experience a longer flight time [8,9]. Thus, high-quality printing requires that the droplet size and velocity, as well as the ink rheology, are carefully tuned to minimize the gap between the main and satellite droplets, and also to minimize the generation of satellite drops [9].

Laserjet Printing Process

Laserjet printing is an electrostatic printing method that involves a laser beam, a photoconductor drum, toner, and a fuser assembly. The laser beam transfers the image to the negatively charged photoconductor drum by rastering the laser across the drum surface in a specific image pattern, creating a positive charge in the image area. When the drum contacts the toner's electrically charged ink, the positive charge from the image area attracts the ink powder and the drum then transfers it to the substrate. The substrate then passes though the fuser assembly which heats and melts the ink. The ink can be fixed on the substrate because of its thermoplastic properties from the polymer present in the toner [8, 10].

Materials and Methods

The inkjet and laserjet printing methods are not only different printing processes, but also have different ink characteristics, all of which will generate unique signatures in the final product. Thus, to verify the signature features for each method, 24 printers, from two different brands, were used. Four of those printers were inkjet and 20 were laserjet.

The printers were used to print a template in triplicate, always using the same substrate (A4 size Boise Multi-Use Copy

Paper 8.5" x 11" and 92 bright) for comparison proposes. Therefore, a total of seventy-two samples for the physical and chemical analyses were utilized. This template had the same text with two different fonts (Times New Roman and Arial) in upper and lower case with the same font size (12) and some color images.

For the chemical analysis, four inks from each printing method were used. These inks are used in the subtractive color model (cyan, yellow, magenta and black (CYMK)). All inks were analyzed using the same parameters even though the inks from inkjet printing method were liquid inks, and those from the laserjet printing method were powder inks.

Physical Analysis

All samples were analyzed using two different pieces of equipment: *i)* Foster and Freeman VSC 6000/HS Video Spectral Comparator (VSC), and *ii)* laser scanning confocal microscope (Keyence VK 200X). Each piece of equipment was used to generate magnified images from the prints to be further analyzed and compared between the different printer types and brands.

VSC Analysis

The VSC is a powerful imaging system, able to analyze a wide variety of document types, and has many options for light examination at various magnifications. Thus, the VSC can be used to reveal a variety of security features and signature characteristics.

The analytical procedure using this equipment consisted of placing the sample on the plate under the VSC canopy to receive a video image on the monitor, varying the magnification of the image until 60x, and also changing the incident illumination types such as ultraviolet (UV), infrared (IR), fluorescent and white light. It was used two wavelengths for the UV light analysis, 365 nm and 254 nm, always using 100% of background light. For the fluorescent light, the wavelength chosen was in the range 585-430 nm. Care was taken to maintain the sample image focus during the whole experiment. For comparative purposes, all examination was performed under the same magnification and illumination conditions.

Confocal Microscopy Analysis

The laser scanning confocal microscope can be used to make non-contact profile measurements using its multi-file analytical software. This equipment was used to identify the topography of the samples to determine differences between the thickness of the ink layers from the inkjet and laserjet printing methods [7]. Samples were fixed on the stage and scanned. The thickness of the layer of ink and roughness of the printed document was measured using the software from the Keyence VK 200X.

Chemical Analysis

The chemical analysis was performed not only in the printed samples, but also using the raw CMYK inks for each printing method. Inks were analyzed using the two different methods: Raman spectroscopy (Foram X3, Foster and Freeman) and Fourier-transform infrared spectroscopy (FTIR) (IRAffinity-1S, Shimadzu).

Raman Spectroscopy Analysis

Raman spectroscopy is an analytical technique in which a laser beam of different wavelength is scattered and it is used to identify functional groups presents on that sample. Analysis was conducted with a 532 nm wavelength laser and measurements were performed at five different locations for each ink color on each specimen. Calibration was performed prior to each measurement using a standard specimen.

The background (substrate) spectrum was also collected and subtracted from the ink spectra to identify specific molecular structure features represented by characteristic peaks that could correspond to some components from the ink.

FTIR Analysis

Like Raman spectroscopy, FTIR spectroscopy is an analytical technique that provides the analysis of the chemical structure of the sample by identifying the functional groups present by bonding characteristics. Before using the equipment, the background spectrum was collected and automatically subtracted from the ink spectrum to have a clear idea of which peaks were from the ink sample.

Eight inks were analyzed with FTIR spectroscopy. The four liquid inks from the inkjet method required little sample preparation. On the other hand, the four laserjet inks needed to be dried because the initial spectra taken without drying exhibited significant noise, determined to be largely from water and water vapor present within the sample.

Therefore, the powder inks were placed in four vials (Figure 1) weighed and then placed in an oven at 95°F. After 1 h, all the inks were dried and compacted into a solid. After drying all the inks experienced an average mass loss of 0.42%. The vials were returned to the oven for more 30 min and were subsequently weighed whereby they no longer exhibited mass loss. The solid laserjet ink samples were then taken from the vail and milled. The powder of the dried laserjet inks was placed again in the new vial and then used in the FTIR analysis.

Figure 1. *Vial with the CMYK laserjet inks after been dried and milled.*

It has been reported in the literature that nearly all inkjet inks are water-based contain water, co-solvents, surfactants, colorants and other additives [9, 11]. Solvents and co-solvents commonly chosen are ethylene glycol ether, propylene glycol ether, or esters [9]. Therefore, many mixtures were prepared in different concentrations of water and ethylene glycol, solvent and co-solvent, respectively. Those mixtures were also analyzed in the FTIR, to compare their spectra with that from the inkjet inks to estimate the solvent composition of the inks.

Results and Discussion

Physical Analysis

VSC Analysis

All 72 samples were analyzed using the VSC under various lighting conditions and magnifications. Figure 2 compares a VSC white spotlight image of the letter "y" printed using inkjet and laserjet.

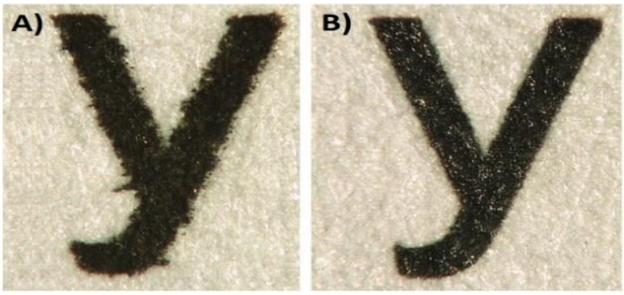

Figure 2. The letter "y" in 12pt. Ariel from A) inkjet and B) laserjet under white spotlight at a magnification of 60X.

All samples showed that the laserjet images have better print quality than that of inkjet. Specifically, the "y" printed in an inkjet printer has a much rougher edge that is noticeable under 60x magnification, and under UV light is even more evident, as shown in Figure 3. Also, it is possible to see with the naked eye, as well as under higher magnification, that the laserjet has a glossier appearance than the inkjet print [11]. Even though the same substrate was used for all of the prints, it is apparent that the substrate for the inkjet printing has different fluorescence than the substrate for the laserjet printing. However, this difference in substrate should not affect the results, and in these experiments the substrate did not obscure any of the features in the document.

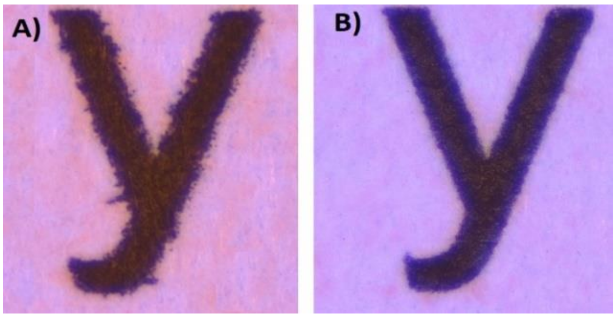

Figure 3. The letter "y" in 12pt. Ariel from A) inkjet and B) laserjet under UV light (254 nm) with 100% of background light at a

In addition, some laserjet prints showed yellow dots spread across the substrate. It was confirmed that the original substrate was free from these marks and the inkjet printed specimens also did not exhibit these features. These yellow dots are generated as a security feature and has encoded information such as date that the document was printed, and information about the printer (serial number) [12].

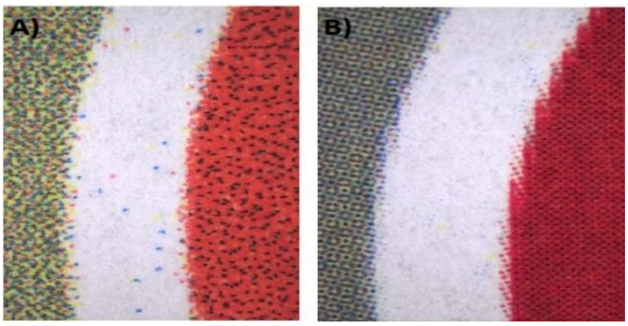

Figure 4. A color image area from A) inkjet and B) laserjet under white light in a magnification of 30X.

Moreover, it was possible to identify some satellites drops on the inkjet print. When the color image was analyzed under high magnification, it was possible to notice that the laserjet prints have a better and well-defined dot pattern compared with the inkjet prints that can lead to better resolution and quality for this printing method. These features are shown in Figure 4.

Profilometer Analysis

The roughness of the as-received substrate was measured in triplicate to identify the thickness of the ink layer in the inkjet and laserjet prints without the background interference. The measurements showed that the substrate has an average roughness of 7.4 µm. Next, the printed documents were analyzed in different regions. Figure 5 shows a height map of the surface of both an inkjet and laserjet print. In both cases the analysis was performed in region containing the letter "y". Clearly the laserjet print leaves a thicker surface ink deposit that is easily observed using this analysis while the location of the laserjet printed feature is not discernable.

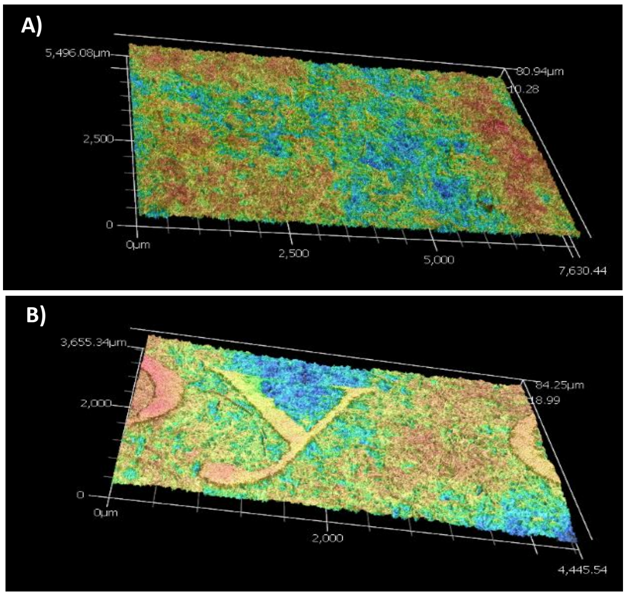

Figure 5. The same image area from A) inkjet and B) laserjet at a magnification of 20X.

The average roughness measured from the inkjet and laserjet image area, represented by Figure 5A and 5B, were 6.51 µm and 6.60 µm, respectively (slightly lower than the roughness of the substrate without any print). However, when the height of the feature was measured specifically within the printed letter, it exhibited a layer thickness of approximately of 10 µm in the laserjet samples, while the inkjet images did not show a significant height variation.

Limited layer thickness observed in the inkjet specimens is likely associated with evaporation of the solvents present in the ink and absorption of the ink into the substrate. This occurs because the inkjet ink is a liquid water-based ink and easily penetrates the substrate while the laserjet ink contains powders that melt and solidify on the surface of the substrate [13].

Chemical Analysis

Raman Spectroscopy Analysis

The Raman spectra of the inks were taken in different points of the sample, that corresponded to three colors (black, red and green). It was possible to notice that even though all spectra with a given printing method have some similar absorbance bands, they were still distinct.

The laserjet spectra were very similar, even in areas of the sample with different colors and with samples using different ink models. The mains peaks are around 1300 cm^{-1}, 1550 cm^{-1}, 1750 cm^{-1}, 2380 cm^{-1} and 2500 cm^{-1} which correspond to the following functional groups ($C-NO_2$), (C=O) and (C≡C) [14]. Those functional groups are present in some thermoplastic resins and an isoparaffinic fluid that are commonly used in laserjet ink formulations [15].

On the other hand, not all spectra from the inkjet samples were as readily identified as the laserjet spectra. The peaks presented by the inkjet inks for the red and green areas of the sample were similar, having the strong absorbance band near the same wavenumber. The green and red area spectra showed strong peaks around 1300 cm^{-1}, 1550 cm^{-1}, 1800 cm^{-1}, 2380, and 2500 cm^{-1} that correspond to the following functional groups (C=C), ($C-NO_2$), (C=O) and (C≡C).

Nevertheless, the black ink spectra showed strong absorbance bands around 1020 cm^{-1}, 1140 cm^{-1}, 1180 cm^{-1}, 1300 cm^{-1}, 1440 cm^{-1}, 1600 cm^{-1}, 1800 cm^{-1} and 2500 cm^{-1} which correspond to the following functional groups (C=C), (C=S), (CH_2), (CH_3), ($C-NO_2$), (C=O) and (C≡C). Thus, the black ink has absorbance band at 1020 cm^{-1}, 1140 cm^{-1}, 1180 cm^{-1}, that the green and red areas do not have.

The large bands at 1300 cm^{-1} and 1600 cm^{-1} can be related with carbonaceous materials, such as carbon black, which is commonly used in black ink formulations [16]. The spectra from the green and red areas also have absorbance bands similar to the black ink, such as the peaks at 1300 cm^{-1}. This is not surprising, because, as can be seen in the Figure 4, those printed areas have some black dots present. The other peaks can be related with residual solvents, surfactants, that have the purpose of improving the wetting of the ink in the substrate, and polymeric binders that will improve the durability of the print and give it a glossy look [9].

FTIR Analysis

The IR analysis for the inkjet inks was made on as received samples, and the resulting spectra were analyzed by comparing the intensity of the main absorbance band, as well as the presence or absence of some characteristic bands [17]. Those spectra were compared between inks, and also between the spectra from nine solutions with different concentrations of water and ethylene glycol. It was observed that most bands present in the ink spectra are complex peaks, that have absorption bands in many areas of the spectrum, which is common in organic compounds present in inkjet ink formulations [18,19].

Through data analysis, it was possible to infer that the solution closely correlated with 50% of water and 50% of ethylene glycol with all the ink spectra, as shown in Figure 6. This finding is not surprising since, as it has been shown that most inkjet inks are water based and have as a common co-solvent ethylene glycol ester [9]. After analyzing the ink spectra, it was possible to identify some specific ink functional groups, as shown in Table 1, that also corresponds to the residual presence of the solvent and co-solvent in the ink.

The dried laserjet FTIR spectra are shown in Figure 7. It can be seen that even though the absorbance bands have different intensities, all inks present almost every peak in the same wavenumber. Table 2 shows some possible functional groups present in the ink composition [17].

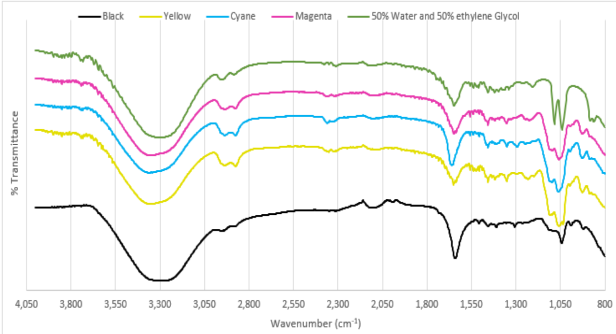

Figure 6. *FTIR spectra from the inkjet ink samples and from the solution with 50% of water and 50% ethylene glycol*

Table 1. Possible functional groups present in the raw CYMK inkjet inks

Wavenumber cm^{-1}	Possible Functional Groups	C	M	Y	K
3700 - 3100	-OH, -NH, C-H	x	x	x	x
3000 - 2800	-CH, $-CH_2$, $-CH_3$	x	x	x	x
2400 - 2000	-C≡N, -C=N+=N-, -C≡C-		x	x	x
1870 - 1650	C=O	x	x		x
1650 - 1550	C=C, C=N, NH	x	x	x	
1550 - 1300	NO_2, CH_3, CH_2	x	x	x	x
1300 - 1000	C-O-C, C-OH, S=O, P=O, C-F	x	x	x	x
1100 - 800	Si-O, P-O	x	x	x	x

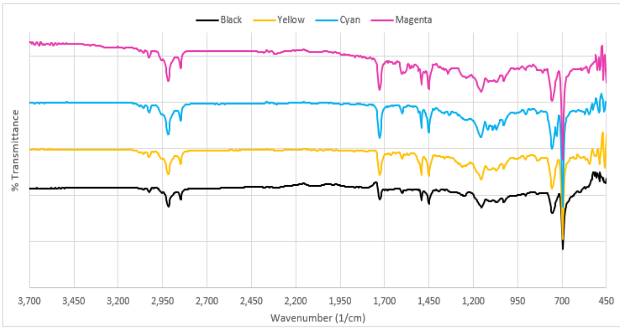

Figure 6. *FTIR spectra from the laserjet ink samples*

Table 2. Possible functional groups present in the raw CYMK laserjet inks

Wavenumber cm^{-1}	Possible Functional Groups	C	M	Y	K
3700 - 3100	-OH, -NH, C-H		x		
3100 - 3000	=C-H, $-CH_2$, or -CH=CH-	x	x	x	x
3000 - 2800	-CH, $-CH_2$, $-CH_3$	x	x	x	x
2400 - 2000	-C≡N, -C=N+=N-, -C≡C-	x	x		x
1870 - 1650	C=O	x	x	x	x
1650 - 1550	C=C, C=N, NH	x	x	x	x
1550 - 1300	NO_2, CH_3, CH_2	x	x	x	x
1300 - 1000	C-O-C, C-OH, S=O, P=O, C-F	x	x	x	x
1100 - 800	Si-O, P-O	x	x	x	x

The results from the Raman Spectroscopy and FTIR are complementary, as all functional groups present in the Raman spectra was also identified in the FTIR analysis.

The inkjet and laserjet inks FTIR spectra were also analyzed using spectral identification software that showed that the raw inkjet inks are composed of water, ethylene glycol, oxides (just for the back ink) and dyes and/or pigments. The oxides can be attributed to pigments in the ink formulation. These findings coincide with the typical inkjet ink components, which are water, colorants, co-solvents, and just 2% are surfactants. The inkjet ink volume fraction can range between 0 – 10% for polymeric binders, which can be represented by the alkyne functional groups, but no specific polymers were found by the spectral matching software [9].

Moreover, the possible compounds found to the laserjet raw inks were styrene, methacrylate, sulfide and dyes and/or pigments. All the suggested compounds matched the possible functional groups shown in Table 2, and consequently matched the those observed in the Raman spectral analysis. The styrene and methacrylate can be linked with the thermoplastics polymers that are present in laserjet inks [15]. The specific thermoplastic polymer used in the toner varied by the manufacturer. The most common polymers are styrene acrylate copolymer and polyester resins [20]. It is possible to confirm the presence of styrene acrylate, amorphous silica, and pigment using the safety data sheet of a common toner. However, it was not possible to identify the presence of the specific wax in the toners as listed in the data sheet by the experimental analysis described here.

The presence of sulfide in the black toner can be a result of the contamination of the ink powder by the polyphenylene sulfide used to coat the fuser roll in laser printers, or due to the presence of sulfide in one or more inorganic pigments colorants.

Conclusion

This study presented a variety of physical and chemical techniques that can be used as a means to identify key characteristics from different printing methods. It was possible to determine from the physical analyses that the laserjet prints have a much more prevalent dot pattern, sharper edges, glossier appearance, and a much thicker layer of ink in the substrate compared to the inkjet prints. The Raman and FTIR spectroscopic analyses also showed that the inks have distinct components in their formulation that can help to differentiate the printing methods. The chemical and physical characteristics obtained can be used to generate a database for authentication software and also help law enforcement agencies to validate documents and goods.

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Author Biography

Ana Sousa finished her B.S. degree in Chemical Engineering from the Salvador University in Brazil (2014), and has earned two specializations, one in quality management and production engineering and another in food safety management. Prior to 2019 she worked as a process engineer focused in improving operational processes, projects development and testing. She is currently a Materials Engineering & Science M.S. degree candidate at the South Dakota School of Mines and Technology.