Pigments in Forensic Geology

Pigments are the coloring agents mixed with a vehicle to make coating such as paints, inks, and cosmetics.

The vehicle is the binding agent and in paints is usually an oil such as linseed oil, or acrylic, resin, casein, wax, gum, honey, egg yolk, and egg whites. In inks the binding agent is commonly iron gall, water with gum arabic, and soluble resin. In cosmetics the binder are waxes and oils.

*PowerPoint Presentation by J. C. Crelling, Southern Illinois University*
OCHRE

- Ochre is a mineral that has been sought and used by humans even before homo sapiens came into existence.

- It has been used as:
  - Body paint
  - Artist paint
  - Sun blocker
  - Medicine (antiseptic and clotting agent)
  - Possible religious symbol for blood, life, etc.
Pigments in Forensic Geology

- Naturally occurring minerals:
  - Hematite \( \text{Fe}_2\text{O}_3 \)
  - Limonite \( \text{Fe}_2\text{O}_3 \ast \text{H}_2\text{O} \)
  - Magnetite \( \text{Fe}_3\text{O}_4 \)

OCHRE
Ochre sticks (crayons) have been found in the graves of *homo erectus* dating to 1.5-1.6 million years.
Pigments in Forensic Geology

OCHRE: Evidence for Mining

- 350,000 - 400,000 years ago at Wonderwerk cave, S. Africa, –ochre with hand axes
- Terra Amata site, France ochre with hand axes
Pigments in Forensic Geology

OCHRE: Evidence for Mining

- 250,000 - 200,000 years ago at Hunsgi in Southern India
- 120,000 years ago at Lion Cave, Swaziland. This is probably the oldest mine in the world.
Pigments in Forensic Geology

OCHRE: Evidence for Mining
Neanderthal Man
150,000 – 32,000 ybp

- Pech de l’Aze, France
- La Chapelle-aux-Saints, France
Pigments in Forensic Geology

Prehistoric Cave Paintings

Pigments Used
- Charcoal, lampblack (soot) C
- Pyrolucite, MnO
- Hematite, Fe$_2$O$_3$
- Magnetite, Fe$_3$O$_4$
- Limonite, Fe$_2$O$_3$ *H$_2$O

There is good evidence that in the cave paintings that many of the colors were a mixture of various pigments, and at some sites there is evidence that ochre was calcined (heated) to get other colors.

Homo Sapiens

~35,000 - 10,000 ybp

Homo Sapiens
Pigments in Forensic Geology

Prehistoric Cave Paintings
Pigments in Forensic Geology
Prehistoric Cave Paintings
Pigments in Forensic Geology

Mineral Pigments in Use from Ancient thru Medieval Times

- Hematite
- Magnetite
- Limonite
- Goethite
- Malachite
- Azurite
- Cinnabar
- Chrysocola
- Lapis Lazuli
- Realgar
- Orpiment
- Cinnabar
- Verdigris (copper acetate - Ancient Greek)
- Van Dyke Brown (17th century peat extract)
Pigments in Forensic Geology

OCHRE

- Naturally occurring minerals:
  - Hematite $\text{Fe}_2\text{O}_3$
  - Magnetite $\text{Fe}_3\text{O}_4$
  - Limonite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Pigments in Forensic Geology

Goethite FeO (OH)

Cinnabar HgS
Pigments in Forensic Geology

Malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
Pigments in Forensic Geology

Lapis Lazuli
(Na, Ca)$_8$Al$_6$Si$_6$O$_{24}$(S, SO$_4$)

Chrysocola
CuSiO$_3$ - nH$_2$O
Lapis Pigments

Michelangelo  

Vermeer
Pigments in Forensic Geology

Orpiment $\text{As}_2\text{S}_3$

Realgar $\text{AsS}$
Pigments in Forensic Geology

Turquoise

CuAl₆(PO₄)₄(OH)₈*5H₂O
Pigments in Forensic Geology

● The pigments described above were also used in Dark Age and Medieval illuminated manuscripts

● Because these mineral pigments are already oxidized or otherwise stable at surface conditions they retain their original brilliance even today
LINDISFARNE
Pigments in Forensic Geology

Some Dye Pigments in Use from Ancient thru Medieval Times

Indigo – blue
Woad – blue
Pomegranate – yellow
Madder – orange yellow
Saffron – yellow orange
Murex - purple

Note: all dyes used were natural vegetable dyes until 1856 when Perkin developed the first aniline dye from coal tar. This was a major achievement and the beginning of organic chemistry.
Pigments in Forensic Geology

Some Pigments Uses in Cosmetics

**Ancient**
- Iron Oxides
- Galena PbS (eye shadow)
- Malachite (eye shadow)
- Cerrusite PbCO$_3$

**Modern**
- Titanium Dioxide (yellow)
- Iron Oxides
- Mica (pearlescent agent)
- Bismuth Oxychloride (pearlescent agent)
Pigments in Forensic Geology

- Because many of the pigments are minerals standard geological techniques such as microscopy, X-ray diffraction, SEM analysis, and optical spectroscopy can be used to discriminate them.

- The organic vehicle or binders can be discriminated by Gas Chromatography – Mass Spectrometry.
Thus, any paint, inks, cosmetics etc. involved in a criminal case can be examined and used as potential evidence.
Locard Case

• In 1912 a bank clerk Emile Gourbin in Lyons, France was suspected of the strangulation murder of his girlfriend, Marie Latelle, but he had a good alibi.

• Edmond Locard took scrapings from under Gourbin’s fingernails and analyzed them.
Locard Case

- He found rice starch and magnesium stearate (binders?) with bismuth, zinc oxide, iron oxide, Venetian red pigment.

- He then found a druggist in Lyon who had mixed these same ingredients in a custom face powder for Marie Latelle.

- When confronted with the evidence, Gourbin confessed.
### Pigments in Forensic Geology

**Dates of First Use for Paint Pigments**

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orpiment (yellow)</td>
<td>ancient</td>
</tr>
<tr>
<td>Red Ochre</td>
<td>ancient</td>
</tr>
<tr>
<td>Smalt (cobalt blue)</td>
<td>1550</td>
</tr>
<tr>
<td>Van Dyke Brown</td>
<td>1690</td>
</tr>
<tr>
<td>Prussian Blue</td>
<td>1704</td>
</tr>
<tr>
<td>Alizarin (Madder)</td>
<td>1830</td>
</tr>
<tr>
<td>Zinc White</td>
<td>1850</td>
</tr>
<tr>
<td>Titanium White</td>
<td>1920</td>
</tr>
<tr>
<td>Manganese Blue</td>
<td>1950</td>
</tr>
</tbody>
</table>
On 18 March 1990 two white male dressed as Boston Police Officers stole 13 paintings worth over $300 million

The investigation went cold until two men offered to be intermediaries in getting the paintings back. The offered a few paint chips reportedly from one of the Rembrandt’s as evidence that they were in contact with the thieves.
Gardner Museum Case

- Walter McCrone, the head of the famous McCrone labs in Chicago, examined the paint chips. He concluded that the paint was consistent with those used by Rembrandt but would not confirm that they were indeed Rembrandt’s.

- The case is still unsolved and the 13 paintings are still missing.
In 1985 a trunk containing pastels drawings by the modern Russian painter Larionov was discovered. Larionov left Russia for France in 1915 and these paintings were apparently left behind and forgotten. When some 200 of these paintings were exhibited in Germany in 1987, some questions about their authenticity were raised.
A few of the paintings were sent to the McCrone Labs. They were examined by optical microscopy and SEM X-ray analysis. The paintings were found to have pure rutile TiO$_2$ as a pigment which was not used until at least 1940, thus the paintings were produced after that year and not before 1915 as purported.
The Case of the Vineland Map

• In 1957 a manuscript “The Vineland Map and the Tartar Relation was offered for sale in Geneva, Switzerland. It was bought by a rare book dealer who sold it to the Yale University library

• The startling thing about the map dated at 1440 was that it showed North America 52 years before the first voyage of Columbus
The Case of the Vineland Map

- Yale published the manuscript in 1965 and it was an instant best seller and a book-of-month club selection.

- A new edition is still in print.
The Case of the Vineland Map

The map was immediately questioned and then studied intensely.

Points putting the map in the 15th century

1. The binding
2. The paper
3. The paleography (writing style)
4. Radiocarbon dating (1434+/- 11 years)
5. PIXIE analysis of ink
The Case of the Vineland Map

Points questioning the authenticity of the map:

1. McCrone analysis finding anatase, a titanium mineral not in use until recently
2. A separate analysis by Raman spectroscopy showing the ink lines with a yellow line containing anatase under the carbon line