Visual, Microscopical, and Microchemical Examination of Paint and Coating Evidence

1 Scope

This procedure applies to Chemistry Unit caseworking personnel who perform visual, microscopical, and solubility/microchemical examinations that are used to characterize and compare a variety of paint and coating specimens.

2 Equipment/Materials/Reagents

a. Stereo microscope (~6X to ~100X) with two lighting conditions (e.g., ring light oriented ~180^{o} from sample, fiber optic light oriented ~45^{o} from sample)

b. Compound microscope with bright field and polarizing light sources

c. Glass microscope slides

d. Scalpel handle with blades

e. Tweezers

f. Probes (e.g., steel, tungsten, wood, Teflon®)

g. Disposable wipes

h. Well slides

i. Pillboxes

j. Compressed gas duster

k. Large, flat-blade spatula

l. Large sheets of untreated kraft paper (or equivalent)

m. Spot plates

n. Acetone (Reagent grade)

o. Xylene (Reagent grade)

p. Chloroform (Reagent grade)

q. Eyedropper bottles and/or disposable pipettes

r. Diphenylamine (DPA) (Reagent grade)

s. Sulfuric acid (Reagent grade)

t. Acetic acid (Reagent grade)

u. DPA solution
Dissolve 0.3 g of DPA in 20 mL concentrated sulfuric acid and then slowly add 10 mL glacial acetic acid. Store the solution at room temperature in a labeled brown glass bottle. The solution will be stable for at least 1 year and can be tested on a positive control sample to determine effectiveness beyond the expiration date.

v. Analytical balance

w. Munsell Book of Color, Matte and Glossy Collections available from the Macbeth Division of Kollmorgen Instruments Corporation, New Windsor, NY

x. Munsell Neutral Value Scale, Matte Edition available from the Macbeth Division of Kollmorgen Instruments Corporation, New Windsor, NY

y. Minolta CHROMA METER CR-241 Colorimeter (or equivalent)

z. PPG RapidMatch® Color Match spectrometer tool with Paint Manager® library (or equivalent)

aa. Digital camera

bb. Digital microscope

3 Standards and Controls

These materials are stable in a laboratory setting and do not expire.

a. Positive Enamel:
Enamel paint standard, such as NAPF PID 6320.

b. Positive Dispersion Lacquer:
Dispersion lacquer paint standard, such as NAPF PID 1910.

c. Positive Acrylic Solution Lacquer:
Acrylic solution lacquer paint standard, such NAPF PID 415.

d. Positive Nitrocellulose Lacquer:
A commercially available colored nail polish with nitrocellulose listed as a main ingredient can be used. A sample should be spread out in a thin layer on a clean glass microscope slide using the product's applicator. Allow the film to dry prior to use as a standard. Store the bottle according to manufacturer's recommendations.

e. Negative Control:
As it does not react with any of the solvents or chemicals used in the scheme, the positive enamel paint standard can be used as a negative control for the other solvents/microchemical tests.

4 Sampling

Refer to the Paints and Polymers Standard Operating Procedure (P&P SOP) *General Approach for Paint and Coating Casework* for guidance for sample(s) selection. Record the samples selected for analysis in the case notes.

5 Procedure

5.1 Visual and Microscopical Examination

Use written descriptions, sketches, photography, or other imaging methods to capture both visual and microscopical characteristics and observations. If the items are suitable for further examination, record a detailed description of each item to include comparative features or any unusual conditions (e.g., commingled material).

1. Process each item separately to prevent cross-contamination

2. Transfer the item from its original container to a suitable substrate (e.g., paper, glass microscope slide, pillbox) to examine both visually and microscopically. Some specimens require processing or preparation prior to examination as described below.

    a. Clothing: Examine each article of clothing visually and microscopically for evidence of a contact paint transfer.

        i. If a potential paint transfer is embedded or abraded onto the fabric, take a cutting which includes a representative portion of the transferred substance and preserve it for future examination. See 2.b. for further instructions regarding smears.

ii. Process each article of clothing as it was received (i.e., individually or collectively packaged) and isolate the debris in the same manner (i.e., one pillbox per package).

iii. Suspend the item from a rack over a large sheet of paper and carefully scrape all surfaces in a downward motion with the edge of a large flat-bladed spatula or similar tool to dislodge any remaining paint evidence.

iv. Collect the deposited debris and transfer it to a pillbox or other container for microscopical examination. Label the top and bottom of the container with the laboratory number, item number, and initial. See 2.c. for further instructions regarding debris.

b. Smears: The considerable force required to cause a paint transfer often results in the paint being abraded and damaged; the layers of a multiple-layer paint system can be mixed together or smeared across a surface.

i. If fused or embedded onto a surface, remove particles and fragments using a scalpel blade, probe, tweezers, or similar tool while observing under a microscope. If the item will be subsequently examined for toolmark comparisons, relatively soft, pliable materials such as wood or Teflon® should be used to dislodge paint from the surface. Metal blades should not be used as they can alter the surface and thereby affect a toolmark examination.

ii. The fabric weave of an article of clothing can be stretched in order to facilitate removal/dislodging of particles of paint.

iii. Transfer isolated particles/fragments to a well slide or pillbox for future examination. Label the slide or pillbox with the laboratory number, item number, and initial.

iv. Smeared paint can be contaminated with material from the surface upon which it is impacted (e.g., fibers, painted substrate, wood) thereby affecting the chemistry and/or color of the sample. If appropriate, take a control sample of the substrate close to but not within the area containing the smear.

c. Debris: Paint evidence can be observed as a mixture with other materials that are not probative for examination by P&P personnel (e.g., fibers, soil, glass).

i. Examine the contents of the debris microscopically, manipulating it with the appropriate tools (e.g., tweezers, scalpel) and isolate any paint-like materials.

ii. Transfer these materials to a well slide or pillbox for future examination. Label the slide or pillbox with the laboratory number, item number, and initial.

iii. To decrease the likelihood that paint evidence has been overlooked, a second P&P examiner can examine the debris. Alternatively, the primary examiner should re-examine the debris on a different day. Results of these subsequent analyses are recorded in the case notes.

d. Liquid paint samples: If appropriate, sample dried material (e.g., cured spray paint on the nozzle) from the container of an uncured specimen. Alternatively, mix an uncured sample (e.g., liquid paint), apply it to a clean glass microscope slide or other suitable substrate as a thin film, and allow it to dry/cure according to the manufacturer's recommendation.

3. Once isolated, observe the surface of the paint and record color, presence of effect pigment(s), morphology, degree of gloss, texture, presence of surface striae, defects, weathering, or any other characteristics that aid in the description of the item.

4. If conducting a comparative examination, observe paint chips for possible physical matches such as a fracture match from broken-edge characteristics and/or surface anomalies (e.g., striae).

a. Fracture matches are the most conclusive type of examination. Record observed fracture matches with descriptive notes and imaging techniques.

b. Include a measuring scale, when practicable. If not, annotate the photograph with the magnification used to capture the image.

c. A second P&P examiner must confirm and record the suspected fracture matches between known and question specimens.

5. Observe the layer structure of any paint specimen(s) by viewing it at ~6X to ~100X magnification.

a. Obvious layers can be exposed/observed by a number of techniques which include, but are not limited to, viewing the sample on edge, cross-sectioning by hand, cross-sectioning by encapsulation and microtomy or polishing, making an oblique (bias) cut through the sample, or taking a series of thin peels through each layer.

b. A combination of techniques can be used to fully characterize the layer structure. The extent of sample manipulation and preparation will depend on the amount of sample available, its complexity, and its characteristics.

6. Record the number and sequence of layers and their relative thicknesses.

7. For each layer, record the description of its color, texture (i.e., primer layer versus color coat, presence of inclusions), presence or absence of effect pigment (e.g., metallic flake, pearlescent, flat), and any other observations (e.g., homogeneity, uniformity of layer thickness across sample, body-filler material evident, tinted clear coat, color-coordinated primer, metal pre-treatment).

8. Microscopical examination of a thin cross-section of a multiple layer paint sample in transmitted light can also be conducted. Higher magnifications using a compound microscope can allow for better detail regarding the number of layers present and the presence/dispersion of effect and/or other pigments. In addition, the thinness of the cross-section also permits better color discrimination. The use of a polarized light source can also aid in the examination of layer structure and characterization of pigments.

9. If appropriate, conduct color measurements on comparative items.

9.1 The tristimulus value of an exposed surface of a paint sample can be measured using the Minolta Colorimeter. Refer to the *Performance Monitoring Protocol (QA/QC) for the Minolta CR-241 Chroma Meter* for more detail.

a. The surface of the sample must be at least 0.3 mm in diameter.

b. Samples should lay flat and possess little or no surface damage or contamination.

c. Measurements obtained on samples being compared need to be collected using the same measurement area (0.3 mm or 1.8 mm diameter). Record which measurement area was used. When sample size permits, three readings are recommended for the 1.8 mm diameter measurement area. A single measurement is recommended for the 0.3 mm diameter measurement area.

9.2 Alternatively, evaluate color designations using the Munsell Book of Color or Neutral Value Scale.

9.3 For automotive paint, the PPG RapidMatch® color matching spectrometer with accompanying Paint Manager® library can be used to determine automotive paint color codes if the sample is at least 3 cm x 2 cm in size.

a. Calibrate the RapidMatch® spectrometry tool prior to each day's use by aligning it flat onto the white surface of the calibration plate, and pressing the

measurement button on the top of the tool. Once the reading is returned on the display window, align the orange-brown metallic surface (i.e., simulated automotive paint) with the spectrometer window, and again press the measurement button. The spectrometer will take a set of three measurements in rapid succession before indicating the tool is ready for use. Record use of the tool in its QA/QC logbook according to the procedures described in section 8.4 of the *General Instrument Maintenance Protocol*.

b. For best results, ensure that the samples lay flat and possess little or no surface damage or contamination.

c. Move the tool on the surface of the paint chip to collect five measurements. Once the measurements are recorded by the spectrometer, interface it to the Paint Manager® library in order to generate a hit list of manufacturer color codes that best align with the color measurements recorded by the spectrometer. Record the results of the library search.

10. In cases involving automotive paint sourcing, determine whether a paint sample is a factory-applied, original equipment manufacturer (OEM) finish or an aftermarket repaint based on the layer structure (e.g., number, sequence, order, relative thickness).

    a. If the sample is clearly an aftermarket repaint with no original layers, report the top coat color and characterization of the evidentiary paint as a non-OEM. Refer to the *General Approach to Report Writing* P&P SOP for guidance in report language.

    b. If the sample appears to be OEM:

        i. Refer to Step 9.1 above for guidance in recording the tristimulus value of the various layers (e.g., basecoat, ecoat).
        ii. Alternatively, refer to Step 9.2 above to evaluate color designations using the Munsell Book of Color or Neutral Value Scale.
        iii. For comparisons of an item's topcoat color to available reference samples, refer to Step 9.3 above to determine manufacturer and color code information or the P&P SOPs *Conducting Color Comparisons Using Automotive Refinishers Color Chips* and *Conducting Motor Vehicle Make-Model-Model Year Searches Using the National Automotive Paint File (NAPF) Database* for make-model-year determination of OEM automotive paint for further details.

5.2 Solubility and Microchemical Tests

Depending on the type of binder, these tests can be destructive or provide no additional information. Therefore, before conducting these tests, consider if the limited, general information

obtained would be probative. This evaluation should be done after binder characterization of the paint layer(s). Refer to Figure 1 in the P&P SOP *General Approach for Paint and Coating Casework* for guidance on appropriate techniques.

1. A flow chart/decision tree for the basic solubility and microchemical tests is shown in Figure 1. These tests are intended for evaluation of individual layers of an automotive finish but can be applied to industrial, architectural, and non-automotive vehicular paints if appropriate.

    a. If the specimen is an enamel (e.g., melamine in Fourier transform infrared spectroscopy (FTIR) spectrum), solubility and microchemical tests are unnecessary.

    b. If the specimen is a lacquer or the binder characterization is not obvious by IR, provided there is adequate sample, proceed with the solubility and microchemical tests.

    c. When conducting solubility and microchemical reactivity tests, analyze negative and positive controls concurrently with the sample(s).

2. Separate a thin peel of each layer from adjacent layers and place the sample on a glass slide or in the well of a spot plate. Subject the layer to one or two drops of acetone and observe the reaction under low power magnification. Record the results.

    a. If the layer dissolves, proceed to step 3.

    b. If the layer does not dissolve in acetone, record it as an enamel. No additional solubility testing is necessary for this layer. However, in the case of a highly filled layer, it may not be readily apparent that a portion of the sample is soluble. See step 5 for further detail.

3. Subject a different thin peel of the same layer to one or two drops of xylene. Observe the reaction under low power magnification. Record the results.

    a. If the layer dissolves, record it as a dispersion lacquer. No additional solubility testing is necessary for this layer.

    b. If the layer does not dissolve, proceed to step 4.

4. Subject a different thin peel of the same layer to one drop of DPA solution. Observe the reaction under low power magnification. The reaction may not occur immediately, so it should be observed periodically for a period of 5 to 10 minutes before a negative conclusion is reached. Record the results.

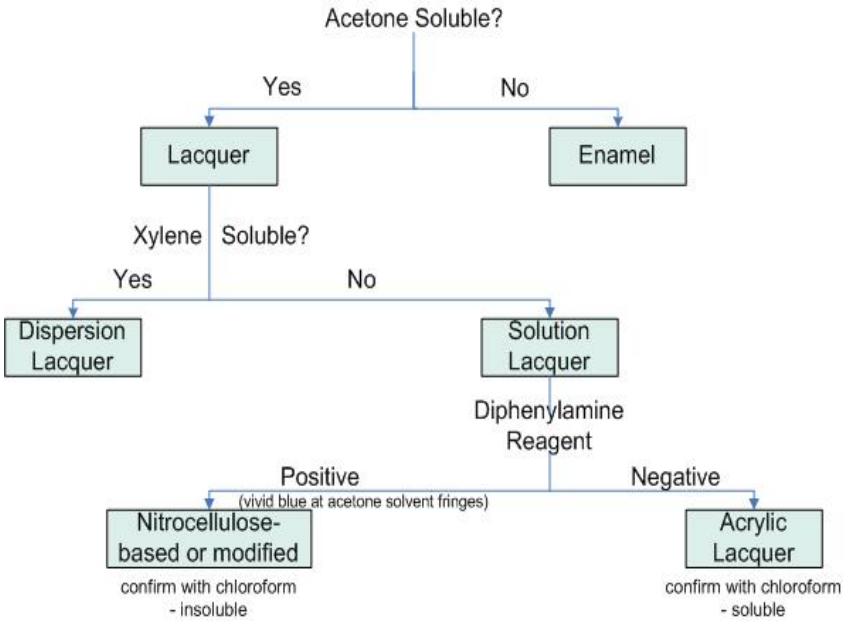
a. A positive reaction is a vivid blue color. This is indicative of a nitrocellulose lacquer. Confirm this result by subjecting a different thin peel of the same layer to one or two drops of chloroform. A nitrocellulose lacquer will not dissolve in chloroform.

Note: Certain dyes and inorganic fillers will react with the concentrated acids in the DPA solution. Record observations such as color changes or effervescence as a point of comparison between two samples; however, these results are not a positive reaction for nitrocellulose lacquer which can be confirmed with observation of the chloroform response.

b. If a vivid blue color is not observed, the reaction is negative. Record the layer as an acrylic lacquer. Confirm this result by subjecting a different thin peel of the same layer to one or two drops of chloroform. An acrylic lacquer will dissolve in chloroform.

5. If the layer being tested is highly filled, it may not be readily apparent that a portion of it is soluble in acetone and therefore it could be misclassified as an enamel. To ensure that a misclassification has not occurred, add one drop of DPA reagent to the thin peel that had been subjected to acetone. If it is a nitrocellulose lacquer, a vivid blue color will appear where the acetone has evaporated around the thin peel. This is indicated in Figure 1 as the acetone solvent fringes.

Figure 1. Basic Microchemical Scheme[1]



6 Instrumental Conditions

Refer to the *Performance Monitoring Protocol (QA/QC) for the Minolta CR-241 Chroma Meter* for instrumental conditions.

7 Decision Criteria

a. For initial characterization, assess physical characteristics known to be exhibited by paint such as color, texture, and layer structure.

b. If physical characteristics of two (or more) specimens being compared differ, cease examinations cease and report the specimens as different.

c. Binder classification by the solubility and microchemical tests utilized in this procedure are described in section 5.2.

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[1] Ryland, S.G. Infrared microspectroscopy of forensic paint evidence. Chapter 6 in *Practical Guide to Infrared Microspectroscopy*. (ed. H.J. Humecki) NY: Marcel Dekker, Inc., 1995.

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

a. Sample size and condition can preclude conducting certain examinations, including color assessment(s).

b. If the sample is a smear, layers can blend and contaminate one another. Microscopical examinations of layer structure, texture, number of layers, color, etc. can be affected.

c. Paint layers less than 15 microns thick can be difficult to distinguish using standard stereo microscopical examinations.

d. Adjacent layers similar in color and texture can be difficult to resolve using standard stereo microscopical examinations.

e. A factory-applied, OEM automotive finish is required for a possible motor vehicle make-model-year determination.

f. The RapidMatch® tool is intended to provide color code information for OEM automotive coating colors and may not be suitable for automotive parts that are repainted or repaired with non-OEM colors. Further, the search may not always yield results.

11 Precautionary Statements

a. As with any procedure involving trace evidence, ensure actions minimize the potential for loss or contamination.

b. Solubility and microchemical tests can be destructive. Consider this factor when evaluating the probative value of such tests.

12 Safety

Use standard precautions for the handling of biohazardous materials, chemicals or sharps. Refer to the *FBI Laboratory Safety Manual* for details.

13 References

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Rev. #	Issue Date	History
0	06/21/06	New document that replaces previous document also titled *Macroscopic, Microscopic, and Microchemical Examination of Paint and Coating Evidence*.
1	09/30/09	Provide reference for sampling plan guidelines and updated references.
2	03/14/12	Updated microscopic/macroscopic to microscopical/macroscopical where appropriate throughout document. Changed "confirm" to "can aid in" in Section 3, 2nd paragraph. Added digital microscope to section 5. Changed "sampling" plan to "sample selection" plan in section 8. Clarified title of the CU colorimeter performance monitoring SOP throughout the document. Updated references in section 17.
3	02/03/14	Changed title, changed "macroscopical" to "visual" throughout to simplify terminology, edited equipment list to be less restrictive regarding material specifications, changed examples in Section 9.1, 2c, edited Section 9.1, 2d to describe sampling of liquid paint when it's cured on container, edited Section 9.1, 4b to expand options for displaying a scale in images, clarified criteria for measurement area in Section 9.1, subsections 9c and 10bic, edited Section 9.1, subsection 10biii to refer to appropriate SOPs not actual procedural steps in those SOPs, removed redundant first sentence in Section 9.2, and updated references.
4	09/18/18	Deleted Introduction, Principle and Specimen sections and renumbered. Modified Scope to describe who document applies to. Removed equipment already described in referenced IOSS SOP and deleted 'Calibration' section and renumbered. Updated remaining sections in the document for clarity. Updated references.
5	01/15/20	Added PPG RapidMatch® Color Match spectrometer tool with Paint Manager® library to equipment list; added section 9.3 to describe use of this tool and section 10f to describe some limitations of the tool. Deleted QA Manager approval per latest LOM revision. Minor edits throughout. Added a reference.

Approval

Redacted - Signatures on File

Paints and Polymers
Technical Leader: Date: 01/14/2020

Chemistry Unit Chief Date: 01/14/2020