Isolation and Identification of Paint Pigments by Sublimation

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The particle size of organic pigments used in modern coatings is extremely fine. Since these individual pigment crystals are typically less than 1 μm in size, they are difficult, if not impossible, to characterize and identify by microscopical means. The occurrence of occasional pigment aggregates may help identify a pigment to a microscopist who is familiar with a variety of known pigments under controlled conditions. More often, however, such observations provide a qualitative basis for comparison of questioned and known paints without leading to identification of the specific pigments involved. Microscopic observations of this type are assisted by the use of a high-magnification oil immersion objective and condenser with numerical apertures of 1.25 or greater. Due to the small working distance available under these conditions, such observations must be made on smears or high-quality thin sections.

Infrared (IR) microspectroscopy of coatings rarely provides direct spectroscopic evidence for the identification of specific pigments because these spectra are normally dominated by the absorption pattern of the polymer component. Notable exceptions are the inorganic pigments and fillers which often exhibit strong, characteristic bands, indicating both their presence and identity. These can be correlated with the results of elemental analysis and microscopy to establish the presence, microscopical character, and specific phases(s) of these components. In the case of organic pigments, minor peaks in the IR spectrum sometimes may be interpreted when an extensive collection of known pigments has been studied previously, and their characteristic absorption peaks have been cataloged (Suzuki and Marshall 1996).

In classical chemical analysis, specific identifications are made on components which have been isolated and purified. For example, in industrial paint analysis, liquid paints are centrifuged, and the residue is washed to isolate pigments and fillers for identification. Isolation, and thus concentration, of paint pigments appears to be an attractive solution to the problem of pigment identification, if it could be performed on a small scale. Modern, cross-linked polymer coatings are insoluble in normal solvents which do not break the cross-link bonds between polymer molecules. Thus, this approach is unsuitable for most original top coat finishes, but it may have some application in the case of repaints.

An approach which has been used for some time in our laboratory and has been successfully employed by many of our students is sublimation. Since many organic pigments sublime under atmospheric pressure at reasonable working temperatures, this appears to be an attractive procedure and has been successful for those pigments which cooperate. The apparatus required is simple and inexpensive. Furthermore the technique can be mastered in a relatively short time. The procedure described in the following paragraphs is currently used. However, the technique has been improved since our first discovery of this phenomenon over 10 years ago, and it continues to evolve.

Materials and Methods

The sublimation apparatus consists of a flat, capillary tube of resistant glass (*e.g.*, Microslides, manufactured by Vitro Dynamics, Inc., Rockaway, NJ). We utilize various path lengths depending on whether we are working with known dry pigment reference samples (greater path length, since it is difficult to charge the tubes with the pigment) or actual paint particles. For case work specimens of known or questioned paint, we normally use a 0.3 mm path length (cat#3530). The tube is charged by inserting the paint particle into one end with a tungsten needle. The particle is then pushed to the center of the tube using a narrow strip of paper about two thirds of the width of the tube and about as long as the tube itself. These manipulations are performed under a stereomicroscope. The tube should have been cleaned previously by wiping the exterior surfaces with a Kimwipe® (Kimberly-Clark Corp., Atlanta, GA) moistened with ethanol.

The tube now is firmly grasped halfway between the particle and one end of the tube with a pair of flat-tipped steel forceps. The broad contact of the forceps acts as a heat sink on the side of the tube, in addition to supporting it. The tube is heated with a microflame (from a modified alcohol lamp or a gas microburner) a short distance from the particle on the side away from the forcepts. The tube is slowly moved so that the particle is directly over the small flame. The tube is watched carefully and moved quickly out of the flame as soon as a cloudiness is observed on the upper surface of the tube. The tube now must be supported in the air and not placed on a surface (which would quickly cool the underside and thus cause the sublimate to rapidly condense as small crystals on the bottom surface of the tube) until it is cool to the touch. If the pigments from the paint sublime, they will crystallize on the upper surface of the tube on both sides of the particle. Depending on the pigments involved, the best formed crystals may be found on the side away from the forceps (usually the better formed, large crystals because the temperature differential between the paint particle and crystallization surface is small, and the crystals grow more slowly) or closest to them (normally the crystals which grow rapidly and thus smaller as their vapors hit the cold region formed by the heat sinking action of the forceps). The charred residue will remain at the bottom center of the tube, and polymer pyroivzates will normally condense beyond the region of the tube where the sublimates crystallize.

Results and Discussion

The pigment crystals frequently take some time to form (allow at least 5 minutes). Their distribution can be observed under the stereomicroscope, but they should be observed under the polarizing microscope, where their characteristics, color, and optical properties all can be studied and compared. Regions of different colors and different crystal habits are frequently observed which often are polymorphs of the pigments caused by the process of sublimation. They will not prevent identification, but the analyst must be aware of this possibility when analyzing them.

This procedure should always be applied to the known paint first (because it is normally available in quantity) to determine if the technique provides useful additional information in a specific situation. When crystals are obtained, they may be identified by IR microspectroscopy. The glass tube is scored in the region of the sublimates and then snapped apart. In some instances, it is necessary to crush the tube to provide easy access to the underside of the tubing to which the crystals cling. The sublimates are individually scraped off with a sharpened tungsten needle and are smeared

COMING EVENTS

✓ First Wed. of Each Month in '96: **New Strategies & Tactics in Image Analysis.** Iowa City, IA. Dr. J.K. Beddow, (319)337-2427, Fax: (319)337-2474.

✓ **Materials TEM Specimen Preparation Workshops.** (AMC Group). Scottsdale, AZ. Dr. Farhad Shaapur: (602)949-4203, Fax: (602)473-9421
Nov. 18/20 '96: Basic Ultramicrotomy
Nov. 21/22 '96: Advanced Ultramicrotomy

✓ **Orientation Imaging Microscopy Workshops** (TexSEM Labs), Provo, UT. (801)344-8990, Fax: (801)344-8997.
Feb. 24/28 '97
June 23-27 '97
Sept. 29/Oct. 3 '97

✓ **Marine Biological Laboratory Courses** Woods Hole, MA:
May 8/16 '97: Analytical & Quantative Light Microscopy
May 20/27 '97: Microinjection Techniques in Cell Biology
Oct. 8/16 '97: Optical Microscopy & Imanging in the Biomedical Sciences.
Carol Hamel: (508)289-7401, eMail: admissions@mbl.edu

✓ Dec. 2/6 '96: **Symposium on Materials Issues in Art and Archaeology V.** (Smithsonian Inst.) Boston, MA. Pamela Vandiver: (301)238-3700, Fax: (301)238-3709.

✓ Dec. 4/6 '96: **26th Annual Conference of the Microscopy Society of Southern Africa.** Durban, South Africa Dr. Fiona Graham, +27-31-260-2174, Fax: +27-31-261-6550.

✓ Dec. 12/13 '96: **Joint Meeting of the Belgian and Dutch Societies for Microscopy.** Gent. Nick Schryers: http://www.ruca.ua.ac.be/"BVM_SBM/progr_net.html

✓ Jan. 8/11 '97: **Atomic Structure of Interfaces Winter Workshop** (Arizona State Univ.) Tempe, AZ. Sharon Willison: (602)965-4424, Fax: (602)965-9004

✓ February 8/14 '97: **Photonics West '97.** (SPIE). San Jose, CA. Marilyn Gorsuch: (360)676-3290, Fax: (360)647-1445.

✓ February 24/28 '97: **LIM Academy: Course in Orientation Imaging Microscopy.** (TSL). Klaus Behnert: (801)344-8990, Fax: (801)344-8997/

✓ March 16/21 '97: **PITTCON '97** - Atlanta, GA. (412)825-3220, Fax: (412)825-3224.

✓ March 31 - April 4 '97: **Workshop on Specimen Preparation for TEM of Materials - IV.** (MRS Spring Meeting). San Francisco, CA. Scott Walck: (513)255-5791, Fax: (513)255-9019.

✓ March 31 - April 4 '97: **Materials Reliability in Microelectronics VII.** (MRS Spring Meeting). San Francisco, CA. Robert Keller, (303)497-7651, Fax: (303)497-5030.

✓ April 4/6 '97: **16th Southern Biomedical Engineering Conference.** (Mississippi State Univ. & Univ. of Mississippi Medical Ctr.) Biloxi, MI. Dr. Joel D. Bumgardner: (601)325-3282, Fax: (601)325-3853.

✓ April 19/22 '97: **SCANNING '97** (FAMS, Inc.) Monterey, CA. Mary K. Sullivan, (201)818-1010, Fax: (201)818-0086

✓ April 27 - May 1 '97: **19th International Conference on Cement Microscopy.** Cincinnati, OH. Louis Jany: (610)261-4429, Fax: (610)261-4430.

✓ May 10/15 '97: **30th Anniversary Scanning Microscopy and Cells and Materials 1997 Meeting.** (Scanning Microscopy International). Chicago, IL. (847)524-6677, Fax: (847)985-6698.

✓ May 19/23 & 26/30 '97: **PASEM 97 SEM Short Course.** (Univ. of Maryland). College Park, MD. Tim Maugel: (301)405-6898, Fax: (301)314-9358.

✓ June 4/7 '97: **24th Annual Meeting of the Microscopical Society of Canada.** Edmonton. Ray Egerton: (403)492-5095, Fax: (403)492-0714.

LEHIGH UNIVERSITY MICROSCOPY COURSES:

✓ June 9/13 '97: SEM and X-ray Microanalysis

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Bethelem, PA. David B. Williams, (610)758-5133, Fax: (610)758-4244.

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✓ June 9/14 '97: **ACHEM 97** - International Meeting on Chemical Engineering, Environmental Protection and Biotechnology. Frankfurt am Main. +49(69)7564-280, Fax: +49(69)7564-201.

✓ June 23/27 '97: **13th Annual Short Course on Molecular Microspectroscopy.** (Miami University) Oxford, OH. (513)529-2874, Fax: (513)529-7284

✓ July 6/9 '97: **CRYO '97 - Low Temperature Microscopy and Analysis.** (Royal Microscopical Society). Univ. of York, RMS: +44(0)1865 248768, Fax: +44(0)1865 791237

over a small area of a polished salt plate. The crystals may be flattened by pressing with the corner of a slide or square coverslip to even out the crystals for spectroscopy. In this way, spectra can be collected easily. We have tried collecting sublimates directly on IR transparent media, but we have not been satisfied with the results. The IR spectra obtained in this manner have been compared directly with collected spectra such as those in the *Atlas of Polymer and Plastic Analysis* (Hummel and Scholl 1978). ■

Hummel, D.O. and Scholl, F. *Atlas of Polymer and Plastic Analysis*, 2nd ed. 3 vols. VCH Publishers, Deerfield Beach, FL, 1978.

Suzuki, E.M. and Marshall, W.P. *In situ* identification of some organic pigments used in yellow, orange, and red nonmetallic automobile finishes using infrared spectroscopy, *Crime Laboratory Digest* (1996) 23:20-21.