Chapter 15.4: Paints and Coatings

Learning Goals and Objectives

Recovered paint samples are often important types of evidence, such as automobiles and from clothing used during burglaries. In this chapter, you will need to understand the following concepts:

- What is the chemical composition of paints and dyes;
- What type of information can these types of trace evidence provide;
- How are paints analyzed in forensic science.

Introduction

Painted objects and surfaces are found throughout society today. Cars, homes, furniture, and so many other objects are coated on their surfaces with paint to provide both protection and beauty to the object. Small pieces of paint are often unwittingly transferred between objects during vehicle accidents, burglaries, robberies, assaults, homicides, and even from simple contact with freshly painted surfaces during a crime. It should not be surprising, therefore, that paint analysis forms an important part of trace forensic analysis.

Paint Composition

Paints are opaque coatings that are typically made up of three components: pigment, binder (sometimes called medium or vehicle) and diluent (solvent). The **pigment** portion of paint consists of very tiny particles of organic and inorganic colored compounds that give the paint its characteristic hue. The **medium or binder** suspends the pigment particles and helps to firmly fix them to the surface. Finally, a volatile liquid **solvent**, such as water or an organic liquid, provides a consistency suitable for spreading the paint on the surface. After spreading, the liquid evaporates, leaving behind the pigments and binder to form the residual paint layer.

A **dye** is distinguished from paint in that a dye is usually a soluble compound that binds directly to the material and does not require any medium to bind the colored material to the surface. In contrast, the pigments in paints are usually insoluble materials that have little or no

Figure 15.4.1. Solid pigments used for paints (Sciencephoto.com No. C010/2529 Rights Managed).

Figure 15.4.2. Typical types of coats in an automotive finish (www.carpaintrepairinfo.com/car-scratch-repair-101).
affinity for the surface and are suspended in the binder to cause it to adhere to the surface of the substrate. For example, cloth is dyed while a metal surface may be painted.

Originally, pigments were prepared from very finely ground, naturally-occurring minerals or inorganic compounds, and modern pigments in many colors continue to be created from both organic and inorganic sources. Historically, dyes usually came from living sources, such as plant or insect-derived compounds. Today, however, both paints and dyes are also created from synthetically prepared organic compounds.

Depending upon the end use, a painted surface may be a simple, single coat of paint or a very complex, multi-layer process. Automotive finishes are among the most complex finishes in order to give the desired color depth and sheen. Automobile paint finishes typically begin with a primer layer that binds tightly to the metal or plastic unfinished piece of the car (Figure 15.4.2). The primer serves as a waterproof, stable foundation upon which to build subsequent colored layers and provides additional protection to the surface.

Primers are designed to either chemically bind tightly to the surface or have physical properties that promote binding. Next, many coats of different paints of varying thicknesses are independently added on top of the primer. Each coat helps to add the depth and luster required for the finish; some may even have metallic flakes embedded within the layer. Finally, an outer clear coat is applied to the surface to provide protection and add the desired shine to the car’s finish. The total process of covering the surface can involve many, many separate layers, such as shown in Figure 15.4.3. The chemical identity of each of these layers, along with their thicknesses can provide a very individualized connection between two pieces of paint evidence.

Upon drying, the binder and clear coat often chemically forms a cross-linked polymer through air oxidation or ultraviolet light irradiation in oil-based paints to form durable, hard surfaces. Two terms are important to distinguish in this process. Drying is simply the evaporation of the solvent from the paint while curing involves a chemical reaction such as polymerization to form the final coating. For

Figure 15.4.3. Typical multilayer automotive paint chip showing the complexity of layers built up to form the final product (http://gk12.ucdenver.edu/lessons/lessonplans/Tennenhouse_Cofrin_forensics.pdf).

Figure 15.4.4. A portion of the infrared spectra for selected paint pigments (http://gk12.ucdenver.edu/lessons/lessonplans/Tennenhouse_Cofrin_forensics.pdf).

Figure 15.4.5. Part of a door panel from a car (left) and the X-ray diffraction scan (XRD) of the paint measured “as-is” directly from the door panel (right) (www.rigaku.com/xrd/miniflex-app023.html).
example, Lacquers are coatings that use simple evaporation to form the coating, leaving behind a hard, solid layer. Lacquer coatings will readily re-dissolved when a solvent is added, however, so they are not usually suitable for coatings where they will come in contact with solvents. Enamels, in contrast, form layers of tough, polymeric material by cross-linking molecules when exposed to oxygen. Latex paints are water-based materials with a binder that is composed of very small polymer particles; when the solvent evaporates they fuse together to form the insoluble coating. Variations upon these basic chemistries are possible, however, that can yield an array of different paint products tailored to specific needs and demands.

**Forensic Paint Analysis**

Paint chips recovered from a crime scene or piece of evidence may provide both class and individual characteristics, depending upon the circumstances. Information about the chemical composition of a paint layer may come from several sources.

Infrared spectrophotometry is commonly employed to analyze the composition of the layer, such as shown in Figure 15.4.4. In this case, the IR spectrum serves as a spectroscopic "fingerprint" for a paint layer to be used in a comparison between two samples. X-ray diffraction has also been used to analyze the paints components, often allowing analysis of the layer as it is received in the laboratory (in situ), as shown in Figure 15.4.5.

Another key method for the characterization of a paint sample is to analyze its color. As described in Section 15.1, paint pigments absorb part of the visible spectrum of light, allowing only some wavelengths to be reflected (or transmitted) from the surface for us to see. In essence, the pigments act as filters, blocking certain wavelengths of light while the reflected wavelengths are allowed pass. In this subtractive color scheme (Figure 15.1.15), the wavelengths of light that are not absorbed form our perception of the color of the object. For example, if the pigments absorb green and blue light, the color appears red to the observer since the components of red light are reflected. Color or hue is experimentally measured using microspectrophotometers that look at the ultraviolet (190 to 380 nm) and visible (380 to 800 nm) ranges of the spectrum.

Gas pyrolysis mass spectrometry is also used in the analysis of paints. In this process, the paint chip is heated to form volatile gases of the components of the paint. These volatile compounds are measured both by the gas

![Figure 15.4.6. Pyrolysis gas chromatogram showing the volatile organic components from a semi-gloss latex paint](www.sisweb.com/.../appnote/app22-a.htm).

![Figure 15.4.7. Moicroscopic analysis of a complex paint coating showing thickness and ID of various layers](www.hirox-usa.com/).
chromatograph (retention time and amount of each fraction) and mass spectrometry (identity of each fraction in the GC). An example is shown in Figure 15.4.6 of the GC trace obtained from the pyrolysis of a type of semi-glass latex point.

The physical properties of a paint sample can also be very informative in a comparison of two samples. The color, order or layers, and thickness of each layer are important to determine (Figure 15.4.7). Additionally, any impurities, weathering, or defects in the paint help to individualize the sample. Databases are available for automotive paint identification that can allow determination of the make, model, and years of manufacture of the vehicle based on paint evidence.

**Hunting a “Fox”**

In 1985, British serial rapist Malcolm Fairley, known as “the Fox”, was caught and convicted largely on the basis of forensic paint analysis. At one particular crime scene in North London, investigators found tiny flakes of a very specific type of yellow paint on a tree about 45 in. off the ground. The paint was analyzed and determined to be unique to the Austin Allegro car model between 1973 and 1975 (called “Harvet Yellow”). This color was relatively rare, only 1500 vehicles with this color had been made in the UK, and investigators began to visit every registered owner of these cars. When investigators visited Fairley, they found him cleaning a yellow Austin Allegro car that has scratches in the painted surface about 45 in off the ground. Fairley was immediately arrested and reportedly broke down and confessed to police during the trip to the police station. Samples taken from the suspect’s car were found to match those found at the crime scene. Fairley was convicted and sentenced to six life terms for the attacks along with an additional 26 years for related offenses. He has, however, already been released under a new identity in the UK after having served less than 20 years of his 146 year sentence.
Chapter 14 References and Bibliography


Karl Ritz, Lorna Dawson, and David Miller (Eds.), *Criminal and Environmental Soil Forensics*, Springer, 2008.
GLOSSARY OF TERMS

Additive color mixing: Adding together two colors of light to give a different color.

Becke line: The halo observed at the edges of a solid, transparent sample when in a liquid with a higher RI than that of the sample. An optical phenomenon used in measuring the refractive index of an object.

Blown glass: Product from a process where molten glass is blown either into a mold to form containers and other shaped-materials or formed freehand to generate art-glass pieces.

Binder: The portion of paint that suspends the pigment particles and helps to firmly fix them to the surface.

Birefringence: A double refraction phenomenon in certain crystalline materials where the refractive index is different depending upon which direction the light goes through the crystal.

Borosilicate glass: Glass with boron oxide added to the silica to improve ability to withstand rapid changes in temperature.

Buoyancy: A method to determine the volume of an irregularly shaped object by determining the mass of the water (or liquid) displaced by the submerged object.

Chemical properties: Properties that can be measured only by attempting to change the chemical identity of the material itself through some sort of chemical transformation.

Color: The way that our eyes and brain perceive different wavelengths of light in the visible range.

Complimentary Color – Pairs of colors that, when mixed in the proper proportions, produce a neutral color (e.g., black or white). Sometimes referred to as “opposite” colors.

Concentric cracks: Fractures in glass that form rings that approximately circle the point of impact.

Conchoidal marks: See “Stress-induced striations”.

Density: Defined as the amount of mass of a material contained in a particular unit of volume, or \( d = \frac{m}{V} \).

Dye: A soluble compound that binds directly to the surface and does not require any medium to bind the colored material to the surface.

Extrinsic properties: Properties that change if the amount of material in the sample changes.

Floatation: A method for approximating the density of a sample by determining the density of a liquid upon which the sample will float.

Float glass method: Method for producing flat glass where a layer of molten glass comes out of a furnace as a continuous sheet that is then floated onto a bed of molten metal, most often tin.

Geology: The detailed study of the Earth and its materials along with the physical processes that act upon them.

Glass: An amorphous material composed primarily of silicon dioxide.

Intrinsic properties: Properties that are the same no matter how much material is present in the sample.

Laminated glass: A form of safety glass where a piece of clear plastic or resin is sandwiched or “laminated” between two pieces of glass.

Paint: An opaque coating that binds to the surface of an object.

Paint solvent: The liquid component of paint that provides the consistency suitable for spreading the paint on the surface.

Physical properties: Properties that can be measured without changing chemical identity of a material.

Pigment: The portion of paint, consisting of very tiny particles of organic and inorganic colored compounds, that gives the paint its characteristic hue.

Plastics: Materials that can be molded; today they are most often made from high molecular weight polymeric compounds.

Proxy indicators: Small amounts of identifiable material from a specific location that can indicate with relatively high accuracy information about the location from which they originated.
Radial cracks: Fractures in glass that extend or “radiate” outwards from the central point of impact, producing a branching??star-like pattern.

Refractive Index: The ratio of the speed of light between two transparent substances (usually the air and another substance such as glass or plastic), calculated as velocity of light in vacuum (or air) divided by the velocity of light in the substance.

Rolled glass method: Method for producing flat glass that uses rollers to press the molten glass into a flat shape, often imprinting a design into the glass.

Soda-lime glass: Glass produced by adding various compounds to the molten silica including sodium carbonate (Na₂CO₃), lime (CaO), alumina (Al₂O₃), or salts (NaCl or others). Are they all added or just one or the other and why? What property does it give to the glass.

Soil (dirt): A mixture of inorganic (mineral) and organic components that are packed together relatively loosely with structural components of solid, liquid, and gaseous fractions.

Stress-induced striations: Rib marks that appear on the edge of broken glass.

Subtractive color mixing: Occurs when mixing pigments together and arises from one color being removed from white light through absorption by the pigment.

Tempered glass: Glass that has been either heated or chemically treated to change the stresses within the glass to make it safer upon breaking.

Viscosity: The resistance of a liquid to flow.

Volume by Displacement: A method to determine the volume of an irregularly shaped object by directly measuring the volume of liquid it displaces when submerged.
QUESTIONS FOR FURTHER PRACTICE AND MASTERY

15.1. A piece of plastic is immersed in liquid “A” and floats on the surface of liquid. The same piece of plastic is immersed in liquid “B” and sinks to the bottom of the liquid. From these data, we can say that the density of the plastic sample is
(a) greater than the density of liquid A but less than the density of liquid B.
(b) greater than the density of liquid B but less than the density of liquid A.
(c) equal to the density of liquid A but greater than the density of liquid B.
(d) equal to the density of liquid B but less than the density of liquid A.
(e) none of the above.

15.2. A piece of glass floats on a liquid's surface. The density of the glass is:
a) greater than the density of the liquid
b) less than the density of the liquid
c) same as the density of the liquid
d) cannot be determined from the information given

15.3. If the laboratory can piece together broken glass from a particular window or a single headlight, then the evidence has _________ characteristics
(a) identification
(b) comparative
(c) individual
d) class
e) cannot determine from the information given

15.4. Which of the following is not a physical property of a substance?
a) boiling point
b) color
c) melting point
d) weight
e) oxidation

15.5. Which plastic has the highest density?
(a) HDPE
(b) foam polystyrene
(c) highly branched polyethylene
d) LDPE
e) LD polypropylene

15.6. A student needs 15.0 g of ethanol (ethyl alcohol) for an experiment. If the density of the alcohol is 0.789 g/mL, how many milliliters of alcohol are needed?
(a) 15.0 mL
(b) 19.0 mL
c) 78.9 mL
d) 17 mL
e) none of the above

15.7. Floatation is a method used by scientists to determine the _ of a particle of glass.
(a) mass
(b) density
c) refractive index
d) weight
e) color

15.8. Which is a true statement about the fracturing of glass;
(a) radial cracks appear first, starting on the side opposite the destructive force.
(b) concentric cracks form first, on the same side of the destructive force.
(c) concentric cracks form first, on the opposite side of the destructive force.
(d) radial cracks appear last, starting on the side opposite the destructive force.
(e) all are true statements.

15.9. In a glass fracture, a fracture always terminates at an existing line of fracture.
   (a) True
   (b) False
   (c) Cannot be determined.

15.10. The order in which the bullets pierced the window (right);
   (a) 1, 2, 3
   (b) 2, 3, 1
   (c) 3, 1, 2
   (d) 2, 1, 3
   (e) none of the above.

15.11. Glass is composed primarily of which two elements?
   (a) O and C
   (b) O and B
   (c) Si and O
   (d) Si and C
   (e) C and Ca

15.12. Refraction is the bending of light waves as they pass through media of different density, shown in the picture at right. Refractive index is determined by
   (a) the speed of light in air divided by the speed of light in a medium (e.g., glass).
   (b) how thick a sample is (e.g., how much sample is present).
   (c) the speed of light in the medium (e.g., glass) divided by the speed of light in air.
   (d) the intensity of the light used in the measurement.
   (e) none of the above.

15.13. A piece of glass floats on a liquid's surface. The density of the glass is:
   (a) greater than the density of the liquid
   (b) less than the density of the liquid
   (c) same as the density of the liquid
   (d) cannot be determined from the information given

15.14. In the picture of a Radial fracture of a piece broken glass), from what direction did the f
   (a) top
   (b) bottom
   (c) left side
   (d) right side

Introduction to Forensic Science
15.15. Explain the difference between chemical and physical properties. Give examples of each.

15.16. What are intrinsic and extrinsic properties?

15.17. What methods are used to determine the volume of an irregularly shaped object?

15.18. Explain the density gradient technique used to determine the relative density of a substance.

15.19. What is viscosity?

15.20. What is refraction? Why does it happen?

15.21. What is the definition of a) angle of incidence b) angle of refraction c) refraction index?

15.22. A sample of glass has an angle of refraction of 24° while the angle of incidence is 18°. What is the refractive index of the glass?

15.23. What is a Becke line? When is it observed?

15.24. What is birefringence?

15.25. What are proxy indicators?

15.26. What are some of the factors that make soil samples unique?

15.27. How does the complexity of a soil sample help a forensic scientist establish or eliminate a connection of the sample to a crime scene?

15.28. What is the difference between float glass and rolled glass? What is tempered glass?

15.29. What is “safety glass”?

15.30. What are radial and concentric cracks in glass?

15.31. True or False: In a stress induced striation the 90° angle side always faces the side away from where the crack originated.

15.32. True or False: In a radial crack, the surface where the crack starts is on the opposite side of the force.

15.33. True or False: In a concentric fracture, the fracture starts on the side nearest the force.

15.34. A car windshield has sustained a series of impacts. What simple rule regarding radial cracks can be used to determine the sequence of the impacts?

15.35. Just like with glass, what two key measurements are usually the first ones made to determine what type of plastic has been sent to the crime lab for analysis?

15.36. What factors go into determining the physical and chemical properties of a polymer?

15.37. What are the typical three components of paint?

15.38. How does a dye differ from a paint?

15.39. What is the difference between drying and curing with respect to paint?

15.40. The use of gas pyrolysis mass spectrography is used to analyze what components of paints?

15.41. When comparing two paint samples to see if they are a match, what physical properties are compared?

EXTENSIVE QUESTIONS

15.42. In the movie, ‘Monty Python and the Holy Grail’, a woman is accused of being a witch. In order to determine if she is indeed a witch her density is to be determined by comparing her ability to float relative to a duck’s ability to float. How does flotation work as a forensic tool to determine the relative density of a sample?

15.43. Explain the difference between additive and subtractive color combinations.

15.44. Light absorption from light sources differ from color perception from pigments. Explain how?