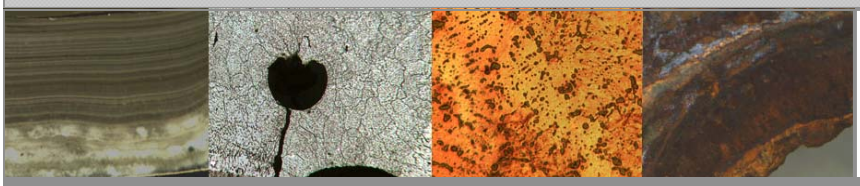
# NUTS & BOLTS



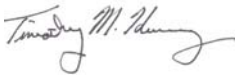
New Hampshire MATERIALS LABORATORY, INC.
*Your Problem Solving Partner*

**FORENSIC PAINT ANALYSIS** **AUGUST 2012 ISSUE 8**

## Welcome to New Hampshire Materials Laboratory

The complexity of the paint industry has grown exponentially in recent decades. An example of how technology has changed the way the paint industry works can be found just by walking into your local hardware store. The variety of paints and stains that can be purchased is amazing and colors can be exactly matched to whatever you want.

With a variety of paints and coatings come a variety of modes by which these products can experience failure. In this issue of the Nuts & Bolts, our senior chemist, Jeff Masse has written an article on Forensic Paint Analysis. It highlights what a modern analytical laboratory can do to help find answers to the problems.



Tim Kenney
Laboratory Director

## Forensic Paint Analysis

### By Jeff Masse

Paint is a suspension of a pigment in a liquid vehicle which enables distribution of pigment over the surface. The liquid vehicle includes solvents, binders and other additives. The complexity of the paint industry has grown exponentially in recent decades to include over 640 different kinds of raw materials and intermediates used in the production of modern paints. A full spectrum of paints that are readily available range from latex household paints, fast drying acrylic paints, enamel automotive paints, and Epoxy based systems. With the variety of paints and coatings come a variety of modes by which these products can experience failure; blistering of exterior household paints, oxidative aging, attack by sunlight, and the blush of amine curing agents to the surface of Epoxy coatings. These failures can all be investigated in a modern analytical laboratory.

***Paint Examinations:***

A paint examination always begins with a microscopic examination of the samples and any materials used for comparison. If a match between two samples is the question, a microscopic exam can first be used to determine if there is a color match between the two samples. Next, a cross section of the paint chip can be mounted and the sequence of layers as well as the relative thickness of the layers can be determined. Much information can often be gleaned from a simple microscopic exam of a paint chip. (Continued on page 2)

Although much information can often be gleaned from a simple microscopic exam of a paint chip, modern analytical techniques allow us to take this comparison well beyond a simple microscopic exam.

Since paint consists of an organic binder as well as inorganic fillers and pigments, we need analytical techniques that can characterize a paint sample in both of these areas. FTIR spectroscopy and EDS spectroscopy are two techniques perfectly suited for the task of paint analysis. We will now give a brief description of these two techniques and their relation to paint analysis.

***FTIR/Micro-FTIR Spectroscopy:***

FTIR is a spectroscopic technique in which infrared light is passed through a thin organic material (such as paint), which has covalent bonds and hence has characteristic absorption frequencies in the infrared region. This produces an infrared spectrum which looks like a series of peaks and valley on an X/Y graph. This spectrum is unique for a given organic material and can be thought of as the materials "chemical fingerprint". This technique is useful both for routine material verification or identification of polymers, paint matching and the identification of trace contaminates via an FTIR microscope.

Micro-FTIR spectroscopy is performed on an infrared microscope which is capable of obtaining spectra of objects down to about 25 microns in size. This means if you can see a tiny speck with the naked eye you can probably get a spectrum to identify it. Micro-FTIR is one of the most powerful techniques available to the modern scientist for paint characterization. Although IR Spectroscopy is not a particularly reliable technique for indicating the presence of a minor constituent of paint, it is excellent for determining the generic type of paint for example, Epoxy, Urethane, Acrylic etc., and for determining if two organic binders are in fact an exact match to each other.

An example, three samples of red paint which cannot be distinguished by color can immediately be distinguished by FTIR if they have a different organic binder (Acrylic, Urethane..). One job which came through our lab which highlights the use of FTIR was that of a polyethylene packing bottle. We dissected it from the bottle and analyzed it by FTIR. It indeed looked like a paint chip. Once we advised our customer of this, they quickly produced a reference sample of bright yellow paint being used within the same building. We are able to identify the source of the contamination in the bottle with a subsequent FTIR analysis that confirmed the two paints matched.

Another example of how the FTIR was used to solve a paint problem came when recently painted prison cells in a nearby jail began to show a thin brown film in patches on the outer surface. We went to the prison and took a sampling of the brown material and identified it as an amine by FTIR. Some paint systems use low molecular weight amines as curing agents. Unfortunately, these curing agents have some water solubility. In very humid conditions the amine curing agent can "blush" to the surface of the paint causing a very poor appearance and certainly preventing the application of a second coat of paint. (Continued on Page 3)

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***Energy Dispersive Spectroscopy (EDS):***

We mentioned above the FTIR was not particularly suited for indicating the presence of minor constituent of paint, such as an inorganic pigment or drying agent. Scanning Electron Microscopy allows detailed elemental analysis as well as high magnification viewing of very small features. The Energy Dispersive Spectroscopy (EDS) features allows the additional advantage of being able to obtain the elemental composition of small objects or surfaces. This combination is useful in studying the inorganic additives and other minor inorganic ingredients used in modern paint formulations. Just as FTIR gives a “fingerprint” of the covalent bonding paint molecules, EDS gives an “elemental fingerprint” of additives which often go undetected by FTIR.

An example of this advantage might be two acrylic automotive paints which match in color (let’s say red as our example) but have different red pigments Cadmium red and Iron oxide. These paints may even have equivalent FTIR scans and the only way to distinguish between these is by EDS, which can easily distinguish between Cadmium and Iron.

A special application of paint analysis is forensic paint analysis. In the past our lab has been involved in forensic paint analysis for legal cases involving vehicle collisions. In such cases, analysis of paint transfers using the techniques described above are often critical in determining if a particular accident reconstruction theory is possible or likely. Modern automobile paints are acrylic enamels and the topcoats (or clearcoats) are also acrylics, which can pose quite a challenge to forensic scientist who may be examining multiple acrylic layers which have been “smushed” together by high speed collision. If the vehicles were of the same or similar color, this can further complicate the sample preparation process. In such cases an FTIR match as well as an elemental EDS match are necessary for unequivocal match establishment between two samples.


**Paint Transfer from Auto Collision**

As the complexity of the modern paint industry has grown, our analytical capabilities of analyzing paints and coatings and their various failure modes have kept pace. Paint analysis problems and paint failures present a unique challenge to the modern scientist, however the combined information obtained from both FTIR and EDS techniques allows for the interpretation and diagnosis of a great variety of paint analysis problems.

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