The Discrimination of Pencil Marks on Paper in Forensic Investigations

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ABSTRACT

Little information is available on the ability to discriminate pencil marks on writing paper, primarily due to the lack of a method to remove pencil marks from the paper substrate. In this study, pencil marks were removed from the paper backing using Duro-Tak 405A, an acrylic-based adhesive. Removed markings were analyzed using a combination of X-ray fluorescence (XRF), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), and chemical extraction. Of the 12 No. 2 pencils studied, all but one pair of samples was discriminated.

Keywords: pencil marks, No. 2 pencils, graphite, paper, forensic investigation, X-ray fluorescence (XRF), scanning electron microscopy/energy dispersive spectroscopy (SEM-EDS), chemical extraction, Duro-Tak 405A adhesive

INTRODUCTION

Whether a particular pencil was used to make a pencil marking is occasionally of probative value in forensic investigations. Very limited literature was found that details this type of analysis. Reference (1) was found to be the most detailed in regards to instrumental and chemical analysis of pencil markings. The results in this study reveal that the removal of writing from the paper substrate is problematic for analysis, and the cutting and chemical extraction of a large amount of pencil markings was required for testing.

References (1, 2) refer to pencil core or “lead” composition as being a combination of graphite, clay, and wax components. The graphite portion determines the blackness of the marking, the clay component the hardness, and the wax allows for smoothness of movement and holding of markings to the paper. The ratio of graphite to clay determines the hardness of the pencil as noted by the designations of a number (English system) or letters (European system). A larger ratio of clay to graphite would result in a harder core. The most common pencil designation found in retail stores is the No. 2/HB; another description for this pencil is a “soft/hard black” pencil. A No. 1 pencil is softer, and a No. 3 is harder. Some refillable pencil cores, like the type used in mechanical pencils, may be composed using a polymer base instead of clay (2).

One reference was located that detailed an instrumental method for discriminating pencil markings in a semi-destructive way (3). This method utilized mass spectrometry to analyze the wax component of the cores only. Seventeen pencils were used to mark a letter A (about 7 × 3 mm) on “soft high rag content paper containing little or no organic or inorganic filler.” Each marking was then scraped from the paper into separate small balls for testing. This method separated the 17 pencils into four groups. Additional testing on hard or soiled paper proved problematic in that the scraping resulted in “gray dust” that was difficult to handle.

Another study (4) utilized inductively coupled plasma mass spectrometry (ICP-MS) to analyze the
elemental content of bulk pencil samples and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to analyze pencil markings directly from a paper surface. Four manufacturers representing 11 total pencil samples were analyzed. They reported success in separating the four manufacturers and some of the “batch” samples within each group. It was noted in the article that one disadvantage of the technique as it relate to forensic laboratories was high instrument purchase and operating costs.

The elements detected — major amounts of silicon (Si) and aluminum (Al), with lesser amounts of magnesium (Mg), sulfur (S), potassium (K), calcium (Ca), titanium (Ti), and iron (Fe) — were expected, based primarily on the clay portion of the core (1, 3). Graphite used in pencil cores was reported to be 97% carbon in cores produced by Faber-Castell and include a blend of amorphous and crystalline graphite (1). The purity of the graphite is expected to vary according to the geographic location of the mine.

More than a dozen countries mine graphite, with China and India being the largest producers. In 2016, China produced 66% of the world’s graphite and consumed 35% (5). Flake graphite, such as the type used in pencil cores, contains impurities identical in composition to the “country rock” from which it was mined (6). Iron and silicon are among the trace elements found in graphite that contribute to the overall elemental profile of a pencil’s core (7).

No procedure was found that detailed an effective method for separating a pencil marking from a paper substrate.
The objectives of this study are to: 1) evaluate a method to perform a non-destructive analysis of pencil markings on paper; 2) determine if instrumental methods, such as XRF and (SEM-EDS) available to most forensic laboratories, can provide meaningful data; and 3) determine if pencils obtained from local retailers of differing manufacturer, brand name, or country of origin can be discriminated.

The first step was to remove a pencil marking from the paper substrate. This need was highlighted by the elemental analysis of pencil markings analyzed by XRF directly on paper. The spectrum was dominated by calcium (Ca) with other elements near background levels. The large Ca presence was expected due to the prominent amounts of calcium carbonate and kaolin clay as fillers in paper (4).

Removal of the pencil marking from the paper backing was investigated using Duro-Tak 204A (Henkel Corp., Bridgewater, NJ). This adhesive, formerly manufactured by National Starch and Chemical, was investigated by Dennis Ward of the FBI for use as a mounting media for SEM-EDS (8). This adhesive is an acrylic-based, solvent-borne product designed as a pressure sensitive adhesive (PSA) for commercial use. The main solvent in this moderately viscous adhesive is ethyl acetate and can be thinned by it effectively. Elemental analysis of this adhesive by XRF and SEM-EDS revealed no significant elemental profile.

A thin film of Duro-Tak was smeared across a clean glass slide and allowed to completely dry. A small ball of the dried Duro-Tak, approximately 300–500 µm in diameter, was used to roll over pencil markings on standard notebook paper while viewing it through a stereomicroscope (Figures 1 and 2). This rolling produced a “cheese ball” type removal of the marking from the paper. The collection was continued along the writing until the ball was coated and most of the adhesive tackiness was gone. Approximately one-half to one-inch length of a pencil line marking was adequate to produce this result. The pencil sampling

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Listed Brand Name</th>
<th>Listed Manufacturer Name</th>
<th>Listed Manufacturer Location</th>
<th>Purchase Location</th>
<th>Collection Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ticonderoga</td>
<td>Dixon Ticonderoga Co.</td>
<td>Mexico</td>
<td>Office Depot</td>
<td>10/29/12</td>
</tr>
<tr>
<td>2</td>
<td>Dixon</td>
<td>Dixon Ticonderoga Co.</td>
<td>China</td>
<td>Wal-Mart</td>
<td>10/29/12</td>
</tr>
<tr>
<td>3</td>
<td>The Write Dudes USA Gold</td>
<td>The Board Dudes, Inc.</td>
<td>U.S.</td>
<td>Office Depot</td>
<td>10/29/12</td>
</tr>
<tr>
<td>4</td>
<td>Staedtler</td>
<td>Staedtler-Mars, Ltd.</td>
<td>Thailand</td>
<td>Office Depot</td>
<td>10/29/12</td>
</tr>
<tr>
<td>5</td>
<td>Crystal Glitz</td>
<td>Design Way Products, division of Musgrave Pencil Co., Inc.</td>
<td>Vietnam</td>
<td>Staples</td>
<td>10/29/12</td>
</tr>
<tr>
<td>6</td>
<td>PaperMate American Classic</td>
<td>Sanford Corp.</td>
<td>U.S.</td>
<td>Wal-Mart</td>
<td>2010</td>
</tr>
<tr>
<td>7</td>
<td>Bic</td>
<td>Bic USA, Inc.</td>
<td>France</td>
<td>Wal-Mart</td>
<td>3/21/16</td>
</tr>
<tr>
<td>8</td>
<td>CaseMate</td>
<td>No mfg. info. CaseMate is a registered trademark name for Wal-Mart, Inc.</td>
<td>India</td>
<td>Wal-Mart</td>
<td>3/21/16</td>
</tr>
<tr>
<td>9</td>
<td>Pentel (refill leads)</td>
<td>Pentel of America, Ltd.</td>
<td>Japan</td>
<td>Office Depot</td>
<td>4/5/16</td>
</tr>
<tr>
<td>10</td>
<td>Dixon</td>
<td>Dixon Ticonderoga Co.</td>
<td>China</td>
<td>Walgreens</td>
<td>3/22/16</td>
</tr>
<tr>
<td>11</td>
<td>Ticonderoga Black</td>
<td>Dixon Ticonderoga Co.</td>
<td>Mexico</td>
<td>Publix Supermarket</td>
<td>3/23/16</td>
</tr>
</tbody>
</table>
was produced by applying moderate pressure to standard writing paper, which produced a line width of approximately 0.5 mm. The remaining marking was still visible on the paper after recovery, minimally impacting any subsequent document examination (Figures 3 and 4). Minimal handling of the document was also required.

The pencil mark was affected by the level of writing pressure, writing style, softness of the graphite core, and nature of paper substrate (2), therefore, the length of writing distance was also affected by the same variables as each may affect the amount of core material deposition.

The Duro-Tak ball was removed from the paper surface and placed directly on a polymer film/sample holder designed for XRF analysis. Each pencil sample was tested in triplicate. The XRF instrument was an EDAX Orbis, operated at 40 KeV at 1000 µA for 1500 Lsec using a 300 µm monocap column.

Following XRF analysis, the Duro-Tak ball was removed from the XRF mount and placed on a carbon planchette for mounting in a FEI Quanta 400 SEM equipped with an Oxford Inca X-act EDS system. Samples were analyzed using an area scan for 360 Lsec at 20 KeV. Samples were run in triplicate. There was very little charging of the Duro-Tak balls in the SEM, presumably due to the grounding effect of the graphite in the samples.

Analysis of the wax component was attempted by extracting first with chloroform, methanol, and hexane on both bulk core samples and Duro-Tak ball-lifted samples. Bulk samples were scraped from the exposed core. Extractions were performed by placing the sample on a glass microscope slide and dropping solvent directly on the sample. Three drops were successively placed on the Duro-Tak ball-lifted samples to allow complete extraction.

TEST SAMPLES

Twelve samples of pencils were obtained from stores in the Atlanta metropolitan area. Some brand names were different but listed as produced by the same manufacturer. Samples were obtained in years spanning 2010 to 2016 (Table 1). Attempts were also made to vary the listed countries of origin. Note: It is unknown to what degree the listed countries reflect the manufacturer of the core portion of the samples. It should also be noted that several brand names did not include a manufacturer’s designation. All samples were designated as “No. 2” or “No. 2/HB.” The pencils selected varied in appearance and included a mechanical pencil refill sample (Figure 5). Some samples were pre-sharpened; others required sharpening to allow for core sampling.

DATA/RESULTS

XRF analysis on the bulk samples revealed all core samples, except for one, to have the same elements detected. The exception was sample 9, the refillable core, which may indicate a synthetic type of graphite. Discrimination of the cores by XRF was based on varying ratios of detected elements. Minor variations were seen between the three samples run for the same core and the final comparisons were based on a sum of the three determinations. Nine of 12 samples were separated by XRF comparisons. See Figure 6 for an example in which samples were distinguished.

Comparisons of the elemental profiles for bulk samples versus the Duro-Tak collections for the same sample are very comparable with exception of the Ca and iron (Fe) levels. The Ca levels were consistently higher and somewhat variable in the Duro-Tak collections and also lower in Fe (Figure 7). Due to the variability in the higher Ca levels in the Duro-Tak collections, Ca level differences were considered significant in performing spectral comparisons, only when their
differences were consistently large.

One possible explanation for the increased Ca is the nature of the pencil marking itself. Stereomicroscopic examination of pencil markings reveals the impression left by the movement of the core tip over the paper substrate. Minute grooves were observed in the paper surface that may dislodge some of the paper filler, which is comprised primarily of Ca. Ca-rich paper filler may explain the increased Ca in the Duro-Tak collections (Figure 8).

The lower Fe levels in the lifted samples may be explained if a greater retention of the graphite portion of the marking occurred. This is possible if the graphite and wax together bind preferentially to the paper in ratio to the clay portion.

Three pairs of samples were not discriminated after the XRF comparisons. The remaining three pairs (pair 1, samples 1 and 11; pair 2, samples 3 and 4; pair 3, samples 6 and 12) were analyzed by SEM-EDS. One of the three remaining pairs, samples 3 and 4, were discriminated based on their magnesium (Mg) levels (Figure 9). Magnesium was detected near baseline levels in the XRF spectra. The remaining two pairs were examined to determine if the wax portions provide additional discrimination.

Three solvents — chloroform, methanol, and hexane — were selected to extract wax from the bulk core samples. Bulk samples were scraped onto a glass slide for testing. Hexane extracted the most wax component material, and therefore, was selected as the solvent of choice. All 12 pencil core samples were extracted in bulk form using hexane to determine the efficacy of the method. Extracts of the bulk samples ranged from a considerable amount of crystalline wax to no crystalline wax observed (Figure 10). Non-crystalline residue was observed in all extractions.

Hexane extractions of control Duro-Tak balls resulted in a small amount of a clear, oily residue ob-
served in successive rings extending outward from the ball (Figure 11). Test samples of lifted material were treated with three successive drops of hexane to allow for more complete extraction. Each drop was allowed to dry before repeating. The extracts from lifted samples resulted in varying amounts of material in similar proportion to the bulk extractions.

No crystalline material was noted in any of the control extracts but was observed in Duro-Tak balls for the same samples, where crystalline wax was extracted from their corresponding bulk samples (Figure 12).

Samples 1 and 11 both revealed extracted crystalline wax and could not be discriminated. It should be noted that both samples 1 and 11 were manufactured by the Dixon Ticonderoga Company and were both labeled as manufactured in Mexico. Sample 6 did not reveal extracted crystalline wax, while sample 12 did. This allowed samples 6 and 12 to be discriminated.
DISCUSSION

The discrimination of the test samples, while largely successful, did not determine to what extent separations could be detected along the length of the same pencil or different pencils packaged together. Additionally, it would be of interest to determine the ability to discriminate pencils manufactured in the same plant over time.

While the lack of discrimination of samples 1 and 11 could be explained by their common manufacturer and marked country of origin, it should be noted that samples 2 and 10 were easily distinguished by XRF and also share a common manufacturer and country of origin. It is unknown if Dixon-Ticonderoga has only one plant in China or Mexico or to the extent graphite material is shipped between different plants. It is also interesting to note that both pairs were purchased in different years, samples 1 and 2 in 2012 and samples 10 and 11 in 2016. This brings to light another variable: the shelf life of pencils in retail stores, which could be considerable. In other words, pencil samples 1 and 11 may represent one manufacturing plant using one source for the core material or different plants using the same core material. Pencil samples 2 and 10 may represent one manufacturing plant using two different core sources or core batches (a different batch may have used different raw materials) or possibly from two different plants using different core sources/core batches.

Additional methods for analyzing the extracted wax component could potentially allow for additional discrimination. Fourier transform infrared spectroscopy (FT-IR) and gas chromatography-mass spectrometry (GC-MS) may be useful methods to consider.

CONCLUSION

The Duro-Tak adhesive proved a time-efficient and effective way to separate pencil markings from a paper substrate, while minimizing damage to the writing. The combined methods of XRF, SEM-EDS, and chemical extractions, are effective in discriminating pencil markings.
REFERENCES CITED


DISCLAIMER

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Figure 10. Crystalline wax from hexane extract.

Figure 11. Hexane extract of Duro-Tak ball.

Figure 12. Crystallized wax in hexane extract of Duro-Tak ball; 400x.
The article, “The Discrimination of Pencil Marks on Paper in Forensic Investigations,” published in *The Microscope* Volume 65, First Quarter 2017, has the wrong image of the “completed and ready Duro-Tak ball” for Figure 2 on page 14. The correct Figure 2 image is included below with related images. *The Microscope* regrets the error.

**Figure 1.** Dried Duro-Tak ball formation.

**Figure 2.** Completed and ready Duro-Tak ball.

**Figure 3.** Duro-Tak ball collection begun.

**Figure 4.** Duro-Tak ball collection complete.