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Black Toner Comparison using Solubility Tests: A Case Report

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This paper describes an actual case examination in which optical methods, solubility tests, and thin-layer chromatography (TLC) were used to determine whether two questioned documents, printed/copied on an office machine(s) using black toner, were produced on or around their purported dates (several years apart), or whether the documents were produced contemporaneously (in close proximity in time, i.e. not several years apart, as dated). In this civil case, based on the results of the optical and TLC examinations of the toner on both questioned documents, the Defendant's expert found and testified that the *black toners in these documents had a connection and were consistent with each other,* and this finding was used as a *chemical* basis for the expert's opinion that the two documents were most probably produced contemporaneously—not several years apart, as dated. This author, retained as a rebuttal expert, repeated the above examinations conducted by the Defendant's expert, and determined that the only chemical *connection* and *consistency* between the two toners was that they both contained a common pigment—carbon black. While optical and TLC examinations could not distinguish between the black toners on the two documents (these results were in agreement with the finding of the Defendant's expert), the solubility tests (chemical extraction of toner samples in chloroform to prepare extracts to be applied on TLC plate for chromatographic analysis) showed that the two toners had significantly different extractability in chloroform; evidence that the toners were of differing chemical composition.

Two common parameters of solubility (extractability) of a solid substance in a solvent are the speed at which the solid dissolves (rate of dissolution/extraction) and the completeness of the dissolution (extent of dissolution/extraction). In this case, the difference in the solubility of the two toners in chloroform was clearly evident and very significant (as in, for example, the drastic difference between the solubility of instant coffee and ground coffee in hot water): one toner was extracted in chloroform almost instantly (within seconds) and completely, while the other toner dissolved only partially (not completely) and the process of dissolution (formation of a suspension of carbon black in chloroform) was slow. Thus, in this comparative examination of two documents produced by electrophotography using black toners, the solubility tests proved to be more discriminating (provided more discriminating power) than the optical and TLC methods.

Introduction

Forensic document examiners often face the task of comparing printed or photocopied documents produced with office machine systems that use dry toner-based electrophotographic technology and black toner (e.g., laser printers, photocopiers, and some types of facsimile machines). Toner is typically a powder that is used in laser printers and photocopiers to form the printed text and images on the paper. During the printing process, toner particles are partially melted by the heat of the fuser, and as a result of that they bind (to each other and) onto the paper. There are many components that make up toner, such as organic polymer resins, pigments (*e.g.*, carbon black used in black toners), dyes, waxes, flow agents, charge agents, and other additives. These components affect toner transfer and color, effectively influencing the consistency of color. Organic polymer resins allow the toner to form a plastic solid after fusing and provide consistency. The pigments and dyes carry the color of the toner. Most of these components can be chemically analyzed for comparison of toner samples.

Multiple analytical methods, such as thin-layer chromatography (TLC), gas chromatography-mass spectrometry (GC-MS), pyrolysis GC-MS, and Fourier transform infrared (FT-IR) microspectroscopy, have been used for toner comparison [1-10]. This paper shows that solubility tests, which have been reported in numerous scientific publications as simple and reliable tools for comparing various materials of documents, including paper, writing and printing inks [6, 11-14], may sometimes be more useful (more discriminating) in toner comparison than TLC.

Case examination – Comparison of black toners by TLC and solubility tests

One of the key questions in the civil case considered here was whether two questioned documents, printed/copied on an office machine(s), were produced on or around their purported dates (several years apart), or whether the documents were produced contemporaneously (in close proximity in time, i.e. not several years apart, as dated).

Visual Analysis

Microscopic examinations showed that both submitted documents, designated as Q1 and Q2, were printed (or copied) using solid black toner on white letter-size copy paper that did not contain a watermark. These and other optical examinations did not reveal any discernible difference between the toners on the two documents.

TLC Analysis

Two toner-on-paper samples[1] were taken from each of the Q1 and Q2 documents, as well as from eight reference documents – known dated documents, designated as "Ks," that bore different dates and that were submitted by the same source (the Plaintiff's office) that has produced the Q1 and Q2 documents. The samples were analyzed by TLC using chloroform (ca. 10 microliters) as the extraction solvent and ethyl acetate / ethanol / water = 70:35:30 (Defendant's expert) and ethyl acetate / isopropanol / water / acetic acid = 30:15:10:1 followed by ethyl acetate / ethanol / water = 70:35:30 (Plaintiff's expert) as the developing solvents.

Neither the Defendant's nor Plaintiff's experts' TLC results revealed any discernible difference between the toners on the Q1 and Q2 documents (see, e.g., Figure 1 below).

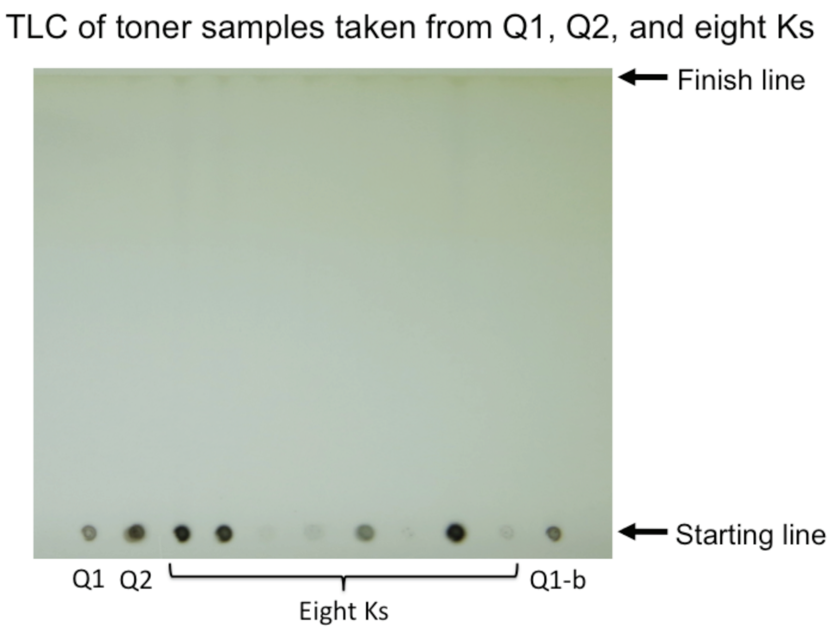

Figure 1. The thin-layer chromatogram obtained for toner-on-paper samples taken from the Q1, Q2, and eight reference documents (photographed under daylight). The TLC plate was developed sequentially in the following two solvent systems: 1) ethyl acetate / isopropanol / water / acetic acid = 30:15:10:1, and 2) ethyl acetate / ethanol / water = 70:35:30. For the TLC analysis, *two* 1-mm toner-on-paper samples were taken from each of the Q1, Q2, and eight K documents, and another *three* 1-mm toner-on-paper samples were taken from the Q1 document (sample "Q1-b").

[1] Samples were taken by a hypodermic needle-like apparatus, the Harris Micro-PunchTM (Electron Microscopy Sciences, Hatfield, PA), which removes ca. 1.0-mm samples (micro plugs) of toner-on-paper. Bored-out samples were removed with a plunger.

[2] The toners on the first, second and seventh of the eight Ks (when counting the Ks left to right in Figure 1 above) have an additional component(s) that appeared on the resulting TLC chromatogram as a long (due to considerable longitudinal diffusion) chromatographic zone located close to the 'finish line.' The presence of the component(s) additional to carbon black in these three toner samples evidences that they are different in chemical composition from the toners on the other five Ks and from the toners on both Q1 and Q2.

As seen from Figure 1, the toner on both documents, Q1 and Q2, contains a single black component distinguishable by TLC—the inorganic pigment carbon black. The TLC analyses evidenced no other colored (pigments, dyes) or non-colored chemical compounds in the toner samples taken from the Q1 and Q2 documents.[2] As the carbon black is not soluble in any organic ('developing') solvent, it did not move from the starting line of the TLC plate while the developing solvent was diffusing up the plate by capillary action and it reached the 'finish line.'

Based on the results of the optical and TLC examinations of the toner on the Q1 and Q2 documents (as well as the above reference documents), the Defendant's expert concluded that *black toners in these [two questioned] documents had a connection and were consistent with each other*.[3] However, it is clear that the only conclusion which can be reached regarding a chemical *connection* or *consistency* between the two toners from the TLC results discussed above (see Figure 1) is that they both contain a common pigment—carbon black. Because carbon black is used in the manufacturing of practically all formulations of black toner available on the world market, this commonality alone is too weak a *connection* to serve as a meaningful basis for the conclusion that the Q1 and Q2 documents "were most probably produced contemporaneously."

Solubility Tests

When toner-on-paper samples, taken from the Q1 and Q2 documents, were chemically extracted in chloroform to prepare extracts applied on a TLC plate for chromatographic analysis, this author noticed that the two toners had significantly different extractability in this solvent.

Two common parameters of solubility (extractability) of a solid substance in a solvent are the speed at which the solid dissolves (rate of dissolution/extraction) and the completeness of the dissolution (extent of dissolution/extraction). In this case, the difference in the solubility of the two toners in chloroform was clearly evident and very significant (see Figure 2 below).

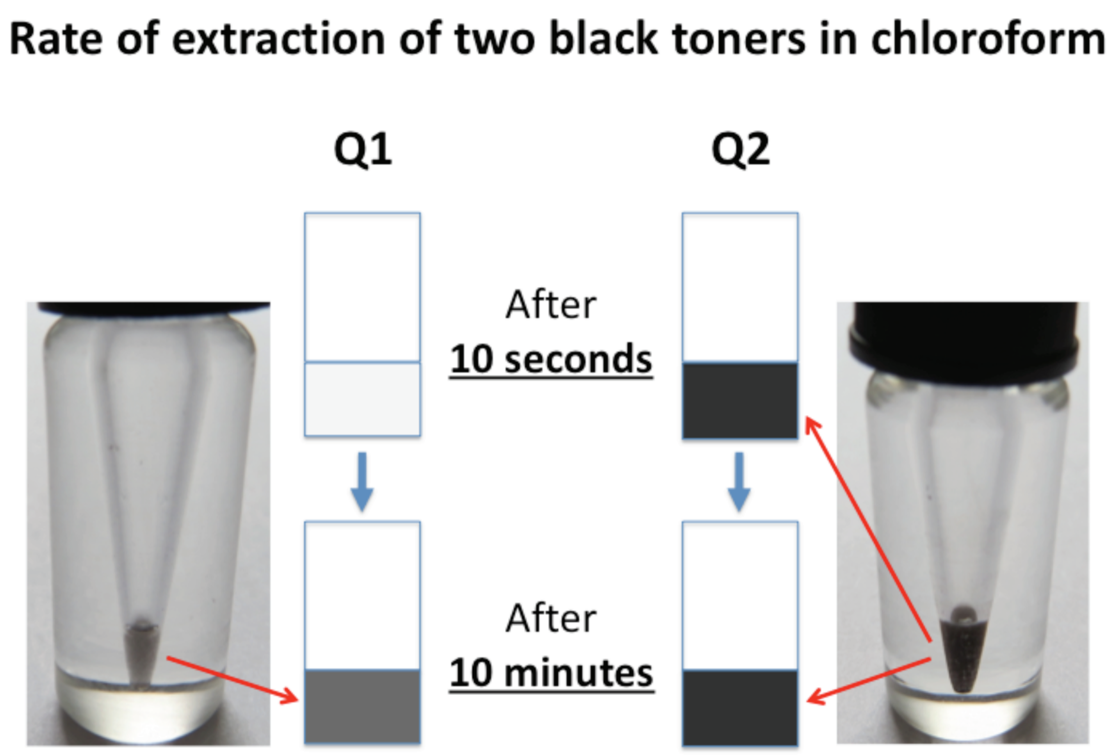

Figure 2. The solubility tests conducted for toner-on-paper samples taken from the Q1 and Q2 documents: the samples were extracted in chloroform, and the color intensities of the extracts were visually evaluated 10 seconds and 10 minutes after the beginning of the extraction process.

[3] This conclusion was used as a *chemical* basis for the Defendant's expert's opinion that the two documents were most probably produced contemporaneously—not several years apart, as dated.

As seen from Figure 2, the Q2 toner was extracted in chloroform almost instantly (within seconds) and completely, while the Q1 toner dissolved only partially (not completely) and the process of dissolution (formation of a suspension of carbon black in chloroform) was slow. These drastic differences in the solubility properties of the Q1 and Q2 toners evidenced that the toners were of differing chemical composition.

Conclusion

This paper describes a real case examination in which toners, appearing 'chemically indistinguishable' by thin-layer chromatography, a relatively complex analytical method, were easily and reliably discriminated by a simple solubility test.

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