Discrimination of Architectural Paints

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Previous work

  - Studied 2000 architectural paint samples using
    - Microscopic examination (layer structure/color)
    - Microchemical tests (solubility testing of binder system)
  - Combination of micro techniques provided 1 in 250,000 chance of a random pair association
    - Emission spectrography (inorganic constituents)
    - Pyrolysis gas chromatography (organic constituents)
  - Provided 1 in $10^6$ chance of a random pair association
Purpose of this study

- Update Tippet’s research to assess more current paint formulations
- Determine if discriminating power improves with advanced analytical capabilities
- Attempt to address the significance of associations
- Translate significance assessments into language that will provide clearer, more “stand alone” reports as recommended in the recent NAS study on forensic science
Samples

- Collected by FBI field and lab personnel, as well as colleagues at other forensic laboratories in North America

- Over 950 samples submitted

- Collected from interiors and exteriors of residences, businesses, and other public places (restaurants, parks, etc.)
FBI Laboratory Architectural Paint Collection Form

Name of person collecting sample ________________________________

Sample color ________________________________________________

Address of sampling location (street, city, state, country)
_________________________________________________________
_________________________________________________________
_________________________________________________________

Building type (e.g. house, apartment, business, industrial site) __________________

Substrate type (e.g. windowsill, wall) __________________________

Environmental location (e.g. interior, exterior, direct sunlight) ________________

Manufacturer (if known) _______________________________________

Approximate age of structure _____________________________________

Date of most recent paint application _____________________________

Number of coats applied _________________________________________
Analytical Scheme

Macroscopic and Microscopic Examinations

- Topcoat color
- # of layers
- Sequence

FTIR

Organic binder
Inorganic pigments & fillers

SEM/EDS

Imaging Inorganic pigments and fillers

Py-GC/MS

Organic binder
Initial Evaluation of Submissions

Samples were divided into groups by topcoat color (blue, red, brown, etc.)

- ~200 classified as “white”

- Remainder possessed some hue
  - Largest group: “off-white” (~300 samples)
Examples of paints in each color category

- yellow/peach
- red
- green
- blue
- brown/tan
- black/gray
- off-white
- white
Macro and Microscopic Exams

- Each sample was initially examined and assessed (e.g. paint or not paint)
  - 15 “not paint” samples observed

- **960 samples intercompared (460,320 pairwise comparisons)**

- If paint, layer structure was determined:
  - Sequence of layers
  - Color and relative thickness of each layer
  - Features such as air voids or delamination
  - Substrates were recorded, but not factored into assessments
Pair-wise comparisons

Samples were compared in more than one color classification as needed.

Red
Red-brown
Brick
Pair-wise comparisons
Visual/micro notes

Ann Print Study
11-19-07
4738

- Taupe
- Cadet gray
- White - panday
- Light gray
- White

- Stone's sand adhered to bottom

Sample collection form static substrate = concrete

Arch Paint Sample 467
- 7 layer system on wooden substrate
- Color variations:
  - 1/4x - mat gray of brown undertones
  - 1/4x - white
  - 1/4x - (bright) turquoise
  - 1/2x - white
  - 1/2x - (bright) turquoise
  - 1/2x - white

- brown (dark) wood
Pair-wise comparisons
Cross-section of a “like” pair
FTIR comparison of topmost (yellow) layer
FTIR comparison of bottom (white) layer
Visual Color Categories

- Off-white: 31%
- White: 21%
- Black/gray: 7%
- Brown/tan: 10%
- Red: 8%
- Yellow/peach: 8%
- Blue: 5%
- Green: 10%
Hued Paint Discrimination: Physical and FTIR assessments

32 pairs remained
White Paint Discrimination: Physical and FTIR assessments

- 197 “white” samples (19,306 pairs)

- 5+ layers - assessed via analyst notes of the physical characteristics
  - None of these 77 samples were comparable.
White Paint Discrimination:
Summary of Physical and FTIR assessments

- Remaining samples grouped as*:
  - 1 layer → 69
  - 2 layers → 47
  - 3+ layers → 36

* Some samples assessed in more than one category

- Topcoat of each analyzed by FTIR prior to microscopic comparisons.
Example of white paint comparison
Discrimination of topcoat by FTIR
Comparable FTIR of topcoats
White vs. Off-White Paint Discrimination: Physical and FTIR assessments

- 54 previously analyzed “hued” samples were directly compared to the “whites”

- Many visually consistent:
  - FTIR conducted on top layer, yielded 12 pairs requiring further assessment.
  - Further microscopic exams discriminated 6 pairs.
  - FTIR of additional layers discriminated one pair.

- 5 pairs remain.
Analytical Scheme

- Macroscopic and Microscopic Examinations
  - 960 samples
  - FTIR
  - 200 topcoats
  - SEM/EDS
  - 43 samples
10 layer paint sample pair
off-white, interior walls

Imaged with BSE to delineate layers
Then attempted FTIR on both surfaces of each chip.
Neither FTIR nor SEM could discriminate samples within this pair.
SEM/EDS

- 31 additional pairs (27 samples) analyzed from hued samples. BEI and EDS discriminated 24 pairs.

- 10 pairs (14 samples) analyzed from white/ off-white group. 7 pairs discriminated.
Analytical Scheme

- **Macroscopic and Microscopic Examinations**
  - 960 samples

- **FTIR**
  - 200 topcoats

- **SEM/EDS**
  - 43 samples

- **Py-GC/MS**
  - 19 samples
7 pairs (14 samples) of hued paints analyzed.
- One discriminated, leaving 6 indistinguishable pairs.

4 pairs (5 samples) analyzed from white/off-white group.
- One pair of 2-layer samples: white over cream
  - Both layers – indistinguishable
- Three 2-layer samples: white over cream
  - Both layers – indistinguishable
Pair discriminated by Py-GC/MS
Pair not discriminated by Py-GC/MS
Discrimination Summary

- Over 950 samples submitted and evaluated
- One 10+ layered pair indistinguishable through SEM
- Ten pairs indistinguishable through Py-GC/MS
Analysis Needed for Discrimination

- Macroscopic and Microscopic Examinations
- FTIR
- SEM/EDS
- Py-GC/MS

960 samples (460,320 pairwise comparisons)

20% 4% <2%

42 indistinguishable pairs = 99.991% discrimination
11 indistinguishable pairs = 99.998% discrimination
### Indistinguishable Pairs

<table>
<thead>
<tr>
<th>Pair Number</th>
<th>Topcoat Color</th>
<th># of layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Dark) Blue</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Brown, Green</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Cream</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Yellow</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>White</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>White</td>
<td>2</td>
</tr>
<tr>
<td>7, 8, 9</td>
<td>Off-white</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Off-white</td>
<td>2</td>
</tr>
<tr>
<td>11</td>
<td>Off-white</td>
<td>10</td>
</tr>
</tbody>
</table>
Conclusions

- Tippet found that two pairs of samples from different sources were comparable. Sample pairs originating from the same source were not included in the discrimination power.

- For each indistinguishable pair in this study, the samples were collected from the same building/structure.

Therefore, no random pairs were observed to be indistinguishable in this study.
Conclusions

- Macro/microscopic exams in combination with FTIR remain the most powerful discriminators for architectural paint systems.

- SEM/EDS and Py-GC/MS can provide additional discrimination and should be utilized if available.

- Single layered or neutral colored samples can contain enough characteristics to allow for a strong association in a comparative architectural paint examination.
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