Forensic Analysis and Databasing of Toners and Inkjet Inks Used in the Production of Fraudulent Documents

Douglas K. Shaffer, Joel A. Zlotnick; U.S. Immigration & Customs Enforcement (ICE) Forensic Document Laboratory, McLean, Virginia USA

Abstract

The identification of the source of a printed document(s) can be important in forensic investigations involving a wide range of fraudulent materials, including counterfeit currency, travel and identity documents, business and personal checks, money orders, prescription labels, travelers checks, medical records, threatening correspondence and financial documents. Determination of the make and model of a printer or photocopier that has been used in the commission of a criminal or illegal activity can provide an important investigative lead for law enforcement officials. The growing complexity of toners and inkjet ink formulations provides an opportunity to identify these printing media to a high degree of specificity, based on their respective chemical compositions.

This paper describes current analytical methods used to characterize commercial toners and inkjet inks, by the identification of their resin, colorant and additives components, and illustrates how these chemical profiles can be compared to authenticate and link forensic documents with a common source(s) in their production history. The creation of a fully searchable database comprised of the recorded chemical and physical properties of commercial jet inks and toners, as well as a library collection of samples of these printing media for comparative testing, is also discussed.

Introduction

The use of office and personal non-impact printing and photocopier machines to produce documents of questioned origin, which are associated with criminal and illegal activities, has become a growing concern for forensic investigators over the past several decades. The emergence and widespread use of high quality toners, inkjet inks and printers has driven the need to develop chemical profiles of these print media as a valuable asset for investigations involving questioned documents [1-4].

Toners

Dry powder toners, which are used in modern desktop printers, photocopiers and fax machines, are formulated with pigments, dyes and resins. Often referred to as *solid inks*, dry toners have an average particle size of 3-20 microns, with some of the new chemically prepared toners (CPTs) approaching the submicron range. Toners consist of a large polymeric resin component and a solid colorant (typically pigment or carbon black) powder component.

Dry electrostatic toners are generally fixed to the paper by means of heat and pressure, which softens the resin polymers to retain a sharp, permanent impression on the print. Resins such as polystyrene, polyesters, polymethyl-methacrylates (PMMAs), epoxides (bisphenols) and polyimides are used as binders. Toners also contain small quantities of additives, including flow promoters, charge modifiers and drum cleansing agents, to optimize performance.

Dry powder toners have been characterized analytically in raw form for manufacturing quality control purposes and, after printing onto paper, in questioned document investigations. Forensic examiners have used infrared (IR) spectroscopic, gas chromatographic-mass spectral (GC-MS), thin layer chromatographic (TLC) and elemental analysis methods to study toner documents in recent years [5-21].

In this study, several dry toners were first examined using Fourier Transform Infrared (FTIR) spectroscopy. As illustrated in Figure 1, three commercial (cyan) toners were compared, based on the composition of their organic binder resins.

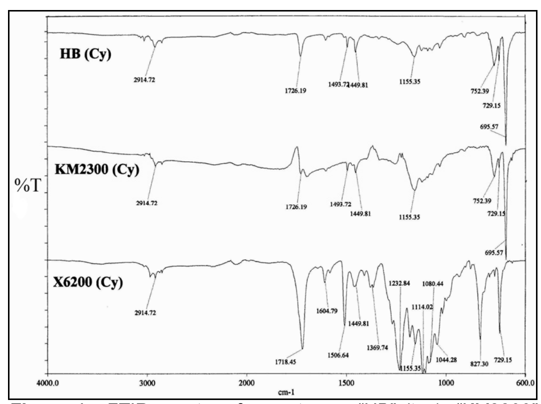

Figure 1. *FTIR spectra of cyan toners "HB" (top), "KM2300" (middle), "X6200" (bottom).*

The FTIR spectra of the top ("HB") and middle ("KM2300") toners were qualitatively similar, and were consistent with a styrene-acrylate copolymer. The bottom spectrum (toner "X6200") was quite different than the other two, with peaks consistent with a bisphenol A-containing (e.g. epoxy) resin.

Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) was conducted on (cyan) toner samples KM2300 and X6200, as illustrated in Figure 2. The resulting pyrograms indicate very different resin formulations for these toner resins.

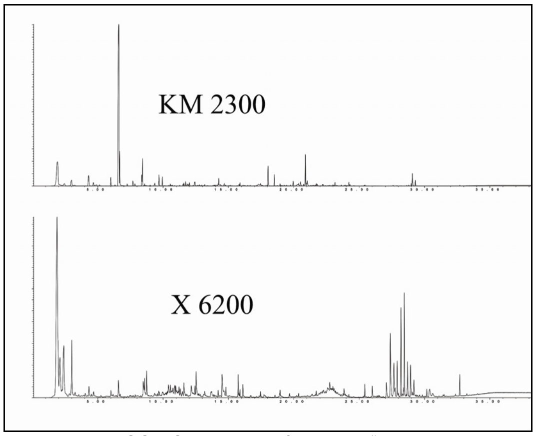

Figure 2. *Py-GC/MS pyrograms for toners "KM2300" (top) and "X6200" (bottom).*

The chemical profile of the KM2300 resin is consistent with a styrene butyl acrylate/butyl methacrylate copolymer, while the X6200 profile indicates an epoxy-type resin originating from bisphenol A. These results are in agreement with the FTIR findings.

Expansion of the central regions of the toner programs illustrates the discriminating power of the Py-GC/MS technique. For the KM 2300 resin (Figure 3), distinct styrene (6.7 minutes) and methacrylate (6.8 and 8.5 minutes) peaks are dominant, while for the X6200 resin, the cluster of peaks centered around 28 minutes is indicative of bisphenol A (e.g. epoxy)-derived compounds (Figure 4).

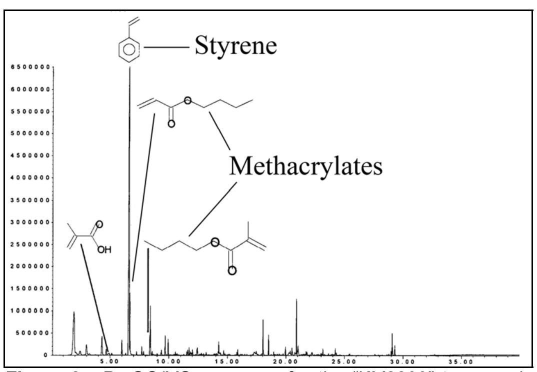

Figure 3. *Py-GC/MS pyrogram for the "KM2300" toner resin showing styrene (6.7 minutes) and methacrylate (6.8 and 8.5 minutes) peaks.*

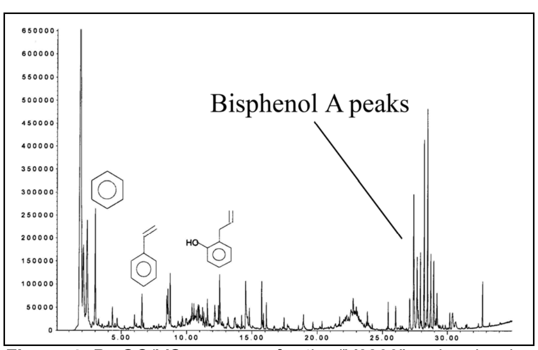

Figure 4. *Py-GC/MS pyrogram for the "X6200" resin, showing bisphenol A (epoxy-type) peaks clustered around 28 minutes.*

Comparison of the X6200 resin with a comparable (i.e. bisphenol A type) resin ("IMEX 2300") illustrates clear differences in composition – e,g, the unique presence of dimethylheptene (5.5 minutes, indicative of polypropylene) and di-t-butyl phenol (17.9 minutes, indicative of an antioxidant) peaks in the IMEX 2300 resin. These diagnostic constituents are shown in Figure 5.

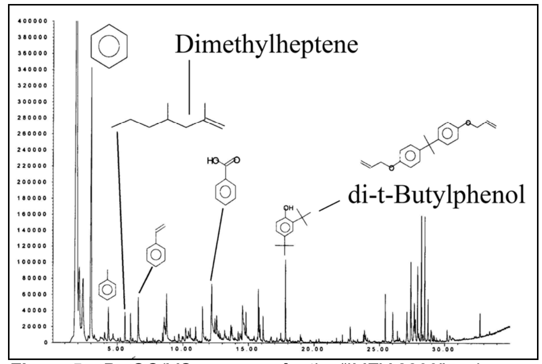

Figure 5. *Py-GC/MS pyrogram for the "IMEX 2300" resin.*

Commercial toners have also been characterized by elemental analysis techniques, including x-ray fluorescence (XRF) and scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDXA). In a study of 162 black powder toners, Trzcinska was able to discriminate between 95.8% of the toner pairs using combined techniques of FTIR and XRF [21], while SEM/EDXA data has been incorporated into a database library for the identification of toners using morphological, elemental and IR spectral properties [22].

Inkjet Inks

The nature of an inkjet ink formulation derives from the stringent requirements of the printing process, including bulk production, in-printhead storage, drop generation and delivery, absorption by the substrate, fixing and drying. Conventional aqueous or nonaqueous inks are necessarily "fluid" to meet these requirements, with viscosity values on the order of 2-10cP. Typical formulations consist of colorants (dyes/pigments, 2-8%, by weight), solvent "blends" (35-80%), humectants (10-30%), penetrants (1-5%), fixatives (1-3%), viscosity modifiers (1-3%), dye solubilizers (2-5%), antioxidants (1-5%) and trace quantities (<1%) of surfactants, pH buffers, chelating agents, biocides and other additives [23].

One of the most practical methods for the chemical characterization of inkjet inks is thin layer chromatography (TLC) [24,25]. TLC analysis of printed inkjet media is based on the separation patterns of colorants from the printed inks as displayed on a "chromatogram." The procedure is most valuable for full color (CMYK) inkjet inks which are based on soluble dyes, rather than pigments, as colorants [26].

A TLC chromatogram showing the band separation patterns for soluble dyes in 15 commercial inkjet inks is presented in Figure 6. The results indicate that consistent (indistinguishable) dye patterns are found in multiple print cartridge types (8 Canon, 4 Epson, 2 Lexmark, 1 Hewlett-Packard) for each of the manufacturers, while the 4 dye-pattern ink "sets" are different from each other.

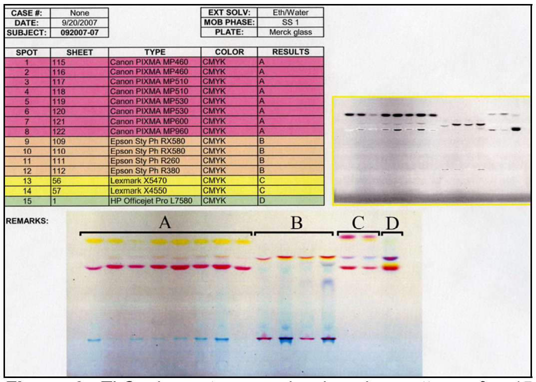

Figure 6. *TLC chromatogram showing dye patterns for 15 commercial inkjet ink formulations and ink classification table.*

The analytical discrimination of inkjet inks has also been reported using Py-GC/MS [27], Desorption-Ionization Mass Spectrometric [28] and Laser Ablation Inductively Coupled Plasma Mass Spectrometric [29] methods. The application of Raman Spectroscopy, recently shown to be quite diagnostic in the structural identification of complex ink dyes [30], may also prove to be a valuable analytical tool for the characterization of inkjet ink formulations.

Experimental

The FTIR spectra were collected using a Perkin Elmer Spectrum One FTIR Spectrometer equipped with a Smiths Detection Universal ATR accessory for sample positioning. Py-GC/MS pyrograms were obtained using a CDS Analytical Model 5250 Pyrolyzer coupled with an Agilent Technologies Model 6890 gas chromatograph/mass selective detector equipped with a 5% phenyl methyl siloxane (30m) capillary column. The pyrolysis chamber conditions included an initial temperature of 50°C, final 750°C held for 15 seconds, cleaning at 1000°C for 30 seconds. The GC oven initial temperature was 40°C for 2.0 minutes, ramp of 8.0°C/minute to 300°C; run in split mode with 50:1 split ratio (split flow 49.7 ml/min, total flow 53.6 ml/min); 300°C initial temp. (On) and 7.0 psi (On). TLC analysis was performed by extracting printed inkjet inks with an ethanol/water (1:1) solution, spotting 5µl of the extracts on Merck silica gel (10x10cm) glass plates and developing the dried plates in a saturated vertical chamber containing "solvent system 5" (butyl acetate/n-butanol/acetic acid/water, 10:41:17:32).

Conclusions

Printed documents containing electrophotographic toners and inkjet inks can be chemically identified and compared in forensic investigations. Dry toners are readily characterized by identifying their polymeric resin profiles (FTIR, Py-GC/MS) and elemental analytical constituents (XRF, SEM/EDXA). Inkjet inks containing soluble dyes are subject to TLC analysis, while FTIR, Py-GC/MS, elemental and Raman spectroscopy are promising techniques, providing that the solvent, resin and color constituents can be isolated from the paper substrate. The creation of searchable database libraries for toners and jet inks, which integrates data from the most diagnostic methodologies for these respective non-impact media, is also under construction.

Acknowledgements

The authors would like to express their thanks to Tom Wampler (CDS Analytical) and Luc Brazeau (Canada Border Services Agency) for providing the Py-GC/MS pyrograms, and to Graham Galliford (Galliford Consulting) and Rick Swantner (Hewlett-Packard) for graciously providing many of the toner specimens.

References

[1] J.E. Lile, A.R. Blair, "Classification and Identification of Photocopiers: A Progress Report," J. Forensic Sci., 21, 923 (1976).

[2] O. Hilton, "The Evolution of Questioned Document Examination in the Last 50 Years," J. Forensic Sci., 33 (6), 1310 (1988).

[3] A.A. Cantu, "Analytical Methods for Detecting Fraudulent Documents," Analytical Chem., 63, 847 (1991).

[4] N.W. Holland, "Photocopy Classification and Identification," J. Forensic. Sci. Soc., 24, 23 (1984).

[5] G.S. Kemp and R.N. Totty, "The Differentiation of Toners Used in Photocopy Processes by Infrared Spectroscopy," Forensic Sci. Int., 22, 85 (1983).

[6] J. Zimmerman, D. Mooney, M.J. Kimmett, "Preliminary Examination of Machine Copier Toners by Infrared Spectrophotometry and Pyrolysis Gas Chromatography, "J. Forensic Sci., 31(2), 489 (1986).

[7] W.D. Mazzella, C.J. Lennard, P.A. Margot, "Classification and Identification of Photocopy Toners by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): Final Report," J. Forensic Sci., 36, 820 (1991).

[8] R.A. Merrill, E.G. Bartick, W.D. Mazzella, "Studies of Techniques for Analysis of Photocopy Toners by IR," J. Forensic Sci., 41 (2), 264 (1996).

[9] G. Tandon, O.P. Jasuja, V.N. Sehgal, "The Characterization of Photocopy Toners Using Fourier Transform Infrared Spectroscopy," Int. J. Forensic Document Examiners, 3 (2), 119 (1997).

[10] N. Mizarchi, Z. Aizenshtat, S. Levy, R. Elkayam, "Classification and Identification of Color Photocopiers by FT-IR and GC/MS," J. Forensic Sci., 42 (2), 353 (1998).

[11] E.G. Bartick, R.A. Merrill, W.J. Egan, B.K. Kochanowski, S.L. Morgan, "Forensic Discrimination of Photocopy Toners by FT-Infrared Reflectance

Spectroscopy," Fourier Transform Spectroscopy 11th International Conference, Athens, GA (August 1997).

[12] R.A. Merrill, E.G. Bartick, J.H. Taylor III, "Forensic Discrimination of Photocopy and Printer Toners I: The Development of an Infrared Spectral Library," Anal. Bioanal. Chem., 376, 1272 (2003).

[13] W.J. Egan, S.L. Morgan, E.G. Bartick, R.A. Merrill, H.J. Taylor III, "Forensic Discrimination of Photocopy and Printer Toners II: Discriminant Analysis Applied to IR Reflection-Absorption Spectroscopy," Anal. Bioanal. Chem., 376, 1279 (2003).

[14] E.J. Levy, T.P. Wampler, "Applications of Pyrolysis Gas Chromatography/Mass Spectrometry to Toner Materials from Photocopiers," J. Forensic Sci., 31 (1), 258 (1986).

[15] W.T. Chang, C.W. Huang, Y.S. Giang, "An Improvement on Pyrolysis Gas Chromatography for the Differentiation of Photocopy Toners," J. Forensic Sci., 38 (4), 843 (1993).

[16] T.O. Munson, "The classification of Photocopiers by Pyrolysis Gas Chromatography-Mass Spectrometry," J. Forensic Sci. 34 (2), 352 (1989).

[17] R.N. Totty, "The Examination of Photocopy Documents," Forensic Sci. Int., 46, 121 (1990).

[18] C.L. Gilmour, "Toner Examination," Can. Soc. Forensic Sci. J., 27, 245 (1994).

[19] J.A. de Koeijer, J.M. de Moel, "Identifying Black Toners using FTIR and Pyrolysis-GC/MS," Problems of Forensic Sciences, Vol. XLVI, 413 (2001).

[20] J.S. Harris, "Dual? Mono? What's the Diff? Determining the Relative Date of Manufacture of a Photocopied Document by FTIR and SEM/EDX of the Toner," Intl. J. Forensic Document Examiners, 4 (2), 182 (1998).

[21] B. Trzcinska, "Classification of Black Powder Toners on the Basis of Integrated Analytical Information by FTIR Spectrometry and XRF Spectrometry," J. Forensic Sci., 51, (4), 919 (2006).

[22] J. Holzapfel, T. Rottes, "Databased Toner Classification," presented at the 63rd ASQDE Annual Conference, Montreal (2005).

[23] S.F. Pond, *Inkjet Technology and Product Development Strategies*, Torrey Pines Research, Carlsbad, CA (2000).

[24] J.A. Zlotnick, F.P. Smith, "Chromatographic and Electrophoretic Approaches in Ink Analysis," J. Chromatography B, 733, 265 (1999).

[25] G.M. LaPorte, "Modern Approaches to the Forensic Analysis of Inkjet Printing: Physical and Chemical Examinations," J. of the American Society of Questioned Document Examiners, 7 (1), 22 (2004).

[26] L.W. Pagano, M.J. Surrency, A.A. Cantu, "Inks: Forensic Analysis by Thin Layer (Planar) Chromatography," *Encyclopedia of Separation Science*, I.D. Wilson, Editor, New York, pp. 3101-3109 (2000).

[27] F. Partouche, B. Espanet, C. Villena, C. Murie, "Forensic Analysis of Inkjet Printings by Pyrolysis GC/MS," Soc. Imaging Science and Technology, Proc. NIP21, p. 216, Baltimore (2005).

[28] D.M. Grim, J. Siegel, J. Allison, "Evaluation of Desorption/Ionization Mass Spectrometric Methods in the Forensic Applications of the Analysis of Inks on Paper," J. Forensic Sci., 46 (6), 1411 (2001).

[29] A. Koenig, "Direct Elemental Analyses of Ink on Paper by Laser Ablation ICP-MS," The Application Notebook (CETAC Technologies), 11, October 2003.

[30] I. Geiman, J. Lombardi, M. Leona, T. Kubic, "Application of Raman Spectroscopy to the Analysis of Questioned Documents," presented at the AAFS 60th Annual Meeting, Washington, DC (2008).

Author Biography

Douglas K. Shaffer received his BS in chemistry from the University of Maryland (1972) and his MS in chemistry from American University (1977). Since then he has worked as a research scientist at Lockheed Martin Laboratories and a forensic chemist at the Maryland State Police Crime Laboratory (trace analysis) and the U.S. Secret Service (questioned documents). Mr. Shaffer is currently employed at the Immigration & Customs Enforcement (ICE) Forensic Document Laboratory, where his work is focused on the development of microanalytical methods to characterize inks, papers and materials associated with questioned documents.

Joel A. Zlotnick received his BS in chemistry from Case Western Reserve University (1996) and his MS in forensic science from the University of Alabama at Birmingham (1998). He was employed for eight years at the U.S. Secret Service as an examiner of counterfeit financial documents, including currency, travelers cheques and money orders. Mr. Zlotnick is currently employed at the Immigration and Customs Enforcement (ICE) Forensic Document Laboratory, where his work is focused on application of forensic techniques to develop operational law enforcement intelligence.