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The Forensic Analysis of Thermal Transfer Printing*†

ABSTRACT: Thermal transfer printing refers to printing processes that utilize heat to produce an image by either physical or chemical means or by a combination of both. As the technology has improved and the supplies have become less expensive, the use of thermal printing in the personal and business markets has increased significantly. Specifically, dye diffusion thermal transfer and thermal mass transfer have become predominant in the production of counterfeit credit cards, drivers' licenses, and other types of documents produced on plastic media. Chemical analysis by means of thin layer chromatography (TLC) has proven to be useful in characterizing various types of inks (e.g., writing and inkjet inks). In this study, the authors examined 81 different samples that included a total of 54 printer samples (43 photographic prints on paper and eleven plastic card samples) and 27 printer ribbons. A new TLC method was developed and tested utilizing a solvent system (80% *n*-hexane, 3% methyl ethyl ketone, and 17% ethyl acetate) that is capable of producing excellent resolution.

KEYWORDS: forensic science, questioned documents, counterfeit documents, identity documents, thermal transfer printing, dye diffusion thermal transfer, thermal mass transfer, printing processes, thin layer chromatography, ink analysis

Thermal transfer printing applies to printing processes that utilize heat to produce an image by either physical or chemical means or by a combination of both. This technology is one of the oldest non-impact printing methods and dates back to the 1930s when it was used for specialized scientific recording instruments (e.g., electrocardiograph charts). Its predominance has evolved in the past two decades with the advent of bar coding, retailer receipts, fax machines, event tickets, and, more recently, the use of high resolution digital photography and plastic identification cards. There are several diverse thermal technologies, but they are generally categorized into thermal direct or thermal transfer methods. It is beyond the scope of this paper to fully discuss the various types of thermal printing methods; however, Komerska (1) provides an excellent review of many of these processes. Rather, the focus of this discussion is the forensic examination of thermal transfer technology, which is commonly encountered in counterfeit credit cards, identification documents such as drivers' licenses and passports, and other documents requiring quality graphics.

It is the tragic events of September 11, 2001, that have particularly caused an increased awareness of identity documents. Many agencies (e.g., Department of Motor Vehicles) are now considering the addition of a multitude of security features such as holograms, security inks, and biometrics, but must maintain reasonable costs, create a high-quality product, and produce the document in a timely manner. Incorporating on-site thermal transfer printing as opposed to utilizing easily accessible color inkjet and laser printing equipment is an excellent compromise to meet some of these needs. Consequently, criminals are becoming more aware of these processes and have begun to reproduce documents using similar printing technologies. In fact, the United States Secret Service maintains a counterfeit document database consisting of over 100,000 specimens including, but not limited to, credit cards, travelers checks, identification cards, and drivers' licenses. Currently, over 5,000 counterfeit credit cards and drivers' licenses on record have been produced using thermal transfer printing. These figures will likely continue to grow as a result of increased awareness, thermal transfer technology improvements, and the utilization of thermal printing in the home and business markets. All these factors should cause a significant decrease in the price of printers and ribbons. As an example, printers priced well over $2,000 in the mid-1990s can now be obtained for less than $500; hence, this makes the technology more accessible.

Two thermal transfer-printing technologies will be discussed. Dye diffusion thermal transfer (D2T2), also referred to as dye sublimation, dye diffusion, or thermal dye, was developed by Sony in 1982 and has been used as a "specialist" application for graphic arts and photographic applications (e.g., medical imaging). D2T2 printers utilize a print head with hundreds of tiny heating elements to molecularly transfer impregnated dyes and similar materials (e.g., fluorescent materials and other compounds without color) from a donor or ribbon onto a receptor or printing substrate. The receptor is a specially coated substrate whereby the surface of the media is designed to chemically accept the dyes from a ribbon. The ribbon consists of colored panels arranged in blocks of yellow, followed by magenta and cyan (YMC), i.e., the subtractive process colors.

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Sometimes the colored panels may be followed by a black panel (YMCK). The black panel is not always present since black coloration can be achieved using the combination of cyan, magenta, and yellow. There are other combinations possible that may include an overlay (e.g., YMCKO or YMCO). The overlay is applied to protect the print with a transparent material after the color portions have been printed onto the substrate. The overlay also enhances light fastness of the final print since it contains UV absorbers, as well as reducing the availability of oxygen. The panels are slightly larger than the substrate and the transfer process that takes place is distinctive. Each panel of the ribbon makes a pass over the substrate, and the amount of dye transferred to the receptor is a function of the amount of energy applied to each heating element. Hence, the gamut of colorants transferred varies in proportion to the amount of heat applied to the print head, resulting in an image with a continuous tone reproduction, i.e., a photographic-like quality image that contains gradient tones of color. D2T2 can provide high resolution, an optical density range that is nearly equal to photography, as well as superior color saturation. The printing ribbon typically consists of multiple layers that may in-

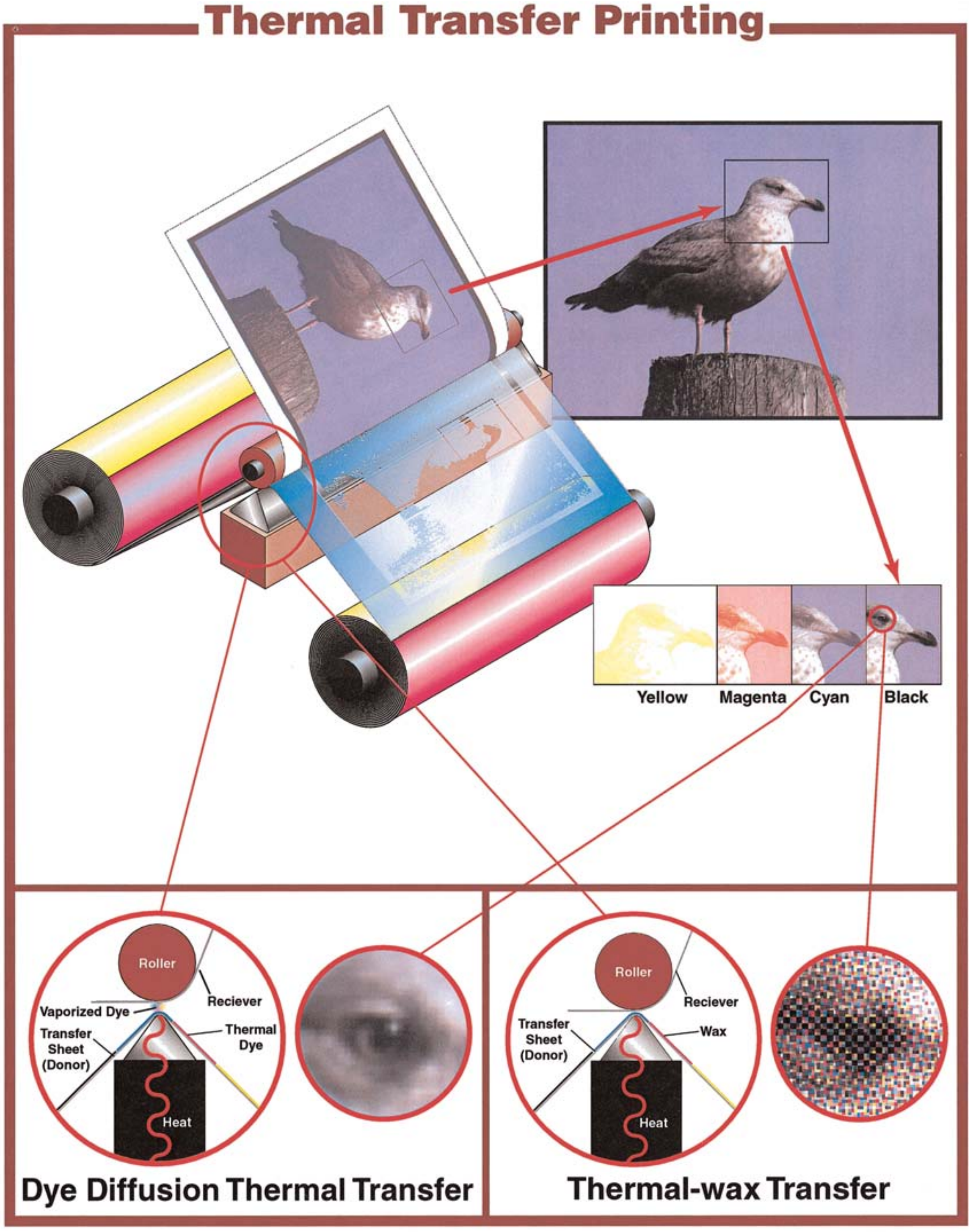


FIG. 1—*The dye diffusion thermal transfer process allows dyes from a ribbon, or donor, to be transferred to a receiver, or substrate. The amount of dyes that diffuses into the substrate is a result of the voltage being applied to the heating element. The second process, thermal wax transfer, is a direct contact process whereby pigment suspensions of colorants are transferred from a ribbon to the substrate.*

clude a slip coat, a polyester or polyethyleneterephthalate base film, and/or a prime coat covered with a layer of dye. Preliminary investigations have indicated that each of the coats may be manufacturer specific. As an example, the ribbon contains a binder polymer that is critical in controlling the rate of release of dyes into the receiver. When a manufacturer opts for a particular binder, a compromise must be reached when considering stability and control versus rapid color buildup. Figure 1 illustrates the dye diffusion process that takes place between the donor and the receiver.

The second thermal printing process is thermal mass transfer (TMT), also known as thermal wax transfer, direct thermal transfer (D1T2), or hot wax transfer. Unlike D2T2, TMT is a bimodal process, which means image transfer is on or off—either the transfer takes place or it does not. The ribbons used are coated with a specially formulated wax that contains a pigment or pigments, which is transferred and dispersed at a special threshold temperature. TMT creates an image by selectively transferring colored wax from a ribbon onto a substrate. The ribbons also consist of yellow, magenta, cyan, and sometimes a black panel and an overlay (YMCKO). Figure 1 also depicts the process that takes place during thermal wax transfer.

Forensic Examination

Due to the differences in their technologies, D2T2 and thermal mass printed documents can be physically differentiated and identified. When viewed under magnification (greater than X10), D2T2 is observed to have a grid-like pattern with severe pixel distortion resulting in a blurry, unfocused quality. Hann and Beck (2) surmise that the blurry feature, characteristic of magnified D2T2 images, is due to the disproportionate temperature on the surface of the heating element. Since the center of each heating element heats up faster than the outside, the center of each pixel will result in a greater amount of dye transfer compared to the edge, with some ink peripherally spreading beyond the edges into adjacent blank pixels. Consequently, variations in the color density and the lack of sharpness as the ink diffuses into the substrate result in an unclear image. Images printed utilizing TMT appear to be sitting on the surface and have a wax-like appearance with well-defined, crisp edges. As well, distinctive "stair-stepping" occurs around the edges of the image, which is the result of bimodal printing, that is, the transfer of colorant is all or nothing. Figure 2 reveals a microscopic representation of each of the processes.

In the past five years, there has been a significant increase in the number of submissions of counterfeit documents produced using thermal transfer technology. Attempting to associate a questioned document with a suspect printer, identify the make and model of the printer used to create a document, or establishing a possible association of multiple documents by means of physical defects and chemical similarities (comparison of plastics, laminates, and/or colorants) may be required. The ribbon consists of colored and overlay panels wound onto a spool, with the spool designed to fit into a specific printer. However, some printers will accept more than one spool. The number and types of spools (e.g., size dimensions and outside spool fittings) available on the market vary widely. Therefore, if a ribbon is the only item submitted for forensic examination, it can provide information about a possible manufacturer and a compatible printer. In addition, if the ribbon was previously used, images will still exist on each of the used color panels and are easily visualized using transmitted light. With this caveat, if a thermal transfer printer is encountered at a crime scene, it would be prudent to remove the ribbon for examination to identify any previously printed documents.

FIG. 2—*The left image is a microscopic depiction (approximately X20 magnification) of a picture produced using D2T2. The right image was created with a thermal wax transfer printer. Note the "blurry" or distorted image produced by the D2T2 printer and the stair-stepped edging in the thermal wax transfer figure when magnified.*

Associating questioned documents produced by dye sublimation printers based on physical properties and/or repeating defects is uncommon, so the forensic examiner often has to resort to a destructive analysis to characterize the chemical components that constitute the final product. These include, but are not limited to, colorants and overlays. Thus, the efforts of this research focused on performing a chemical analysis of colorants and overlays from ribbons, paper, and plastics.

Chemical analysis of writing inks by means of thin layer (planar) chromatography (TLC) is widely accepted in the field of forensic science since it is very effective for separating and identifying various colored components such as dyes and their by-products (3–7). Undoubtedly, the chemical composition of thermal printing inks can be quite complex since there are many factors to take into consideration when formulating quality inks. In a vastly competitive environment, manufacturers are vying for market share, so increased emphasis is placed on developing thermal transfer inks that have the proper hue, resistance to fading (light fastness), and thermal stability (generally up to 400°C). As a result, companies will allocate significant amounts of resources into research and development, resulting in proprietary ink formulations that are often difficult to mimic. The authors hypothesized that the chemistry of the inks will vary from one manufacturer to the next, often making the forensic analysis discriminating. In addition, since the technology of these printers has been rapidly advancing, it was suspected there might be detectable changes in ink composition from model to model within a manufacturer. TLC can be used to determine the composition of dye components found in printers by comparing them with known standards. In fact, the U.S. Secret Service currently maintains a library of standards consisting of various makes, models, and manufacturers of office machine systems utilizing a wide variety of printing technologies (e.g., inkjet, toner, and solid ink) for comparison and/or identification. TLC is not an adequate procedure for identifying unknown compounds unless a complete collection of standards exists. Cantu (8) discusses the importance of obtaining samples from all manufactures on a regular basis since deficiencies in a comparative library will weaken the forensic conclusion and increase the number of non-matches. The importance of establishing a library of standards cannot be overemphasized, but maintaining a collection of standards is a formidable task that obviously requires significant resources and maintenance. Indeed, this is not always a practical solution for every forensic facility to achieve, so any law enforcement agency needing an ink analysis that requires a library of standards can do so by contacting the nearest U.S. Secret Service office.

Prior to this study, neither the solvent systems nor the extraction procedures utilized for writing inks (6–7) or inkjet inks (9) were feasible for the analysis of documents produced using thermal transfer printing. After conducting a thorough review of the literature, no references could be found pertaining to the chemical analysis of documents produced with thermal transfer printers, so the authors initiated research to effectively compare the colorant components of different manufacturers based on the development of a new TLC solvent system to be used on silica gel plates.

It should be emphasized that the TLC method is generally suitable for matrices containing colorants that are resolvable on a TLC plate, i.e., dyes. Since the TMT ribbons mainly contain pigments as colorants, this approach would likely not be feasible for the chemical comparison of documents produced using solely TMT. Further, the great majority of counterfeit specimens produced using thermal transfer printing are produced with D2T2 machines. However, documents may be produced whereby the color portions (CMY) are created utilizing dye diffusion, and the black portions (e.g., text and barcodes) are produced using TMT. Therefore, a single printer is capable of manufacturing a document by means of dye diffusion and TMT. Analysis of pigments from TMT ribbons might be better suited for analysis using Fourier transform-infrared spectrometry (FT-IR), Raman spectroscopy, and/or scanning electron microscopy–energy dispersive spectrometry (SEM-EDS).

Methods and Materials

Using a standard procedure for TLC analysis of inks involves sampling, extraction, spotting, developing, visualization, and interpretation. Extractions using pyridine were performed on 81 different samples, which included a total of 54 printer samples (43 photographic prints on paper and 11 plastic card samples) and 27 printer ribbons, all from various manufacturers. Five millimeter hole punches were removed from the paper samples, small cuttings measuring approximately 5 by 5 mm were cut from the ribbons, and scrapings, using a scalpel, were removed from the plastic cards to minimize the amount of plastic removed. In all instances, an arduous effort was made to obtain samples with all four process colors (e.g., CMYK). The extracted samples were dissolved and spotted on silica gel 60 pre-coated EM Science® glass plates (EM No. 5721-7) with a layer thickness of 250 μm. The plates were placed in an oven (100°C) for approximately 5 min, and, once removed, were immediately placed in a TLC chamber with a solvent system composed of 80% *n*-hexane, 3% methyl ethyl ketone, and 17% ethyl acetate. The solvent front was allowed to elute for 4 cm.

Each colored section of the ribbon was tested separately (e.g., C+M+Y+K+O) and in combination (e.g., all sections of the ribbon combined). This allowed for the examination and documentation of each component. Therefore, if a questioned document was submitted for analysis and was not produced using all the process colors, a comparison with library standards would still be feasible.

The TLC plates were first visualized using the 254 and 366-nm wavelength settings using an ultraviolet (UV) source manufactured by UV Products®. The Foster and Freeman® Video Spectral Comparator 2000 High Resolution (VSC 2000 HR) was used to document and record the TLC plates in black and white and color modes. The VSC 2000 HR was also used to observe and record infrared luminescence (IRL) properties on the TLC plate produced from the D2T2 dyes and/or overlays.

Results and Discussion

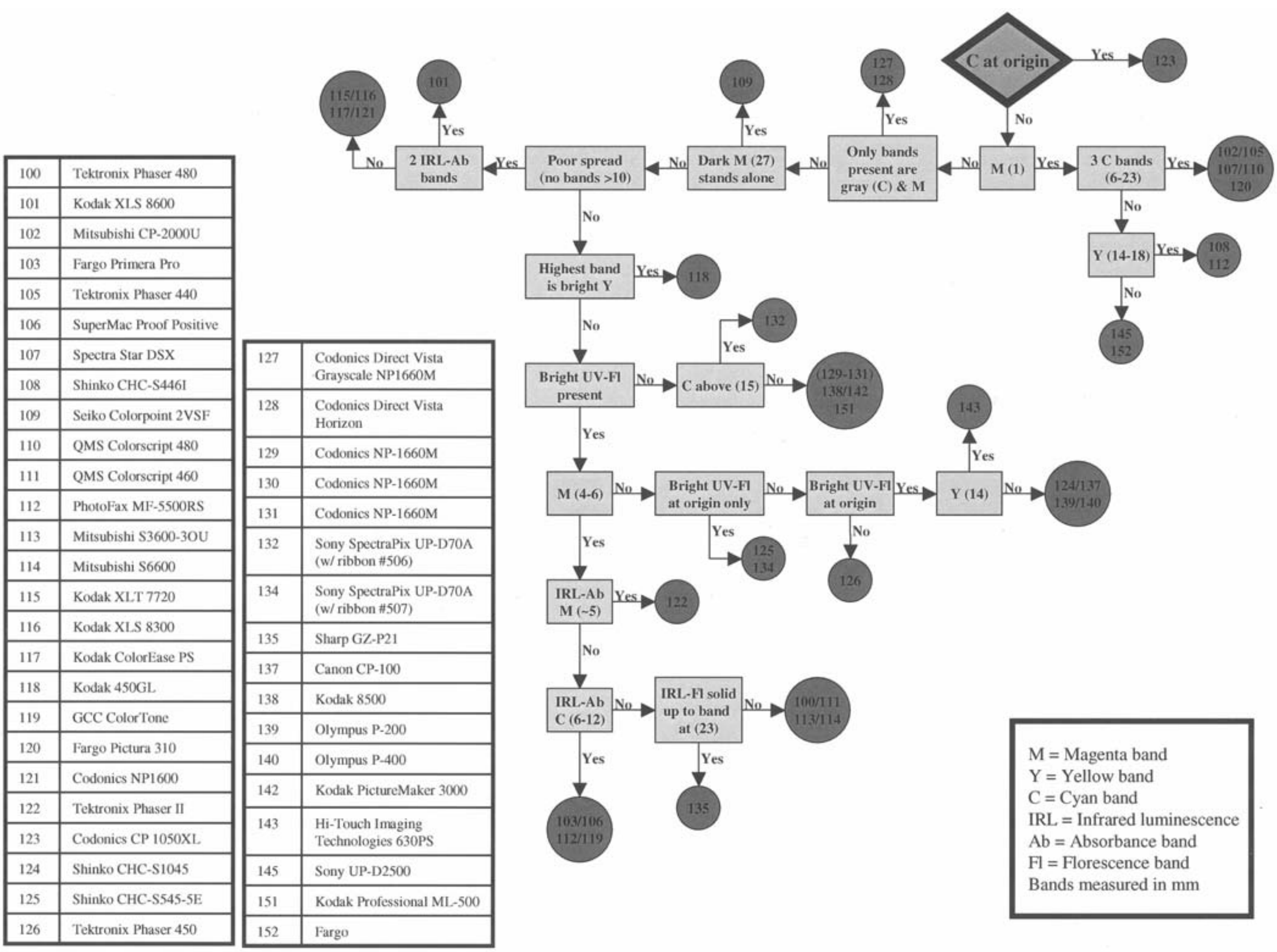
In this study, the general TLC method employed, including the extraction procedure and solvent system (80% *n*-hexane, 3% methyl ethyl ketone, and 17% ethyl acetate) was capable of producing excellent resolution of chemical constituents on the TLC plate. The results were reproducible, but some important factors were noted. First, the authors discovered that it was critical to place the TLC plate in the mobile phase chamber immediately following removal from the oven because allowing the glass plate to stand in ambient conditions resulted in poor resolution. A second observation was that the solvent system had to be relatively new or fresh, i.e., running less than three separate plates in the same solvent system or changing the solvent system every 2 h. The root cause of this phenomenon was likely due to the change in the ratio of solvents in the TLC chamber as they volatilized. When the glass plates were added to the solvent system, the heat from the glass probably accelerated the changes. Further research is needed to determine if other systems exhibit the same phenomena and if the loss in resolution is due to humidity or some other factor. At present, no other TLC plates have been tried since the protocol developed here works well provided the heating to developing steps are carefully followed. Finally, TLC plates needed to be documented immediately following development. Some colored bands faded and the UV characteristics became less apparent following exposure to light. The plates were digitally imaged, placed in plastic sleeves, cataloged into a binder, and stored in darkness to minimize their degradation from exposure to light.

Polyester TLC plates (60 Å, 250 μm) coated with silica gel (Whatman® Catalog Number 4410221) were tested since they have been used to record thousands of ink standards (e.g., writing, stamp pad, and inkjet) in the U.S. Secret Service International Ink collection. They are suitable for library cataloging for two reasons. First, they are not breakable and easily stored. Second, the plastic TLC plates are used to perform a preliminary screening comparison because they are low-resolution plates that are generally not affected by environmental factors such as temperature, humidity, and other development conditions. However, the colorants from D2T2 printers were not sufficiently resolvable using the plastic TLC plates.

Research through industry contacts, printer catalogs (10), and Internet resources indicates that there have been over 50 printer manufacturers and 250 models of dye diffusion printers available on the market from the mid-1990s until the time of this publication. However, this is a dynamic and competitive market that constantly undergoes technological change, so some manufacturers are no longer in business and some printer models are now obsolete. The dye sublimation printer industry can be generally divided into two sectors: personal or specialty applications and plastic card printers. D2T2 printers are capable of producing high-quality photographic-like images and, at one time, were predicted to replace traditional silver halide photography. Technological advances in inkjet technology have proven to be a strong competitor and have significantly eroded the market share in the personal printer arena. Notwithstanding, D2T2 personal or specialty printing continues to find niche areas such as medical imaging, specialty on-site photographic prints (e.g., holiday photographs found in malls and shopping centers), and direct printing from cameras without a computer interface. Some examples of manufacturers of these types of D2T2 printers include Canon, Casio, Kodak, Olympus, Mitsubishi, Panasonic, Sharp, and Sony. Typically, questioned documents produced in this manner are infrequently submitted to the forensic laboratory. The latter sector, that is, companies that specifically manufacture printers for card personalization, are encountered more often for forensic analysis. They are designed to print directly onto plastic substrates, making them more common for the production of counterfeit credit cards and identity documents. There are over 30 companies worldwide that produce plastic card printers and include Atlantek, DataCard, DigiCard, Eltron, Fargo, Magicard, and NISCA. There are also original equipment manufacturers that do not produce the card printer, but use a version of the original manufacturer's printer, while marketing a machine under their name. However, printer manufacturers oftentimes do not manufacture their own ribbons; rather, they are obtained from a different source.

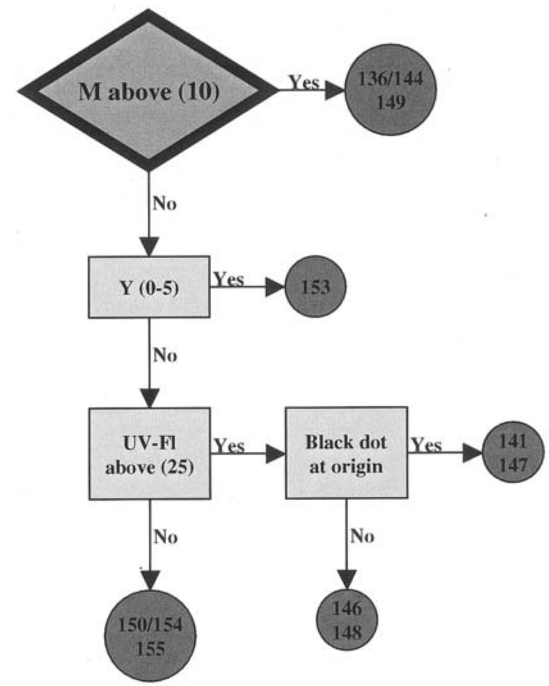
An understanding of the relationship between printer manufacturers and ribbon makers is essential when attempting to draw conclusions following a forensic examination. Currently, there are five major manufacturers of ribbons, which include Dai Nippon Printing (DNP), Hansol, ICI Imagedata (ICI), Kodak, and Sony. 3M also manufactures laminate or overlay materials for select card printer manufacturers. A conversation regarding this topic with an industry representative did help enlighten the authors with some facts surrounding the relationship of printer manufacturers and ribbon producers (e-mail communication with John Knotts, Vice President Sales and Marketing, ICI Imagedata, October 10, 2002). Each of the ribbon manufacturers produces a product that is compatible in a variety of printers. For example, ICI makes ribbons for some Nisca, Fargo, Eltron, and Datacard printers. Furthermore, a single printer may be compatible with multiple ribbons. For example, the Atlantek Model 85DSL plastic card printer is configured to use ICI and DNP ribbons. However, many printers are configured and color tested with a manufacturer's ribbon. Therefore, if a different ribbon, other than the original, is used in a D2T2 printer, the color might be altered on the picture since the firmware in the printer is configured using a given color gamut from the original ribbon. Although the intricacies of the relationship between printer and ribbon producers appear to be complex, with information provided by manufacturers, it is feasible to create a flow chart or database to account for these relationships, ensuring that the forensic examiner forms accurate conclusions.

Since maintaining a comprehensive library of standards requires continual updating, the number of samples contained in any collection is continuously changing. At the time of this study, by utilizing TLC analysis, 43 photographic-like prints from 21 different manufacturers were differentiated into 19 categories. Figure 3*a* demonstrates how the TLC results from the prints were documented and differentiated into their respective groupings. Many of the final groups of printers that could not be discriminated contained printers from the same manufacturer and/or printers from different manufacturers that utilize the same ribbon (e.g., Kodak



A

FIG. 3—*Flow charts depicting class characteristics for: (a) 43 photographic prints that were chemically analyzed using TLC; (b) eleven plastic card printers subjected to TLC analysis; (c) 27 D2T2 ribbons based on physical characteristics, and; (d) 27 D2T2 ribbons based on TLC results. The rectangles represent the various features observed on TLC plates that allowed for discrimination such as IRL, UV properties, and Rf values for the colored bands. The numbers within each of the circles signifies the printer or ribbon manufacturer. Multiple entries within a circle represent a group of printers or ribbons that could not be further differentiated.*

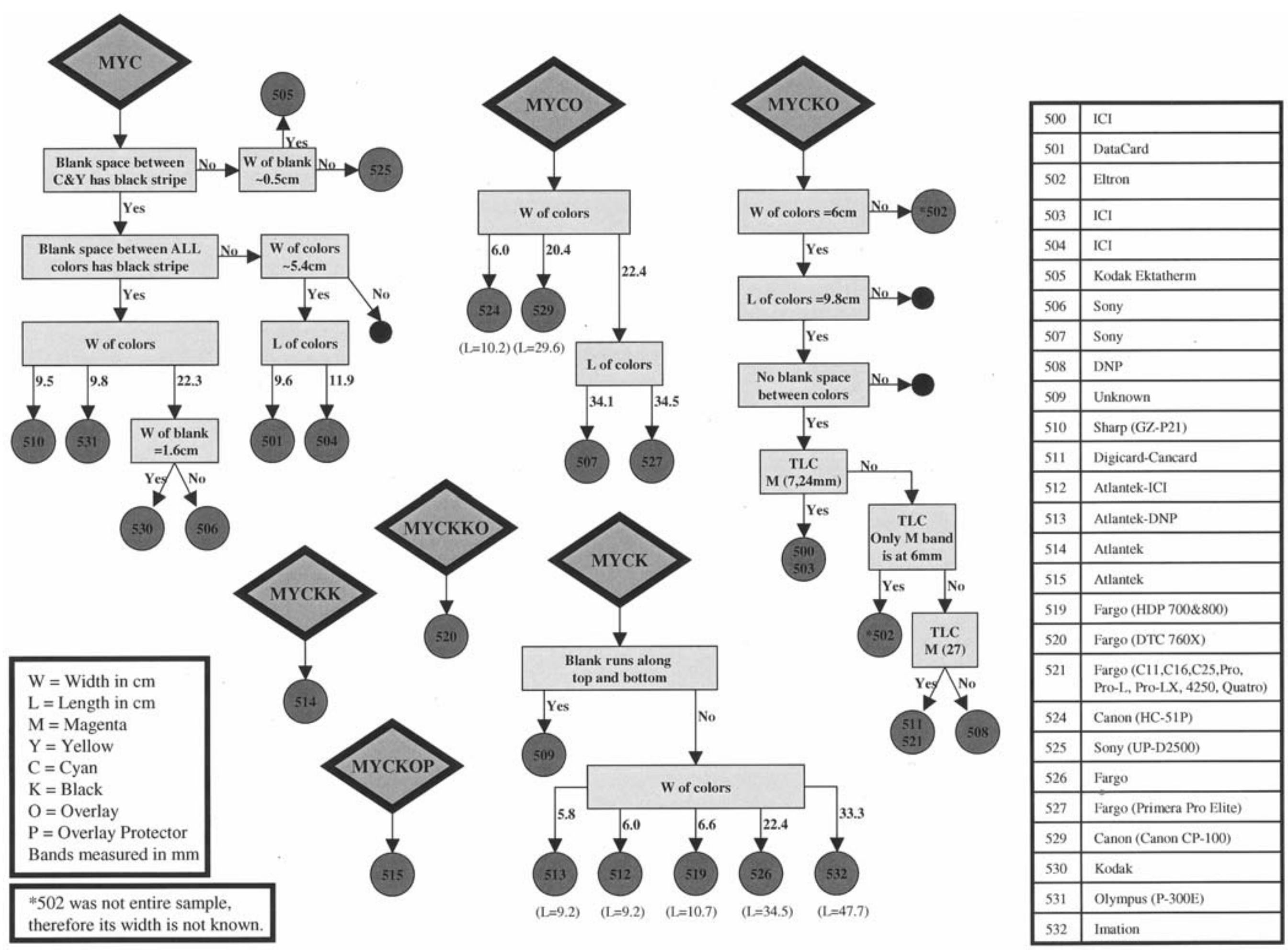


136	US Premiere
141	Cancard
144	Fargo HDP 700&800
146	Fargo Persona C16
147	Fargo Persona C11
148	Fargo Persona C25
149	Fargo DTC 700&500
150	Atlantek 85DS
153	Atlantek Model 60G Web Printer
154	Eltron P720 Card Printer
155	ColorX

M = Magenta band
Y = Yellow band
C = Cyan band
Fl = Florescence band
Bands measured in mm

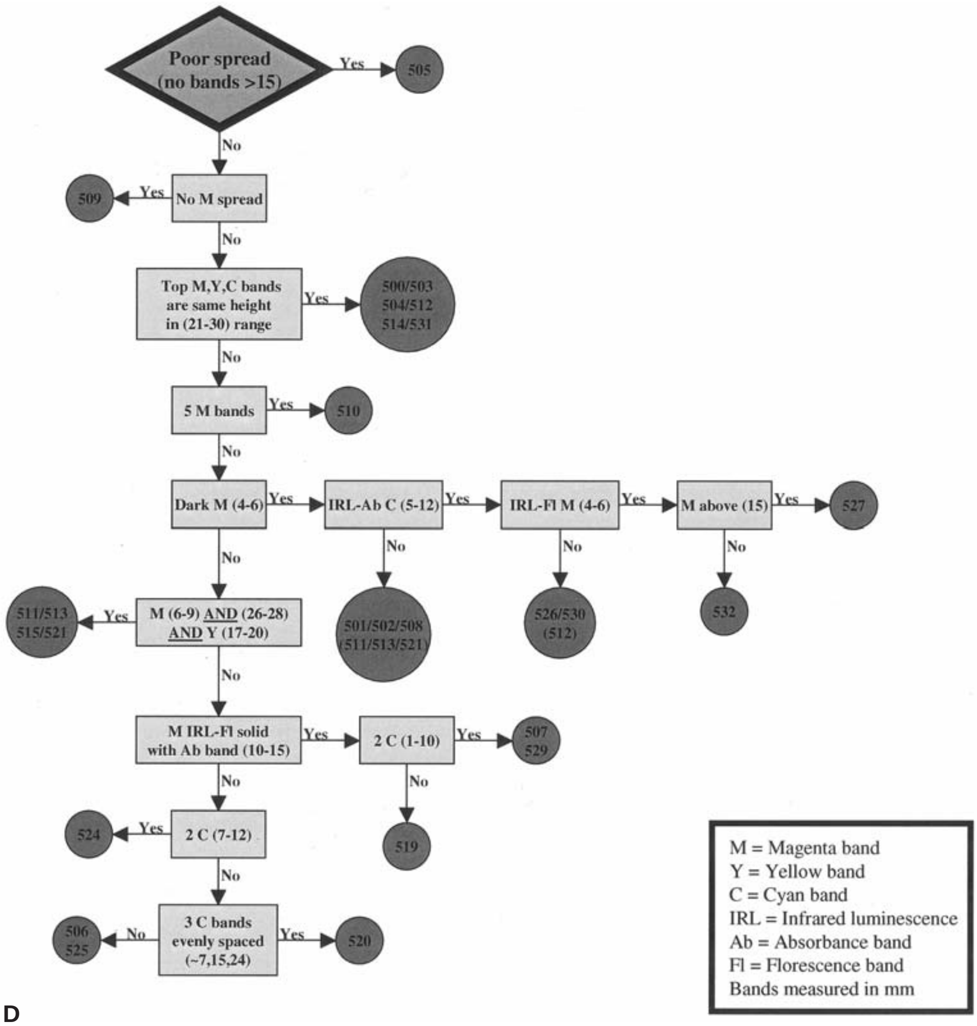
B

FIG. 3—*(continued)*



C

FIG. 3—*(continued)*



500	ICI
501	DataCard
502	Eltron
503	ICI
504	ICI
505	Kodak Ektatherm
506	Sony
507	Sony
508	DNP
509	Unknown
510	Sharp (GZ-P21)
511	Digicard-Cancard
512	Atlantek-ICI
513	Atlantek-DNP
514	Atlantek
515	Atlantek
519	Fargo (HDP 700&800)
520	Fargo (DTC 760X)
521	Fargo (C11,C16,C25,Pro, Pro-L, Pro-LX, 4250, Quatro)
524	Canon (HC-51P)
525	Sony (UP-D2500)
526	Fargo
527	Fargo (Primera Pro Elite)
529	Canon (Canon CP-100)
530	Kodak
531	Olympus (P-300E)
532	Imation

FIG. 3—*(continued)*

and Codonics). Plastic cards printed on eleven different printers, obtained from six different manufacturers that make up over 99% of the world's plastic card printer market, were chemically discerned into five groups (see Fig. 3*b*). The final samples analyzed included 27 ribbon samples. Taking into consideration that a ribbon could potentially be submitted for forensic analysis from a crime scene, physical and chemical analyses were conducted to determine the feasibility of identifying the ribbon. The physical examination of the ribbons proved to be very discriminating: 92.6% (25 of 27) of the ribbons were discernible based on a combination of the number, type, length, and width of the panels, as well as the presence or absence of spacings (see Fig. 3*c*). The ribbon samples were appropriately grouped into 14 different categories following the TLC analysis. Figure 3*d* illustrates a flow chart of the differences resulting from the 27 ribbons following chemical analysis. It is important to note anyway that the ribbons analyzed varied in the number and types of panels (e.g., YMC, YMCK, and YMCKO), thus providing for an inherently discriminant physical and chemical analysis. Regardless of this, the analysis of the ribbons and printers demonstrates that there are significant differences that will permit forensic examiners to associate two or more questioned documents and/or to determine a brand or model of thermal transfer printer based on class characteristics, i.e., chemical analysis of colorants and overlay materials.

The flow charts constructed for this study are beneficial to portray the differences among printers and ribbons. However, in practice, the examiner must remain cognizant of the possibility of not sampling all process colors from a document produced via D2T2 because of the difficulty to discern definitive colors. Consequently, when comparing TLC results, all possibilities should be accounted for if there is a lack of color or colors on a TLC plate. As an example, if a questioned document is created on a D2T2 printer using cyan, magenta, and black, it may be difficult for the examiner to physically identify the absence of yellow, unlike inkjet- and toner-produced documents where the colors are typically differentiated using 10 to 20X magnification. A comparison should then be conducted with the cyan, magenta, and black components in known standards, with no consideration to yellow constituents, which may effectively increase the number of matches.

Conclusion

Thermal transfer printing has become a widely accepted printing technology for the creation of genuine documents requiring photographic quality images. Unfortunately, criminals have discovered the capabilities of thermal transfer printing and are rampantly utilizing the technology for the creation of counterfeit identifications and credit cards. This is evident in the number of submissions of questioned documents produced with D2T2 and TMT printers in the past five years. Because of availability, quality, and price reduction, D2T2 printing has become the prevailing thermal transfer color technology for counterfeiters. In this paper, the authors have successfully developed a discriminating analytical protocol for the examination of documents produced using D2T2 printers. TMT printing is more common for the production of black text and bar coding because of the crisp, sharpened images it is capable of creating. Further research in the area of chemically analyzing TMT-produced documents is much needed. A reliable and relatively simple technique, thin layer chromatography, has proven to be sufficient for the analysis of colorants in inks for the past several years. A new solvent system consisting of hexane:methyl ethyl ketone:ethyl acetate (80:3:17) for the mobile phase used in silica gel TLC development was tested for resolution and reliability. The newly developed mobile phase proved to be effective for sufficiently resolving the dye components from a substrate containing sublimated dyes. Further, tests were conducted on 81 samples, including paper and plastic prints, as well as D2T2 ribbons, from various manufacturers. In many instances, physical and chemical analyses proved to be suitable tests to differentiate printers. Typically, the production of printers and ribbons is mutually exclusive, so the creation of a library of standards is quite complex. However, with information from various sources, the most important being the manufacturers, a database has been created to outline many of the intricacies of which ribbons are compatible with a given printer and vice versa.

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