

Forensic Paint Analysis and Comparison Guidelines

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(SWGMAAT)
(formerly the Technical Working Group on
Materials Analysis [TWGMAAT])
Paint Subgroup
May 2000 Revision
(Originally Published as the January 1999 Revision)**

This document is intended to be a suggested revision to the original ASTM E1610-94 Guide. This revision is the product of the Paint Subgroup of the Scientific Working Group for Materials Analysis (SWGMAAT). Its ultimate acceptance as an [ASTM](#) document will be the responsibility of ASTM Committee E-30 on Forensic Sciences. You are invited to submit constructive feedback on the [Document Comments Form](#).

1.0. Scope

1.1. Forensic paint analyses and comparisons are typically distinguished by sample size that precludes the application of many standard industrial paint analysis procedures or protocols. The forensic paint examiner must address concerns such as the issues of a case or investigation, sample size, complexity and condition, environmental effects, and collection methods. These factors require that the forensic paint examiner must choose test methods, sample preparation schemes, test sequence, and degree of sample alteration and consumption suitable to each specific case.

1.2. This document is an introduction for the forensic examination of paints and coatings. It is intended to assist personnel who conduct forensic paint analyses in the evaluation, selection, and application of tests that may be of value to the investigation. The guidelines that follow describe methods to develop discriminatory information using an efficient and reasonable order of testing. The need for validated methods and quality assurance guidelines is also addressed. This document is not intended to be a detailed methods description or rigid scheme for the analysis and comparison of paints but a guide to the strengths and limitations of each analytical method. The goal is to provide a consistent approach to forensic paint analysis.

1.3. Some of the methods discussed in these guidelines involve the use of dangerous chemicals, temperatures, and radiation sources. This document does not address the possible safety hazards or precautions associated with its application. It is the responsibility of the user of these guidelines to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2.0. Reference Documents

2.1. ASTM D16 Terminology Relating to Paint, Varnish, Lacquer, and Related Products¹

2.2. ASTM D1535 Method for Specifying Color by Munsell System

2.3. ASTM E308 Test Method for Computing the Colors of Objects by Using the CIE System

2.4. ASTM E1492 Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory²

3.0. Terminology

3.1. For definitions of terms used in these guidelines other than those listed, see ASTM D16 Terminology Relating to Paint, Varnish, Lacquer, and Related Products.¹

3.2. Descriptions of Terms Specific to this Guide:

3.2.1. Binder: A nonvolatile portion of the liquid vehicle of a coating, which serves to bind or cement the pigment particles together.

3.2.2. Coating: A generic term for paint, lacquer, enamel, or other liquid or liquefiable material that is converted to a solid, protective, or decorative film or a combination of these types of films after application.

3.2.3. Discriminate: To distinguish between two samples on the basis of significant differences; to differentiate.

3.2.4. Discriminating Power: The ability of an analytical procedure to distinguish between two items of different origin.

3.2.5. Known Sample: A coating sample of established origin.

3.2.6. Paint: Commonly known as a pigmented coating.

3.2.7. Pigment: A finely ground, inorganic or organic, insoluble, and dispersed particle. Besides color, a pigment may provide many of the essential properties of paint such as opacity, hardness, durability, and corrosion resistance. The term pigment includes extenders.

3.2.8. Questioned Sample: A coating sample whose original source is unknown.

3.2.9. Significant Difference: A difference between two samples that indicates that the two samples do not have a common origin.

3.2.10. Additive (modifier): Any substance added in a small quantity to improve properties. Additives may include substances such as driers, corrosion inhibitors, catalysts, ultraviolet absorbers, and plasticizers.

4.0. Quality Assurance Considerations

4.1. A quality assurance program must ensure that analytical testing procedures and reporting of results are monitored by proficiency tests and technical audits. General quality assurance guidelines may be found in Trace Evidence Quality Assurance Guidelines (1).

5.0. Summary of Practice

5.1. Physical and Chemical Features

Paint films are characterized by a number of physical and chemical features. The physical characteristics may include color, layer sequence and thickness, surface and layer features, contaminants, and weathering. Chemical components may include pigments, polymers, and

additives. These features can be determined and evaluated by a variety of macroscopical, microscopical, chemical, and instrumental methods. Limited sample size and sample preservation requirements mandate that these methods be selected and applied in a reasonable sequence to maximize the discriminating power of the analytical scheme.

5.2. Questioned and Known Samples

Searching for differences between questioned and known samples is the basic thrust of forensic paint analysis and comparison. However, differences in appearance, layer sequence, size, shape, thickness, or some other physical or chemical feature can exist even in samples known to be from the same source. A forensic paint examiner's goal is to assess the significance of any observed differences. The absence of significant differences at the conclusion of an analysis suggests that the paint samples could have a common origin. The strength of such an interpretation is a function of either or both the type or number of corresponding features.

5.3. Motor Vehicle Identification

An important aspect of forensic paint analysis is the identification of the possible makes, models, and years of manufacture of motor vehicles from paint collected at the scene of a crime or an accident. The color comparison and chemical analysis of the undercoat and topcoat systems requires a knowledge of paint formulations and processes, collections of paint standards, and databases of color and composition information.

5.4. Sample Documentation

The test procedure selected in a paint analysis and comparison begins with thorough sample documentation. Some features of that documentation are described in ASTM E1492 Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory.² Analysis generally begins with appropriate nondestructive tests. If the initial tests are inconclusive or not exclusionary, the examination may proceed with additional tests that are selected on the basis of their potential for use in evaluating or discriminating the samples of interest or both.

6.0. Significance and Use

6.1. These guidelines are designed to assist the forensic paint examiner in selecting and organizing an analytical scheme for identifying and comparing paints and coatings. The size and condition of the sample or samples will influence the selected analytical scheme.

7.0. Collection of Suitable Samples

7.1. The potential for physical matches between known and questioned samples must be considered before selecting the method of paint sample collection. Care should be taken to preserve the potential for a physical match.

7.2. Questioned Samples

7.2.1. Questioned samples should include all loose or transferred paint materials. Sources of questioned samples can include tools, floors, walls, glass fragments, hair, fingernails, roadways, adjacent structures, transfers or smears on vehicles, or transfers to or from individuals such as damaged fabric with paint inclusions. Items with paint transfers should be appropriately packaged and submitted in their entirety for examination whenever possible. If sampling is necessary, the procedures listed in Trace Evidence Recovery Guidelines (2) may be used. When paint evidence is recognized, every effort should be made to manually remove it before using tape lifts to collect other types of evidence. If paint is collected with tape lifts, be aware of the possible difficulty encountered when attempting to manipulate paint samples bearing adhesive residues. In addition, components of the adhesive could contaminate the paint sample and change its apparent chemistry.

7.2.2. Smear transfers can exhibit mingling of components from several layers or films that could preclude application of some of the analytical methods discussed in these guidelines. Because of the difficulties associated with collecting smeared or abraded samples, the entire object bearing the questioned paint should be submitted to the laboratory whenever possible.

7.2.3. When contact between two coated surfaces is indicated, the possibility of cross transfers must be considered. Therefore, if available, samples from both surfaces should be collected.

7.3. Known Samples

7.3.1. When feasible, known paint samples must be collected from areas as close as possible to, but not within, the point or points of damage or transfer. These damaged areas are usually not suitable sources of known samples. The collected known samples should contain all layers of the undamaged paint film. Substantial variations in thickness and layer sequences over short distances can exist across a painted surface. This is particularly true in architectural paint and automotive films where the curves, corners, and edges are often impact points and may have been subjected to previous damage, sanding, or overpainting. If necessary, several known paint samples should be taken to represent all damaged areas. Known paint samples collected from different areas should be packaged separately and labeled appropriately.

7.3.2. The surface underlying the suspected transfer area should be included for analysis when possible. Adjacent sections removed from a wall, ceiling, door, window, implement handle, and automobile door, fender, and hood are examples of items that can be valuable for assessing questioned and known sample differences and for evaluating the possible cross transfer of trace materials.

7.3.3. Paint flakes can be removed from the parent surface by a number of methods. These include but are not limited to the following: lifting or prying loosely attached flakes, cutting samples of the entire paint layer structure using a clean knife or blade, or dislodging by gently impacting the opposite side of the painted surface. When cutting, it is important that the blade be inserted down to the parent surface. It should be noted that no one method of sampling should be relied upon exclusively.

8.0. Procedure

8.1. Discussions of forensic paint analysis are provided in dated but detailed form by Crown (3), and more recently by Nielsen (4), Thornton (5), Maehly and Stromberg (6), and Stoecklein (7).

8.2. A reasonable scheme for forensic paint examinations is outlined in [Figure 1](#). A variety of potentially useful techniques for the discrimination of paint binders, pigments, and additives are listed. The major steps in Figure 1 correspond to the discussions presented in this section (e.g., [8.8. Solvent/Microchemical Tests](#)). For any given comparison, not all the techniques listed in Figures 1A, 1B, and 1C are necessarily required. Sample size, condition, and layer structure complexity should be considered when determining which techniques to use. The forensic coatings examiner should always use the more specific and least destructive tests prior to those that require more sample preparation or consumption. A review of the general technique descriptions, listed in [8.8. Solvent/Microchemical Tests](#) and the subsections that follow, provides guidance for the selection of appropriate methods.

8.3. Figure 1 does not imply that other examinations should be excluded or that the order of the procedures in the chart is irrevocable. Samples that are neither constrained by amount nor condition should be subjected to analyses that will determine the color and texture of the paint as well as the number, order, colors, and textures of the layers in a multilayered sample. In most cases, instrumental techniques should be employed to analyze and compare both the pigment and binder portions of the sample. A combination of techniques, which provides discrimination

between as many types of paints and coatings as possible, should be used. These techniques should also be selected to provide either or both classification or component identification information to be used in significance assessments. For samples that are limited in layer structure complexity, techniques for the comparison of both the binder and pigment portion of the coating must be used. The choice of techniques may change depending upon sample characteristics. For instance, pyrolysis gas chromatography (PGC) may be used for identifying and comparing the binder portion of samples that exhibit a low binder concentration. Likewise, scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDS), X-ray fluorescence (XRF), and X-ray diffraction (XRD) may be used for identifying and comparing the pigment portion of samples that exhibit a low pigment concentration.

8.4. The flowchart in [Figure 2](#) is a guide to the determination of the possible origins of a motor vehicle paint in an investigative case. It is usually possible to differentiate motor vehicle repaint from the original equipment manufacturer (OEM) paint by microscopical examination. If no OEM paint is present, then only the vehicle color can be reported. For OEM paint, the color of the topcoat layers and of the undercoat layers will each be useful in identifying manufacturer, model, and year. Often the two systems provide complementary information. In most cases a range of possible makes, models, and years will be generated by the search. Further specific information can often be developed through chemical analysis of the individual layers. Any of the techniques shown in Figure 1 can be used, depending on the databases available. Reference collections and databases may fall into one of the following categories: books of color chips produced by automotive refinishing paint manufacturers for use by body shops and automotive repair facilities, manufacturer topcoat and undercoat colors, chemical standards, street samples collected from damaged motor vehicles, OEM information on paint formulations, and collections of infrared spectra or pyrograms of known paints. Examples of databases include the Royal Canadian Mounted Police/Scientific Working Group on Materials Analysis (RCMP/SWGMAT) database, the National Automotive Paint File maintained by the Federal Bureau of Investigation, the Collaborative Testing Services reference collection of automotive paints, and the Georgia Bureau of Investigation Paint Library of infrared spectra.

8.5. Sample Description

8.5.1. The first step in forensic paint analysis is the visual and macroscopical evaluation, description, and documentation of the original condition of the sample or samples. Occasionally, this can be the final step in an analysis if exclusionary features or conditions in the sample or samples are identified during the initial evaluation.

8.5.2. The initial evaluation should begin with a critical review of the chain of custody, package sealing, and identification markings of the sample or samples and any potential cross-contamination between samples. If the items are found to be suitable for further evaluation, a detailed accounting and description of the paint fragments and any commingled material should be documented. This involves describing the general condition, weathering characteristics, size, shape, exterior colors, and major layers present in each sample. This description can be accomplished by examining each item using a stereo microscope.

8.5.3. Written descriptions, sketches, photography, or other imaging methods must be used to document each sample's characteristics. The goal is to produce documentation that will be meaningful to a reviewer in the absence of the recording examiner. The resulting notes must be sufficient to document the conclusions reached in the examiner's report. Although documentation is discussed at this point in the guidelines, it is an essential part of all steps in an analysis.

8.6. Physical Match

8.6.1. The most conclusive type of examination that can be performed on paint samples is the physical matching of samples. This may involve the comparison of edges and surface striae between samples or the comparison of surface striae on the underside of a questioned paint

fragment to those of a parent surface. Either or both the edges or striae in question must possess unique characteristics.

8.6.2. Physical matches must be documented with descriptive notes. Photography, photo transparency overlays, or other appropriate imaging techniques may be a useful adjunct. When imaging methods are used to document a physical match, the examiner must ensure that the method employed is dimensionally accurate and has associated measuring scales. Images must be well-preserved and retained as part of the documentation.

8.7. Sample Preparation and Layer Analysis

8.7.1. The layers in a paint film are identified by viewing the sample edges at magnifications ranging between 5x and 100x. The obvious layers are generally visible without sample preparation. Definitive paint layer identification usually requires sample preparation techniques such as manual or microtome sectioning, edge mounting and polishing, or both. A combination of techniques may be required to fully characterize the layer structure. The extent of sample manipulation and preparation will depend on the amount of paint available and its characteristics.

8.7.2. Paint layer structure can be observed by using a scalpel blade to make an oblique cut through a sample. The larger surface area created by this angled cut may enhance layer visualization and assist in the detection of layer inhomogeneities. The preparation of thin-sections and the separation of paint layers can be accomplished with a scalpel blade. Preliminary solvent tests can be conducted on the manually prepared sections and layer fractions.

8.7.3. Subtle differences in color, pigment appearance, surface details, inclusions, metallic and pearlescent flake size and distribution, and layer defects may require microscopical comparisons of the edge, oblique cut, and surface views of known and questioned paint samples. These comparisons must be carried out with both samples positioned side by side and in the same field of view.

8.7.4. Cross sections (embedded or thin-section preparations) may provide additional information as to the layer sequence, layer thickness, color, pigment distribution, pigment size, and composition of the individual layers that may not be possible to obtain with gross examination. Embedded preparations can be prepared by polishing, microtomy, or both. Thin-sections can be prepared using a variety of microtomy techniques. Examination and analysis of the cross sections can be conducted using a variety of analytical techniques that may include light microscopy, UV-visible microspectrophotometry, infrared microspectrophotometry, and electron microscopy. Laing et al. (8), Allen (9), and Stoecklein and Tuentje (10) offer a concise discussion of thin-section paint analysis.

8.8. Solvent/Microchemical Tests

8.8.1. Solvent/microchemical tests have long been used for attempting to discriminate between paint films of differing pigment and binder composition that are otherwise similar in visual and macroscopical appearance. They have been described previously in the general references for this section ([Subsection 8.1.](#)). The tests are based not only on dissolution of paint binders but also on pigment and binder color reactions with oxidizing, dehydrating, or reducing agents.

8.8.2. Solvent/microchemical tests are destructive and should be applied first to known samples in order to evaluate their efficacy to a specific case, and they should be used only in situations in which an adequate questioned sample is available.

8.8.3. Solvent/microchemical examinations should be applied to both questioned and known materials concurrently. The effects of various tests are recorded immediately and then at reasonable intervals for the duration of each test. It is desirable to apply such tests not only to

intact paint films but also to peels of each individual layer to avoid interaction with neighboring layers and to observe the dissolution process more critically.

8.8.4. Reactions such as softening, swelling, curling or wrinkling, layer dissolution, pigment filler effervescence, flocculation, and color changes are some of the features that may be noted. The results of these tests are inherently difficult to quantify. Therefore, they are primarily used for preliminary classification and comparison.

8.9. Polarized Light Microscopy (PLM)

8.9.1. PLM is appropriate for the examination of layer structure as well as either or both the comparison or identification of particles present in a paint film including pigments, extenders, additives, and contaminants. Extenders and other components of a paint film are generally of sufficient size to be identified by their morphology and optical properties using this technique. Although some pigment particles are too small for definitive identification by this method, exclusionary features may still be evident between samples.

8.9.2. Suitable samples for examination by PLM include but are not limited to thin peels, thin-sections, pyrolysis and low-temperature ashing residues, sublimation condensates, and dispersed particles in a solvent oil or other mounting medium.

8.9.3. The use of PLM for the identification of paint components requires advanced training and experience. Preparation and identification of paint components by PLM are discussed by McCrone (11) and Kilbourn and Marx (12).

8.10. Vibrational Spectroscopy

8.10.1. Infrared spectroscopy (IR) may be used to obtain information about binders, pigments, and additives used in various types of coating materials. Because the paint fragments to be analyzed are often quite small, a beam condensing or focusing device is normally required, and a Fourier transform infrared (FTIR) spectrometer is recommended. Both transmittance and reflectance techniques may be used for the analysis of coatings, but in most cases, transmittance methods are preferred because all the sampling wavelengths are subjected to the same pathlengths and most of the reference data of coatings, binders, pigments, and additives consist of transmittance spectra. In addition, transmittance data are not significantly affected by collection parameters such as type of refractive element used, angle of incidence chosen for analysis, or the degree to which the sample makes contact with the refractive element. These factors affect spectra obtained using internal reflectance methods.

8.10.2. If a multiple-layer coating system is to be subjected to an infrared examination, optimal results can be obtained if each layer is isolated and analyzed separately. Methods that use solvents to assist in the sample preparation should be used with caution because they might alter the sample or result in the production of residual solvent spectral absorptions.

8.10.3. An infrared microscope accessory permits the analysis of a small sample or a small area of a sample. Samples of individual layers may be prepared manually using scalpels, blades, needles, forceps, or other similar tools. Peels or sections can be placed on a salt plate or appropriate mount for analysis. The infrared microscope accessory may also be used to sequentially sample individual layers of a multiple-layer coating system that has been cross-sectioned either manually or by microtome. Generally, it is desirable to press such a sample after sectioning to produce a wider width for each layer and to produce a more uniform thickness. The aperture for an individual layer should be chosen so that its edges are as far from the adjacent layers as practicable. This minimizes the amount of stray light produced by diffraction that may be detected. All spectra of individual layers should be examined to determine if absorptions of adjacent layers are contributing to the spectrum.

8.10.4. Certain types of coatings, including automotive undercoats and many types of architectural coatings (particularly those with low luster finishes), usually contain significant amounts of inorganic pigments. These pigments tend to have most of their significant infrared absorptions in the lower frequency spectral regions, and several have all of their absorptions in the region below 700 cm^{-1} . An FTIR spectrometer equipped with cesium iodide (CsI) optics and a deuterated triglycine sulfate (DTGS) detector can collect spectral data to 220 cm^{-1} . The DTGS detector is less sensitive than the mercury cadmium telluride (MCT) detector used with IR microscopes, and the DTGS detector also requires a longer time to acquire each spectrum. CsI optics also have the disadvantage of lower energy throughput compared to potassium bromide (KBr) optics. Thus, a far-IR instrument requires longer analysis times.

8.10.5. Transfers of coatings resulting in smears on various substrates may be sampled in situ using an appropriate attenuated total reflectance (ATR) accessory or an ATR objective for an infrared microscope. As a control, the substrate itself (not a metal) should also be analyzed to verify that its absorptions are not contributing to the spectrum of the smear. Any contributions from the substrate should be considered. If the substrate is a metal or highly reflecting, it may be possible to obtain a reflection-absorption spectrum of the smear using the reflectance mode of an infrared microscope accessory. This produces a double-pass transmittance spectrum of the material, and a background spectrum of the substrate itself (or uncoated mirror) should be used as a reference.

8.10.6. General information about the forensic analysis of coatings using infrared spectroscopy is discussed by O'Neill (13), Suzuki (14), and Ryland (15). Forensic infrared microsampling of coatings using a beam condenser is described by Tweed et al. (16), Rodgers et al. (17), and Schiering (18). Analyses using infrared microspectroscopy are described by Wilkinson et al. (19), Allen (20), Bartick et al. (21), and Ryland (15). The identification of specific binders, pigments, and additives using infrared spectroscopy is described by Rodgers et al. (17, 22, 23), Norman et al. (24), Ryland (15), and Suzuki et al. (25-27). Infrared spectral data for a number of binders, pigments, additives, and solvents are presented in a compilation produced by the Federation of Societies for Coatings Technology (28).

8.10.7. Raman spectroscopy can also be used to obtain information about binders, pigments, and additives used in coatings. Because this technique is based on light scattering rather than absorption, Raman spectra provide information that is complementary to that produced by infrared spectroscopy. Some paint components, for example, may give rise to both infrared absorption bands and Raman bands, but the relative absorption or scattering intensities of these bands will differ significantly between the two techniques. Other paint components may have vibrational modes that produce no infrared absorption bands but may produce Raman bands. In addition, Raman spectroscopy can be useful for the analysis of inorganic pigments and additives because it, like far-infrared spectroscopy, can provide information about low-frequency vibrational transitions.

8.10.8. In most cases, Raman instrumentation using near-infrared lasers will be needed to avoid strong fluorescence produced by various paint components. Because near-infrared excitation produces considerably weaker Raman scattering than visible excitation, dispersive instruments equipped with diode array detection systems or Fourier transform Raman spectrometers are recommended. Some applications of Raman spectroscopy for the analyses of coatings are discussed by Kuptsov (29) and Claybourn et al. (30).

8.11. Pyrolysis Gas Chromatography (PGC)

8.11.1. Pyrolysis gas chromatography (PGC) is a destructive technique that uses pyrolytic breakdown products to compare paints and to identify the binder type. As noted by Burke et al. (31), Fukuda (32), Ryland (15), and Cassista and Sandercock (33), this method of analysis may offer improved discrimination of chemically similar paints. Several pyrolysis systems and techniques are available to the forensic scientist and are discussed in overviews by Blackledge

(34), Challinor (35), Saferstein and Manura (36), Irwin (37), Wampler (38), Freed and Liebman (39), and Liebman and Wampler (40).

8.11.2. Pyrograms, the chromatograms of the pyrolytic products, are influenced by numerous sample characteristics and instrumental parameters. These may include sample size, shape and condition, ramping rates, final pyrolytic temperature, type of capillary column or columns, gas-flow rates, temperature programs, and detector type or types. The resulting patterns of peaks in the known and questioned sample pyrograms are used for comparison purposes. If pyrolysis and chromatographic conditions are kept constant over time, then PGC can be used as an aid in the characterization of binder types by comparison with pyrograms of paints or resins from a reference collection.

8.11.3. The applicability of this technique depends on the paint type, layer complexity, and the amount of sample consumption that can be tolerated. PGC analysis may be conducted with as little as 5-10 micrograms of sample. Run times are typically 20-40 minutes in duration. PGC is best applied to individual paint layers for purposes of both binder classification and comparison. With multilayered paint samples, layer thickness variations, sample orientation in the pyrolysis accessory, and incomplete pyrolysis make reproducible pyrograms more difficult to obtain.

8.11.4. The user must ensure that reproducibility is maintained and that there is no sample carryover between runs. The necessity and frequency of replicate and blank runs must be established for each system and sample type.

8.11.5. The identification of pyrolysis products may be accomplished by pyrolysis gas chromatography-mass spectrometry (PGC-MS). Besides the detection of binder components, the reconstructed total ion chromatogram may contain information about additives, organic pigments, and impurities. McMinn et al. (41) and Challinor (42) provide discussions of mass spectrometric detection for PGC.

8.11.6. Information about the binder composition of some samples can be increased if the paints have been derivatized during pyrolysis. The use of derivatizing reagents such as tetramethyl-ammonium-hydroxide (TMAH) is discussed by Challinor (43-45).

8.12. Microspectrophotometry

8.12.1. Color analysis has a long history in the pigment, paint, dyestuff, and fabric industries and has led to numerous approaches to color measurement and description. Absorption spectroscopy, to discriminate the color of visually similar or metameric paint samples is discussed by Cousins (46). Colors can be described by systems such as those of Munsell and the Commission International de l'Eclairage (CIE), as described by ASTM Standard Method D 1535 and Test Method E 308. These systems can be used to classify colors for database systems, but usually absorption spectra of known and questioned samples are directly compared in forensic color comparisons.

8.12.2. Microspectrophotometry may be required to provide objective color data for paint comparison because of the typically small size of samples. The technique can be applied to the outer surfaces of paint films by diffuse reflectance (DR) measurements with visible spectrum illumination.

8.12.3. Diffuse reflectance measurements of paint surfaces are affected profoundly by surface conditions such as weathering, abrasion, contamination, and texture. This fact can provide useful discriminating information when an examiner is faced with distinguishing different surfaces that were originally painted with the same paint formulation. Careful reference sampling is essential to the success of color comparisons of such surfaces.

8.12.4. Diffuse reflectance techniques can also be used on the edges of thin paint layers much as it is on outer paint surfaces. Before analysis, questioned and known samples can be mounted side by side on edge and polished to a smooth surface using a polish of 3-micron grit size or less. Microtomed samples without surface defects may be used without polishing. The requirement for consistent surface finish characteristics for all samples is achieved easily if the known and questioned samples are mounted and prepared in a single mount.

8.12.5. When required for the discrimination of similarly colored paint layers, the surface finish of a polished sample must approach the size of the smallest pigment particles present.

8.12.6. Comparison of paint layers by transmission microspectroscopy of thin cross sections offers a more definite form of color analysis for these samples, compared to reflectance techniques. Transmission microspectroscopy demands the most care in preparation. Consistent sample thickness and choice of measurement size and location are essential for meaningful comparisons. Although thin cross sections can be manually prepared, improved reproducibility can be achieved using a microtome. Even when using a microtome, the slice thickness, blade angle, cutting speed, lubrication, and mounting block stiffness or resilience must be selected and controlled carefully. A discussion of these parameters is presented by Derrick (47).

8.13. Scanning Electron Microscopy

8.13.1. Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDS) can be used to characterize the morphology and elemental composition of paint samples. The SEM rasters an electron beam over a selected area of a sample, producing emission of signals including X-rays, backscattered electrons, and secondary electrons. Emitted X-rays produce information regarding the presence of specific elements, and the electron signals produce compositional and topographical visualization of a sample.

8.13.2. X-rays are produced as a result of high-energy electrons creating inner-shell ionizations in sample atoms, with subsequent emission of X-rays unique to those atoms. The minimum detection limit under many conditions is 0.1 percent. Elements with atomic numbers greater than or equal to 11 are customarily detectable. Detection of elements with atomic numbers greater than or equal to 4 is possible using a detector with an organic film window or a windowless detector. Analysis can be performed in a rastered beam mode for bulk-layer analysis or static beam (spot) mode for individual particle analysis. Goldstein et al. (48) present a general treatment of all aspects of SEM and X-ray microanalysis.

8.13.3. Comparison of the composition of layers is generally performed by a nonquantitative method, such as direct spectral comparison or peak ratioing. Because accurate quantitative EDS requires sample homogeneity to a level of several microns, quantitative methods are not generally used for paint analysis. In order to produce a representative spectrum of a paint layer, the summing of spectra from multiple areas or the use of a beam raster area larger than 30 square microns is often required. The homogeneity of modern household paints and their examination by SEM-EDS is discussed by Gardiner (49).

8.13.4. The analysis of individual pigment particles in paint layers by static beam (spot) analysis can be useful. However, variations in the absorption and fluorescence factors caused by particle size and shape and fluorescence contributions from adjacent particles preclude the application of small, single-particle, X-ray correction routines.

8.13.5. The depth from which X-rays are produced (the analytical volume) is dependent upon beam energy, composition and density of the sample, and energy of the X-rays. Generally, the primary X-ray spatial resolution obtained in the analysis of paint systems is less than 10 μm . Secondary X-ray fluorescence further enlarges the analytical volume beyond the scanned image area visible in the SEM image. Optimal results are obtained from samples prepared in cross

section, either by microtomy or polishing. The low bulk density and low average atomic number of organic polymer-based paint layers make them susceptible to electron and X-ray penetration that can yield analytical X-ray contributions from adjacent layers. Care must be taken to ensure that the EDS data generated are representative only of the paint layer of interest or that any adjacent layer contributions are reproducible.

8.13.6. Additional sample preparation methods such as thin peels or stair stepping may be used. Stair-step sample preparation and analysis allows larger areas to be analyzed and possibly avoids inhomogeneity concerns but faces the potential for penetration into the underlying layer and difficulties in obtaining flat analytical surfaces and reproducible layer thicknesses. If samples are prepared as single-layer peels, the concerns of penetrating or sampling adjacent layers or both are avoided. Elements in low concentrations may not be as readily detected in these thin peels without longer count times.

8.13.7. Mapping of elements across the cross section of a multilayer paint can be useful for explaining or demonstrating elemental distributions and elemental associations. However, elemental maps are generally not quantitative and may lack the sensitivity to demonstrate minor sample differences.

8.13.8. Because a wavelength dispersive spectrometer (WDS) generally has better spectral resolution, lower detection limits, and superior light element detection capability than EDS, its use can supplement EDS to more completely characterize the elemental composition of paints. For example, WDS may resolve overlapping Ti K and Ba L lines, which is not possible by EDS. Because WDS has critical X-ray focusing requirements, the sample analyzed must generally be flat, and the analysis area must generally be smaller than that allowed for EDS. Goldstein et al. (48) present a complete discussion of wavelength and energy dispersive spectrometers.

8.13.9. The elemental composition of paint smears that cannot be lifted from a substrate can often be estimated by subtraction of the substrate's X-ray spectrum from the combined smear-substrate spectrum. However, commingling of the smeared paint with substrate surface contaminants, the low mass of the smear, and typical inhomogeneity of paint can produce significant deviations of the smear spectrum from that of the original paint.

8.13.10. Atomic number contrast images are produced in the SEM by the collection of backscattered electrons. These images are used to characterize and compare the structure of paints, including layer number, layer thickness, distribution and size of pigment particles, and the presence of contaminants.

8.14. X-Ray Fluorescence Spectrometry (XRF)

8.14.1. XRF is an elemental analysis technique based upon the emission of characteristic X-rays following excitation of the sample by an X-ray source. XRF analysis is less spatially discriminating than SEM-EDS because of its larger analytical beam size and the greater penetration depth of X-rays compared to electrons. However, the limits of detection for most elements are generally better than for SEM-EDS, and the higher energy X-ray lines produced by higher energy excitation typical of XRF can be useful during qualitative analysis.

8.14.2. Because of the significant penetration depth of the primary X-rays, XRF analysis will generally yield elemental data from several, if not all, layers of a typical multilayer paint fragment simultaneously. Because variations in layer thickness may cause variations in the X-ray ratios of elements present, this technique can be used only comparatively or qualitatively. Fischer and Hellmiss (50) present a general discussion of the forensic applications of X-ray fluorescence. Howden et al. (51) discuss XRF analysis as applied to single-layer household paints.

8.15. X-Ray Diffraction (XRD)

8.15.1. XRD is a nondestructive technique for the identification of the crystal form of pigments

and extenders or fillers. This method is usually not suitable for the identification of organic pigments. X-ray diffraction techniques for the analysis of paint compounds are discussed by Snider (52).

8.15.2. XRD instruments usually employ a copper target X-ray tube to generate the X-ray beam and a diffractometer to measure both the diffraction angles and peak intensities characteristic of the crystal structure. Beam/sample geometry is critical in producing the correct diffraction pattern.

8.15.3. Commercially available databases of diffraction patterns of crystalline materials can be used to facilitate qualitative analysis. Because the diffraction pattern of a mixture may be difficult to interpret, the identification of each component may require information provided by other analytical techniques such as elemental analysis.

8.15.4. Most paints need no sample preparation. Surface contaminants (e.g., sand particles), however, should be removed. Individual layer analysis is preferred over multilayer or bulk analysis in order to associate components to their respective layers.

Figure 1

Paint Comparison Guide

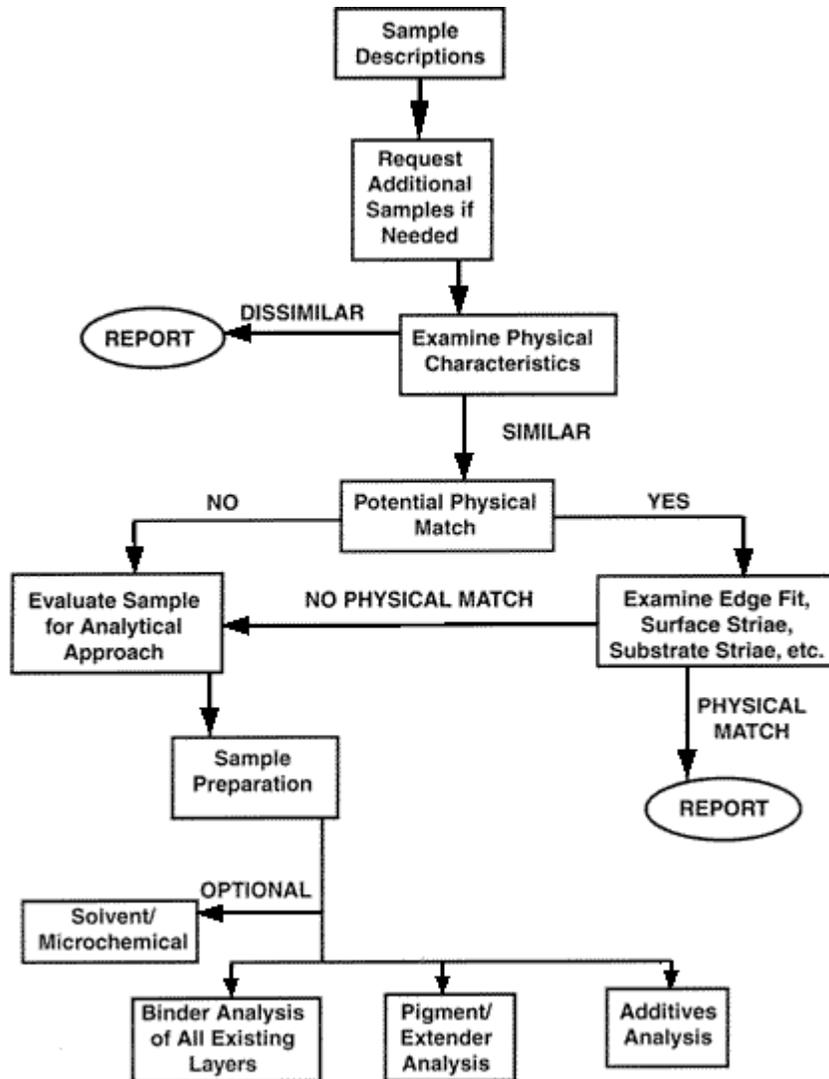
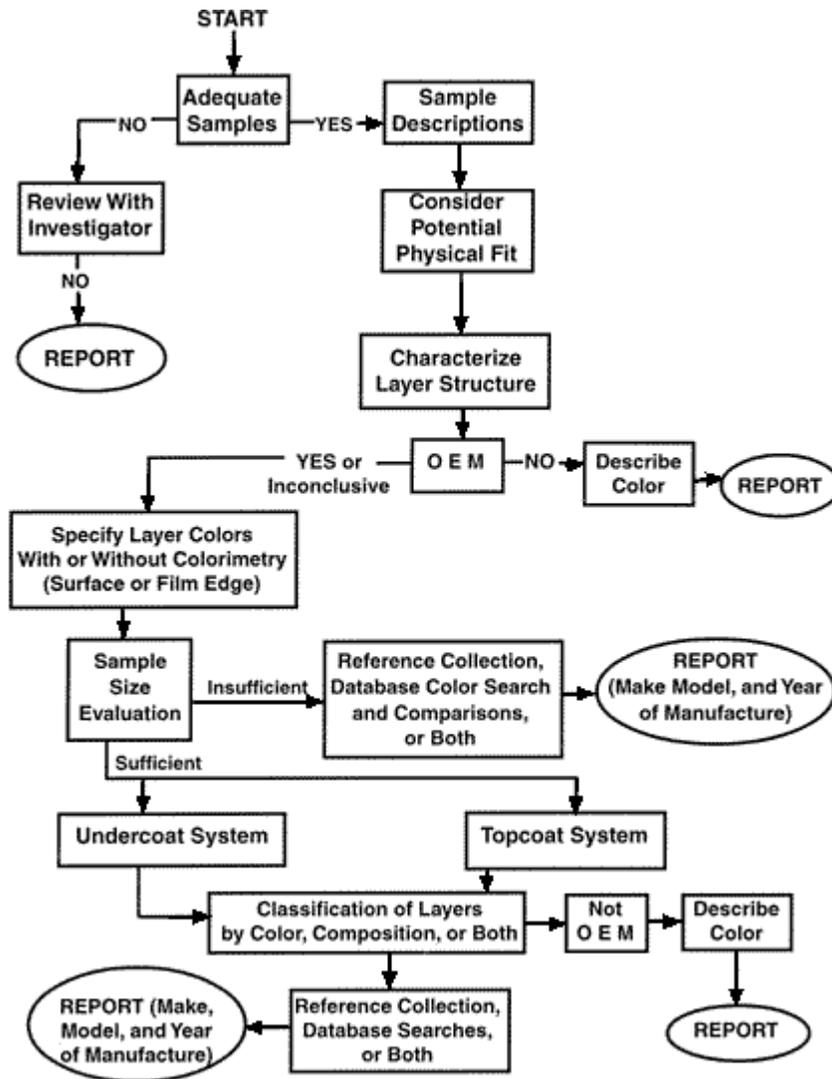


Figure 2

Guide to Motor Vehicle Identification



9.0. Other Techniques

9.1. Fluorescence Microscopy

9.1.1. Fluorescence microscopy of thin or bulk cross sections, as an aid in differentiating samples or various layers within intact paint fragments, is discussed by Stoecklein and Tuentje (10). When using an excitation wavelength of 365 nanometers, the technique may be sensitive to differences in organic pigments, additives, and film-forming components. Allen (53) reports it to be most useful with light-colored architectural coatings.

9.2. Low-Temperature Ashing

9.2.1. The low-temperature asher is a device in which an oxygen plasma is used to remove organic materials from a complex matrix. Materials that produce volatile oxides (principally organic components) are removed from the matrix with minimal elevation of the sample temperature in contrast to pyrolysis systems. Ashing usually continues until all such volatile oxides are removed.

9.2.2. Inorganic pigments, extenders, and some additives in the different layers of the ashed paint film will remain after the organic material is volatilized. The relative size and morphology of the different particles, noted during previous tests, serve to help identify and separate these residue components for additional analysis. A brief description of the technique is provided by McCrone and Delly (54) and Brown (55).

9.2.3. Ashing residues can be analyzed by a variety of methods, including PLM, SEM-EDS, analytical electron microscopy (AEM), or XRD techniques.

9.3. Solvent Extraction

9.3.1. Solvent extraction can be used to separate some of the organic components from paint films, depending on the paint system or systems in question. The objective of the procedure is to recover a solute that can be examined by IR, GC, or GC-MS techniques. It is especially useful for coatings where the volume of pigments or extenders is very high. The identification of the binders by FTIR is often only possible after separation of the pigments and extenders.

9.3.2. When using solvent extraction, separation of paint layers is very important. If this is impossible, it is important that identical conditions (e.g., time, and temperature) be applied to both the known and questioned samples.

9.4. Analytical Electron Microscopy

9.4.1. Analytical electron microscopy (AEM) is the term applied to the use of transmission electron microscopy (TEM) in conjunction with both selected area electron diffraction and EDS. The combination of techniques can provide more definitive identification of some pigment grains that cannot be identified conclusively by PLM because of their extremely small size or opacity.

9.4.2. AEM requires that the sample be sufficiently thin to permit transmission of the analytical electron beam. It is thus applied only to dispersions of extracted inorganic particulates, such as those recovered from low-temperature ashing, dissolved paint layers, or ultramicrotomed sections of a paint film (56).

9.5. Cathodoluminescence

9.5.1. Cathodoluminescence (CL) is the emission of radiation from the sample in the visible light region and neighboring wavelengths following excitation by electrons where these, originating from a cathode and accelerated in an electric field, strike upon an insulator or semiconductor (e.g., inorganic pigments or fillers). This phenomenon can be observed through the use of specially equipped optical or scanning electron microscopes.

9.5.2. Cathodoluminescence can be performed on embedded sections as an aid in differentiating samples or various layers within intact paint fragments. The technique has been found to be most useful for characterizing and comparing multilayered white or beige architectural and marine paint fragments (57).

10.0. References

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11.0. Endnotes

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