The PAINTINGS SPECIALTY GROUP ANNUAL VOLUME 3 1990

THE AMERICAN INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

THE

PAINTINGS SPECIALTY GROUP ANNUAL

VOLUME THREE

Papers presented at the Eighteenth Annual Meeting of the American Institute for Conservation in Richmond, Virginia

> Compiled by Christine Daulton

> > 1990

The Paintings Specialty Group Annual is published by the Paintings Specialty Group (PSG) of the American Institute for Conservation of Historic and Artistic Works.

Responsibility for the methods and/or materials described herein rests solely with the contributors and these should not be considered official statements of the Paintings Specialty Group or the American Institute of Conservation.

The Paintings Specialty Group is an approved division of the American Institute for Conservation of historic and Artistic Works (AIC) but does not necessarily represent AIC policies or opinions.

The Paintings Specialty Group Annual is distributed to members of the Paintings Specialty Group. Additional copies may be purchased from the American Institute for Conservation of Historic and Artistic Works, 1400 16th Street N.W., Suite 340, Washington, D.C. 20036.

The Paintings Specialty Group Annual has been printed offset on 60# Gladfelder's Supple, a recycled/acid-free paper made by the Gladfelder Paper Company and adhesive bound by the Mennonite Publishing House Herald Press, Scottdale, Pennsylvania.

TABLE OF CONTENTS

Condition, Change, and Complexity: New Interpretations of Albert Pinkham Ryder's Paintings by Ingrid C. Alexander, Jacqueline S. Olin, Roland H. Cunningham, and Yu-Tarng Cheng	1
STUDIO TIPS II - 1990: A Session of Brief Contributions for the Paintings Specialty Group by James Bernstein, Steven Prins, Martine Barras, Margaret Contompasis, James Hamm, and Jill Norton Sterrett	9
The Treatment of a Water-Damaged Painting by William P. Brown	22
Condition, Change, and Complexity: The Media of Albert Pinkham Ryder by David Erhardt, David von Endt, and Jia-sun Tsang	28
Maerten van Hemskerck's <i>Panoramic Landscape</i> <i>With the Rape of Helen:</i> Preliminary Report on the Analysis and Treatment by E. Melanie Gifford	36
To Clean or Not to Clean: The Analysis and Treatment of an Early 20th Century Painting by Susan Lake and Jia-sun Tsang	41
The Extractable Components of Oil Paint Films by Jia-sun Tsang and David Erhardt	45
When Trees in Blossom Becomes Winter: Problems in Treating a Reworked Painting by Ernest Lawson by Serena Urry	51
A Radioisotopic Assay for the Direct Measurement of Residual Detersive Materials on a Paint Film by Richard C. Wolbers	60

GUIDELINES FOR AUTHORS

- 1. The Annual is a compilation of papers presented at the Paintings Specialty Group Session at the Annual Conference of the AIC. The Annual is designed to be an informal publication whose primary function is to fulfill the needs of its immediate membership. It is a forum for the dissemination of ideas and information, whether of a formative or a conclusive nature.
- 2. The Annual is a non-juried publication. Papers will not be edited by the compiler.
- 3. Papers should be submitted camera-ready.
- 4. Margins should be one-inch on all sides.
- 5. Type should be letter-quality or better. Dot matrix printers should be avoided if possible.
- 6. Copy should be single-spaced, with double-spacing between paragraphs.
- 7. Pages should be left unpaginated (they should be paginated in pencil on the verso of each sheet for clarity to the compiler).
- 8. The title and author's name should appear at the top of the first page (no title page), with the affiliation and/or the address of the author at the foot of the first page.
- 9. Authors are encouraged to submit illustrative material. The placement of figures or photographs should be clearly indicated, whether in the body of the text or at the end of the text, with appropriate captions or reference numbers. Authors are responsible for the layout of all illustrations, either by pasting up line-drawings or by marking the intended placement of photographs on the page with a box drawn in blue pencil. As a rule, only black and white photographs can be reproduced. These should be of reproduction quality. Black and white photographs from color slides are usually inadequate. Authors are encouraged to make good quality black and white photographs at the time of documentation. Photographs should be submitted separately from the text (not pasted-up). The one-inch margin on all sides should be maintained in the layout of the illustrations. There is no absolute limit on the number of photographs, but authors are encouraged to be judicious in their use of photographs. The compiler may request limitations when necessary.
- 10. Authors are responsible for the content and accuracy of their submissions and publication in the *Annual* does not constitute endorsement by the Paintings Specialty Group or by the American Institute for Conservation of Historic and Artistic Works.
- 11. Authors of papers whose scope is of general interest to the conservation community are encouraged to submit their articles to the Editor of the Journal of the American Institute for Conservation, 1400 16th Street N.W., Suite 340, Washington D.C. 20036. Authors of articles already published in the *Annual* which have been well received and have stimulated further discussion should also consider submitting them to the Journal.

FOREWORD

In this third volume of the Paintings Specialty Group Annual some small but important changes have been made. While it remains a non-juried anthology of papers presented at the Paintings Specialty Group session at the Annual Conference of the AIC, an effort has been made to make this publication a better reference source for our members and others interested in this field. Thus, the papers used for both text and cover are acid-free and the cover is resin coated to reduce wear. Title and volume now appear on the spine of the publication and guidelines for authors are included. This latter addition will, we hope, enable authors to better prepare for the annual meeting and insure an earlier publication date than we have yet been able to achieve. While we feel it is important that all our members benefit from the information presented at the Annual Meeting, we do not seek to compete with the Journal of the American Institute for Conservation. We encourage all our authors to continue submitting their material to the Journal.

I would like to thank all the contributors to this volume and to the members of the Book and Paper Group whose very professional *Annual* provided the inspiration for our own improvements. I would also like to offer a special thanks to Mr. Glenn Millslagle of the Mennonite Publishing House for his assistance and advice and to Jay Krueger for his suggestions and support.

Christine Daulton December 1990.

CONDITION, CHANGE AND COMPLEXITY: NEW INTERPRETATIONS OF ALBERT PINKHAM RYDER'S PAINTINGS

Ingrid C. Alexander, Jacqueline S. Olin, Roland H. Cunningham, Yu-Tarng Cheng

Albert Pinkham Ryder is considered by many to be the first modern American painter and his experimental working methods have generated a great deal of commentary in the literature. For example, an artist friend criticized him for adding wax to his paintings, to which Ryder supposedly replied, " I only used one candle."

Jonah, in the collection of the National Museum of American Art, is one of Ryder's most important works (fig. 1).¹ Begun in the 1880's, a period that saw the creation of his most significant pieces, Jonah represents a major departure from the early landscapes and points to a period when Ryder preferred dense color and glazes. The painting is also a prime example of the sort of transformation some of his canvases underwent. Also, one of the most significant discoveries in the technical study of Jonah is a portrait beneath the painting.

Ryder worked nearly 10 years on <u>Jonah</u> constantly enriching and seeking the desired balance between color and form. He said, "Art is long. The artist must buckle himself with infinite patience."² Ryder appeared to have had infinite patience while reworking and was unconcerned with how long his revisions took.

His obsessive reworking is responsible, in part, for the degradation in so many of his works.

*Conservation Analytical Laboratory, Smithsonian Institution, Washington, D.C. 20560

Some of the changes in Jonah are documented in an engraving made by Elbridge Kingsley and published in 1890.³ The sea is calm. The boat has a mast and a tattered sail. The rayonnant around God's head is broad and imposing. In Ryder's new interpretation of the scene, passages of thick color dominate the upper portion of the painting, particularly around God's head. The rayonnant has been intensified with strong strokes of color and is more stylized.

Autoradiography has provided valuable information concerning the changes in Ryder's paintings as well as the substructure and the characteristics of his brushwork. To date, 20 paintings have been examined by this method.

In the autoradiograph of Jonah, there are the typical jots and dabs of paint applied spontaneously that are visible in many autoradiographs of his paintings (fig. 2). The 5th autoradiograph, in the series of 12, is taken 3 hours after activation. The film is in contact with the painting for 3 hours and dominated by the activity of manganese, associated with umber. The autoradiograph also captures Ryder's expressionist handling of paint, considered so revolutionary at the time. Ryder defines the contour of the boat with a broad sweeping stroke. Traces of the mast of the boat are still visible. The frenzied, multi-directional brushwork corresponds to areas of revision. A later autoradiograph, no. 11 (2 weeks after activation), shows the expansive aureole (fig. 3). The antimony-rich area, associated with Naples yellow, is painted in a thick, dry application.

The discovery of a portrait of a woman under <u>Jonah</u> was certainly a surprise. She is in a three-quarter position at a 90° angle to the picture plane in the bow of the boat. A cross-section of a sample from this area shows evidence of the painting beneath. The lower ground is the commercially prepared one consisting of zinc white + barium sulphate. Dark lines of pigment correspond to the portrait. Above this, the dirt of years has settled in. Ryder applied a layer of lead white to block out the portrait and proceed with Jonah. There is also a hint of the red priming below the area of white sea foam which is primarily made up of lead white with hints of chrome yellow.

We encountered a number of pentimenti in several paintings examined. In the painting, In the Stable, also from the National Museum of American Art, there are shifts in the positioning of the legs of the white horse and the head of the brown horse (fig. 4). Ryder appears to painstakingly seek the greater impact as the two horses glance at one another. Also, a major change was made. In the x-ray radiograph, a groom is seen sweeping between the two horses. The 4th autoradiograph shows that Ryder once painted him carrying a feed bag before deciding to paint the figure out of the composition. A variety of paint handling is visible in this autoradiograph. Carefully applied, striated strokes are used in the foreground and in the background. The artist has also adopted a broad and rapid brushstroke to define the contours of the white horse.

The autoradiograph also provides a view of the cracking. We know that the painting was dark and cracking shortly after it was finished. When William Macbeth purchased the painting in 1911, Ryder strongly protested his desire to have it restored, fearing the color effects he had strived for, would be damaged.⁴ The deep browns of this painting, where the cracking is concentrated, were areas once believed to contain bitumen. Analysis has shown there is no bitumen present. The cause of the extensive cracking is related rather to Ryder's painting thickly. Also, his experimental methods of

paint application contributed to the deterioration seen in so many of his paintings. Jonah and In the Stable exemplify Ryder's particular use of color. The artist often used a red priming in selected areas to impart the rich warm tones he preferred. He used a restricted palette of traditional earth colors.

A cross-section from <u>In the Stable</u>, prepared from a sample of the rooster's head, shows one of the types of layering that we have discovered (fig. 5). Thin, regular layers of paint above a thin zinc white ground. There are several layers of red which vary in color. Some red lake has been added to intensify the haematite red of the undercolor.

A cross-section from Jonah, on the other hand, reveals indeed that Ryder used wet-into-wet painting. The sample is taken from a figure in the boat. There is a thick layer of paint composed of umber, Prussian blue and chrome yellow. There is a blending and juxtaposing of the blue and yellow to create a green color. He rarely used a green pigment to create his greens.

In conclusion, the technical studies have revealed a conventional palette used in an unconventional fashion, a technique of application that runs the gamut from careful layering to spontaneous wet-into-wet techniques. There is evidence of preparatory sketches in umber, quite bold and rapid, to define the initial ideas in a composition. He often returned with a very small brush to work over details important to him. Ryder then would rework and revise sometimes for years. His experimental approach led to the creation of some remarkably innovative paintings at the turn of the century.

NOTES

- 1. Elizabeth Broun, <u>Albert Pinkham Ryder</u>, Washington, 1989, 235-238.
- 2. Albert P. Ryder, "Paragraphs from the Studio of a Recluse," <u>Broadway Magazine</u>, 14 (September, 1905), 10-11.
- 3. de Kay, Charles, [Henry Eckford, pseud.], "A Modern Colorist." <u>Century</u> <u>Magazine</u>, 40 (June, 1890), 256.
- 4. Ryder to Macbeth, 6 November, 1911, Macbeth Gallery Papers, Archives of American Art.



fig. 1. Jonah, National Museum of American Art, Smithsonian Institution, Washington, D.C.



fig. 2. Jonah, autoradiograph 5, Conservation Analytical Laboratory, Smithsonian Institution, Washington, D.C.



fig. 3. Jonah, autoradiograph 11, Conservation Analytical Laboratory



fig. 4. In the Stable, autoradiograph 4, Conservation Analytical Laboratory



fig. 5. cross-section from In the Stable, photographed at 110x

STUDIO TIPS II - 1990 A Session of Brief Contributions for the Paintings Specialty Group

James Bernstein, Session Chair, Conservator in Private Practice, San Francisco, CA.

Steven Prins, Conservator in Private Practice, Santa Fe, NM.
Martine Barras, Conservator, Conservation Analytical Laboratory, Suitland, MD.
Margaret Contompasis, Graduate Student and James Hamm, Associate Professor, Art Conservation Program, Buffalo State College, Buffalo, NY.
Jill Norton Sterrett, Paper Conservator, San Francisco Museum of Modern Art.

Just when you thought it was safe to return to the studio, it was time for STUDIO TIPS II, the sequel. Never the final word but hopefully better than no word at all, these sessions are where colleagues let down their guard and reveal what really goes on behind those studio doors. So, if you enjoyed last year's "LUST FOR TIPS", and thought maybe that it was "GOODBYE, MR. TIPS", get set, you're sure to enjoy this session. Regretfully, the highlights of the presentations, namely the funny slides, could not be included in <u>Postprints</u>. You will have to return next year to catch the humorous visuals and anecdotes!

Conservation Slide Labeling

We've all been surrounded by mountains of slides ready to be labeled. This labeling system, using individual index moulding stamps, makes the inevitable chore both neat and time efficient.

While you can choose specific phrases that are most often used in your studio, there is a certain stock set of phrases used in conservation photodocumentation. Such a set includes the following:

Before Treatment	During Treatment	
Before Inpainting	Partially Cleaned	
Detail:	Detail of Damage	
Edge Detail	Raking Light	
Specular Light	Ultraviolet	
X-Radiograph	Former Restoration	

After Treatment Reverse Detail of Media Transmitted Light Infrared Signature/Inscription

The procedure for using the stamps is fairly self-explanatory. After slides are organised on a light box, simply stamp the appropriate phrase or phrases on the margins of the slide mount. It should be noted that most stamp inks will give best results on cardboard mounts.

Custom labeling stamps are available through most local stamp manufacturers. When ording stamps, choose a font in either 10 or 12 point. Using either of these point sizes, all of the above phrases will fit on a two inch slide mount. As shown on the next page, up to three phrases can be stamped on each of the wider margins of the mount.



Date and pricing stamps (available in most stationery stores) are useful for stamping an artwork's job number and/or registration number. The red projection dot is easily inserted at the lower left corner of the mount, using the eraser on the end of a new pencil as a stamp.

While there will still be some amount of handwritten information to include on each slide, labeling stamps make an effective and efficient way to keep your slide library orderly.

Jill Norton Sterrett

Magnetized Photo Labeling System

This system, presented at last year's "Studio Tips", is being described in this year's <u>PSG Postprints</u>. The underlying concept is to include as much clearly legible labeling in the documentary photos as is possible at the time they are taken. This insures accurate identification and labeling at any time in the future.

Items to consider including in photographs are:

Conservator Job #	Accession #	Date of Photo
Owner	Artist	Subject
Grey Scale	Color Scale	Rule Scale
Raking Light Scale		

For this purpose, I like the Magna Chart® magnetic labeling system. The Magna Visuals Company manufactures a wide variety of magnetized letters, numbers, words (e.g., months, days), symbols, continuous write-on/wipe off ribbons, markers and self adhesive tapes, in a variety of colors and sizes. With these products one can produce customized photo labeling (and work flow charts) to suit preferences and needs. Self-adhesive magnet strips can be adhered to the backside of color, grey, and rule scales; Flat bar plaques can be cut to any length to write pertinent data upon (using removeable marking pens); and individually cast letters and numbers can be slid into magnetized lengths of track for use throughout to document each stage of treatment. For instance, at the beginning of a treatment I assemble a nameplate bar with the client's name and the artwork job #. This plaque is retained on a work board and used for each photodocumentary stage of the conservation treatment.

The magnetized I.D. items can be used on plates of smooth steel sheeting that are secured to the top or bottom bar of the photo easel. For pieces not in use, a wall mounted magnet board such as those offered by Magna Visual or a home-made wall plate facilitates ready visibility and easy access. To make one's own custom easel or wall plates, I use galvanized metal sheeting (available from hardware stores) which is cut to size, smoothed with files (to remove corner and edge burrs), cleaned with steel wool and detergent (to roughen and degrease the surface), and then rinsed and wiped dry. The sheet metal is then sprayed with Krylon High Heat Black Enamel Spray Paint (for barbeques and auto engines), also available from hardware stores. After the paint has dried for several hours, the enamel is "baked" onto the metal by placing the sheet in a vented oven, under infrared lamps, or by using a hot air gun. Obviously, the painting and heating stages have to be done outdoors or in a well ventillated and safe environment (such as in a spray booth). The resulting easel and wall plates are tough, smooth, and egg-shell matte, with finishes that hold up incredibly well to years of use.

On my photo easel, I have attached a plate along the bottom that measures $30'' \times 3 1/2''$. This provides plenty of room for whatever labeling is needed.

For undersize pictures or for edge or corner detail shots, I recommend making a selection of "mini-plates". These are rectangles of sheet metal (e.g. 4" x 6") that are bent into a " — " shape, with offset bends that vary from 1/4" (for thin panels) to 1-3/4" deep. These are finished black as described above. The plates can then be slid behind paintings, with the face part holding the magnetic letters flush with the front plane of the artwork. Tiny pin-sized holes can be punched or drilled into the sides or back faces of these plates to enable push-pinning to the sides of an easel, a supporting foam board (hidden behind the artwork), or inobtrusive locations on the stretcher reverse or edge.

I recommend the pre-spaced white letters and numbers on black backgrounds: Days (#MH-37: 1 thru 31 White on Black, $7/8" \times 7/8"$); Months (#MH-17: JAN-DEC White on Black, $1" \times 2"$); Letters (#PMA-21, 3/4") and Numbers (PMN-21, 3/4"); and the corresponding Magna Plate Letter and Number Holder bars (MPC-23: $7/8 \times 57/8"$, MPC-24: $7/8 \times 77/8"$, MPC-25: $7/8 \times 97/8"$). You will need several sets of the letters, numbers and holder plates if you wish to keep working assemblies of Client and Job # headings. For a full description of the Magna Chart Magnetic Visual Control Systems request a catalog from: Magna Visual Inc., 9400 Watson road, St. Louis, MO 63126-1596. Tel. (314) 843-9000 or (800) 622-6273.

James Bernstein

New pHep+ Pen with Automatic Temperature Compensation

Hanna Instruments now offers an improved "electronic Paper" pH pen, that features automatic temperature compensation for relatively quick and easy pH readings of aqueous working solutions such as detergent mixtures or resin soaps. The pen is Model # 00624-20, white in color (not to be confused with the lesser model, without temperature compensation, which is red), available from Markson Science Inc., 10201 S. 51st Street, Pheoniz, AZ, 85044, Tel. (800) 528-5114. Approximate cost: \$50.

James Bernstein

Wet Silicone Release Paper

For use in setting down flaking and cleavage, keep a roll of silicone release paper in a jar of water (a small proportion of ethanol (2-5%) can be added as surfactant. To use, simply cut off a piece of the size required, blot with paper towel to remove surface water, and use as you would any release film with a warm tacking iron. The presence of the water in the paper support does not effect the release properties of the silicone coating in the various papers I have used in this manner. The heat of the tacking iron drives the moisture out of the paper and through the silicone coating to the work surface. By helping to plasticize/relax the paint and ground, the moisture facilitates flattening of cupped and tented paint at lower temperatures than might otherwise be necessary. This is especially useful with synthetic emulsions/ resins used as heat-seal/hot-melt adhesives. As always, care must be taken not to damage impasto (a cushioning layer should be used where appropriate) and blanching may occur in some paint and varnish layers, so testing is always required. I prefer the double coated silicon release paper from SEAL Co. It is available in rolls as follows: #929 (26" x 20 yds); # 905 (34" x 30 yds); # 934 (42" x 30 yds) and # 986 (50" x 35 yds).

Steven Prins

Filler Additive

Last year Jim Bernstein noted that he adds a small amount of acrylic gesso to Polyfix or other vinyl filling putty to give it greater opacity and whiteness. I have adapted a similar approach, but for different reasons. I generally add Golden's Titan Buff acrylic paint to commerical vinyl putty, to create a warm, off-white filler. The addition of the acrylic not only modifies the color; it gives the hardened putty better finishing properties. It reduces the fills sensitivity to water (proportionately to the acrylic added) and it makes the filling material easier to tool. Other acrylic colors can be added to emulate the color of tinted grounds or imprimatura. One important caution to consider: as more acrylic is added to the vinyl putty, the resulting fills will be increasingly less soluble in water and will require increased amounts of aromatic hydrocarbons for removal.

Steven Prins

WilsonArt® Backing Panels

Last year, Jay Krueger introduced WilsonArt® Phenolic Resin laminates ("Formica®like" material) as a semi-rigid interlayer for linings. This material is also available without the colored/textured surface. The backing material is thinner (30mil), lighter, and free of the melamine finishing layer used in the printing process. It is however slightly more susceptible to dimensional changes from wetting and high humidity. This has not proven to be a problem wih paintings of modest to moderate size (up to 40 x 40 inches). Some distortions, however, are apparent in the full sheets. Each sheet should be thoroughly sealed with a size, such as Acryloid B-72.

Recently, we have had success in fabricating supports for oversized paintings from this material. A laminate is prepared from two layers, each pieced together to the appropriate dimensions, with the seams offset in each layer to prevent deformations along the joins. The seams are then filled with epoxy and the 'panel' treated as any other interlayer in a lining.

Grinding Colors for Inpainting

Hand grinding of dry pigments for inpainting is laborious, time consuming, messy, and often the results are less than satisfactory. In studios where fairly large amounts of color are used the following alternative may prove very useful. For small studios or individual practitioners, obtaining access to the equipment described below can be a real blessing. I am referring to jar-rolling mills, manufactured by several companies in the U.S. and also available from scientific supply houses.

Instead of the ceramic jars intended for use on such mills, small cylindrical glass jars (2-4 oz.) are used. Pigment, medium and diluent are introduced to the jar, along with cylindrical burundum grinding medium of the proper size. The pigment/medium proportions may be estimated from wetting parameters available in paint industry literature, and can be adjusted as necessary after initial grinding and dispersion. Better too little medium than too much if a full bodied paint with good covering properties is to be obtained

The jars are banded in groups of seven, six outer jars around a center jar. These bundles are then stacked and bound together in corrugated cardboard. In this manner as many as 42 colors may be ground in a single session on most single tier mills. Grinding can be done as long as necessary/desired with virtually no effort. Just turn on the machine; turn it off when it is done. It is a good idea to band colors of similar grinding and dispersive characteristics together so that difficult pigments can be conveniently left on for a longer time.

Before use for color, it is a good idea to work the interior of each jar with the grinding cylinders and some corrundum grinding powder to reduce interior irregularities which might leave pockets of unground pigment; this also roughens the polished glass to make a better grinding surface. Fisher Scientific provides a single tier mill for around \$600. They also carry the burundum medium in two sizes. These materials are also available from the Paul O. Abbe Co., 139 Center Ave., Little Falls, New Jersey 07424. The jars are best obtained from a local packaging supplier. Gustav Berger once told me that he simply uses the jars in which the pigments (I recall that he used Holbein's) were provided.

Steven Prins

Tube Colors for Inpainting

The variety of pigments and quality with which they are ground and dispersed makes artist colors very attractive for restoration. But oil colors should not be used, as the medium present is well known to discolor and cross-link. Blotting on paper, a common practice, is not sufficient to reduce the oil content to safe levels. This is evidenced by the simple fact that the colors left on their blotters will quickly form a horny skin of polymerized paint. The solution is to extract the oil with an excess of solvent and decant it from the pigment. This is done in a small jar. Xylenes are the solvent of choice as they are compatible with virtually every medium likely to be used by conservators. Squeeze a volume of paint in a jar, add 4-5 volumes of xylenes, stir well and shake vigorously, let stand for several days, then decant off the excess solvent. In the case of mixed colors, the various components may separate dring the extraction process, particulalry if they vary in density. These will have to be remixed, by stirring or with a knife on a stone, after removal of the excess solvent. A second

washing can be done, but at this point the amount of residual medium in the pigment is very small.

Keep the jars well sealed with sufficient xylenes to cover the pigment. In time the pigment will settle into a firm cake on the bottom of the jar. To use, scoop out a little color, place it onto a blotter, and remove it to the palette for mixture with the medium of your choice. If only one medium is used, you may prefer to introduce it to the jar after decanting of excess xylenes, mix thoroughly (use of a roller mill is again helpful), and keep well sealed until used.

Example: One of the special colors shown in presentation slides was a genuine **Naples yellow** from Becker's of Stockholm. Genuine lead-antimonate keeps its true color when used to scumble over darker tones, without the livery discoloration seen in common substitutes composed of cadmium yellow and earth pigments. Little known in the United States, Becker's purports to produce a fine line of traditional oil colors.

The extraction process is also useful with watercolors for the preparation of pigments for various aqueous media, cellulose gums, tempera emulsions, etc. Water will extract media from watercolors or gouaches in a similar process to produce well ground, dispersed pigments for use in aqueous media, ie. cellulose gums, tempera emulsions, etc. Again, a little color will go a long way if properly cared for. Steven Prins

New Pigs on the Block

Two of Europe's fine color houses are now distributing dry pigments in the United States: Sennelier and Oude Holland. The Oude Holland pigments are especially attractive in their antique-style apothecary jars. They are also made by traditional methods and carefully ground to preserve the optimum color characterisitcs of each pigment. Look for these colors at art suppliers in your region.

Can anyone explain why neither Lefranc & Bourgeois nor Maimeri offer Prussian blue in their 'Restoration'' palettes???

And if only someone would produce orpiment and realgar. Well, someone does! Kremer of Germany has opened a retail outlet in Manhattan. A great source for all sorts of art/conservation materials, they offer pigments (dry and dispersed in water), natural and synthetic resins, gums, and even two grades of sturgeon glue. They still prepare rare pigments such as orpiment, realgar and lapis lazuli in dry powders. Kremer is located at 61 East 3rd Street, New York, NY 10003. Tel. (212) 995-5556; FAX (212) 995-5616.

Steven Prins

Gold Finger

Conservator Carolyn Tallent relates an inexpensive alternative to gold powders, used by her and Denise Domergue in the Conservation of Paintings, Ltd. studio in Santa Monica, California. The procedure is to extract the titanium coated mica flakes used in Liquitex® (or other proprietary) Acrylic Irridescent Gold and Silver colors. The pigment is fairly easy to extract. Simply dissolve a blob of the wet paint in a jar of water and allow the flakes to settle out. Pour off the water and re-suspend the pigment in fresh water. Repeat this until the water appears clear. Let the water evaporate and the dry flakes can then be used as pigment easily mixed with other colors in the resin of your choice.

Carolyn Tallent

[Ed. note - see the **Painting Specialty Group Postprints 1989** "Studio Tips" for the manufacturer sources of the Mearl and Afflair irridescent dry pigments.]

Epoxy Mends with REN 306

For those who use epoxy mends, as initially described by Gustave Berger, I have found that REN 306, a castable epoxy resin formulated by Ciba-Geigy as a structural adhesive for wood and adapted to the conservation of wooden panels some time ago by Barbara Heller and Andrea Rothe, makes an excellent adhesive for canvas repairs.

The damaged area is prepared as with any mend, locally flattening deformations of the support, realigning threads, etc. The threads are then lightly sized with B-72 (I prefer it in ethanol, about 3-5%). A temporary band-aid of BEVA® 371 Film is attached to the reverse of the canvas with a warm tacking iron. This acts as a dam to restrict the flow of the epoxy. If a suction plate is available, it can be used to keep the system in plane while the mend is effected. I simply press a piece of 10 mil mylar onto the BEVA film, which generally adheres well without heat. When the painted surface is satisfactorily aligned the epoxy is laid in from the front of the painting. Working time is about 20 minutes. After 5-6 hours, the excess REN is cut away with a scalpel and the surface of the paint is cleared with xylenes. At this point, if the mend is not satisfactory it can be reversed and the procedure repeated. Otherwise, the area is left under flat weights for at least 24 hours, until the epoxy has hardened.

With acrylic surfaces, which will not allow the use of xylenes, the BEVA Film is adhered to the painted surface and the mend effected from the reverse. Such mends are not entirely reversible, but they make sound repairs which are less likely to deform with time and environmental changes than any other system of which I know.

Steven Prins

Microcrystalline Wax for Lining Adhesive

Walnut Hill Enterprises manufactures a white, microcrystalline wax (W-155) with a melting point of about 155°F which makes an excellent lining adhesive without the addition of gums and/or resins. A highly refined petroleum byproduct formulated as a hot-melt laminate adhesive, it is more stable and poses less risk of deleterious effects on paint, ground and canvas than wax-resins. From my experience it provides equally good adhesion, remains flexible, and has a non-tacky surface at room temperature. Avialable from: Walnut Hill Enterprises, Inc., P.O. Box 599, Bristol, PA 19007. Steven Prins

Commercial Encaustics for Wax-resin Fills.

R & F Encaustics, composed of purified beeswax, Damar resin, and pure, high quality pigments, offer a convenient starting material for conservators who use tinted wax-resin filler materials. They are available in a fairly broad range of colors based on a traditional palette. They can be easily mixed together on a warm surface to effect a wide variety of colors and values. Most ground colors can be matched with the earth colors available, and black and white. Dry pigments can also be added to expand the available palette. As they have not been analyzed and tested, we have only begun using them on a limited basis until more information becomes available from the manufacturer. But they seem to have pretty good working properties. In bulk they are hard and have a dry, non-tacky surface that carves very well. In thin layers they exhibit remarkable flexibility, yet are firm enough to carve as well as model. In warm weather, however, they may remain too soft to polish. R & F is located at P.O. Box 248, Rifton, NY 12471, Tel. (914) 384-6403. If you cannot find their encaustics in an art store near you, they can also be ordered by mail from Artisan of Santa Fe, 717 Canyon Road, Santa Fe, NM 87501.

Steven Prins

Design Modification for Pomerantz Stretcher

In adapting Louis Pomerantz's stretcher design to my own needs, I have replaced the original hex-nut used to adjust tension with Tite-joint screw mechanisms. This simplifies production. Additionally, the adjustment of tension does not require an open-end wrench of the correct size; a nail or metal rod will do as well as the tools provided by the manufacturer.

Steven Prins

Glass Solution Jars

Square tablet jars, featured in Richmond, are "just right" in every way. They have wide mouths, a good height-to-width ratio $(3 1/2" \times 1 3/8")$, and hold 80ml. or 2 3/4 ounces of solution. They are fitted with leak-proof polyseal (polyethylene cone) caps and because they are square, they store compactly and hold more material than round jars of the same proportion. When mounted snugly in a "u" shaped wooden block or rack, these jars become operational with one-hand as they do not spin when the lid is screwed off and on. They are small enough for test solution blocks and large enough for working solutions or on-site kit use as well. Conservation Materials, Ltd. now makes these jars available to conservators in a convenient 20 count pack (Stock # 3609-020 @ \$13.50 per pack): 1165 Marietta Way, Sparks, NV 89431 Tel. (702) 331-0582.

P.S. - clearly readable I.D. labels for solutions or powders can be generated on a computer and printed directly onto self-adhesive label pages, such as the $1'' \times 3''$ labels used for mailing addresses.

James Bernstein

New in the Kitchen: Houseware Products for Studio Use

Bamboo Skewer Swabs

Carrie Ann Calay reminds conservators that bamboo barbeque skewers make great swab sticks for aqueous solutions, since bamboo swells less than wood making it easier to remove and change the cotton head. For solvents, hardwood dowels are recommended as the wood grips the cotton better and the solvent has less tendency to wick up the stick than as with bamboo.

Carrie Ann Calay

MiniPolyethylene Seal Ware, or Who Left the Polyfix® Uncovered?

Japanese grocery markets and houseware stores have fascinating selections of kitchen gadgetry and accessories. Seek out the mini polyethylene seal ware that comes in numerous shapes and sizes, including many much smaller than available in American markets. In addition to being excellent for storing wads of Wasabi (green chili horseradish paste, which loses its kick anyhow when it is stored...) these mini "Tupper"-type wares are perfect for keeping fresh working quantities of Polyfix® filling putty or favorite studio-made mixes. For best results fill the container to its capacity (to reduce the airspace, thus extending the lifespan of the putty). For additional humidification, cut off a small piece of sponge, moisten and tape to the inside of the lid.

James Bernstein

Mini Hot Plate

The Salton "Hot Spot" Beverage Warmer, Model MW-1, designed for keeping a mug of coffee warm, is a perky mini hot plate for warming gelatin glue or other solutions where one only needs to keep the solution warm, not boiling. This item, sold in kitchen and houseware stores for \$20 or less, makes a wonderful studio gift for a conservation colleague. The low-profile warmer with a 3- 1/4" heating surface provides less chance of beaker accidents than with tall profile industrial models that often overheat and seem potentially hazardous. It is fitted with a power indicating pilot light and a cord line switch. I wouldn't be without mine (thank you, Carrie Ann Calay) and I think other conservators would find it ideal as well.

James Bernstein

T-Fal Saucier "Cook and Stir"

There is no need to stand at a hotplate and stir, when the T-Fal "Cook and Stir" is available to do the job. This motorized sauce maker, invented to cook and stir sauces in the kitchen, is ideal for cooking starch pastes, cellulose gums, animal glues or other aqueous solutions. It features a 26 oz. teflon lined bowl, a continuous-stirring plastic blade that scrapes thickened paste from the bottom and sides (turning the material back into the bowl and preventing scorching), and an adjustable heat setting (from no heat to high).

Two tips for the preparation of wheat starch paste are 1) pre-soak the starch in water overnight to produce a superior paste; and 2) make a dome lid of aluminum foil to cover the top of the "Cook and Stir". This prevents loss of moisture and keeps the heat level elevated during the cooking, producing a glassier starch.

Approximately \$75 in cost, the "Cook and Stir" is available from Bookmakers, 6001 66th Ave. Suite #101, Riverdale, MD 20737. Tel: (301) 459-3348; or Premier Center, 3450 Delaware Ave., Kenmore, NY 14217, Tel: (716) 877-3574.

James Bernstein

Making Your Own Spatulas

A great assortment of stainless steel spatulas may be found in kitchen and houseware sections of variety and hardware stores. These instruments, often longer, broader and more varied in shape then those available from conservation or woodworking tool suppliers, may be easily modified for use in painting conservation. Giant or 'Killer' spatulas are particularly helpful for large lining or mount removal projects (murals for example). Suitable spatulas are strong, stiff yet flexible, round-edged, and thin. Off-the-shelf spatulas are generally too thick and square at the edges and need to be customised. First, any sharp corners or points of the spatual are removed by filing. Next, one side (the top side) of the spatula is filed downward along the edges to produce a tapering effect. This keeps the cutting edge of the spatula downward, so the blade does not cut into the original (top) canvas or board.



Any blade roughness is then polished smooth with wet emery paper. The spatula edge will require periodic fine tuning and resharpening as it is used and becomes dull.

James Bernstein

Speedy Spatulas

Inspirational paper conservator Robert Futernick once showed me his slick trick for getting spatulas to fly. Simply apply a small amount of silicon fluid or spray to a cotton blotter and then periodically strop the spatula blade against the blotter surface while in the process of removing a lining, backing or mount. The spatula will glide along with noticeably improved speed and smoothness.

James Bernstein

Potential Treatment for Discolored Acrylic Emulsion Medium

We have been working on a project involving the research and treatment of a Robert Goodnough (1917 -) colorfield painting (1970) which shows a significant degree of yellow discoloration in the background field. Telephone conversations with the artist have indicated that he typically would coat his cotton duck canvas with Liquitex matte medium and then paint distinctive, scattered, hard-edge paint "islands" in acrylic pastel hues. These paint islands seemingly float in a sea of bare canvas, which has discolored irregularly and no longer reads properly.

The owner recalls that this problem was objectionable as early as the mid 1970's, indicating that the yellow discoloration had occurred fairly early in the life of the painting. The color of the Liquitex matte medium closely resembles deposits from cigarette smoke. Initial tests have indicated that, although cigarette smoke residue may have contributed somewhat to the present appearance of the painting, this is not the major cause for the discoloration.

Part of our research focus is on the cause for the rapid discoloration of the Liquitex acrylic medium. Attempts to reproduce this discoloration using mock-ups have been successful. Further testing is already planned to narrow the list of possible deleterious materials, but conversations with Mark Golden at Golden Artist Colors, Inc. have lead us to suspect a kind of negative interaction between the matting agent in the Liquitex and the original manufacturers sizing on the canvas.

Recalling that light bleaching was used successfully by Dr. F. C. Tahk in 1979* to enhance fire damaged oil based films, preliminary testing was undertaken to determine whether light bleaching would have application to acrylic resin based films as well. Tests were conducted on the fortunately wide and discolored tacking margins of the Goodnough painting, and on the beforementioned mock-ups. These tests have indicated that a reasonable degree of success can be expected from light bleaching for one to two weeks under fluorescent lamps. Equivalent real time exposure under ideal gallery conditions at levels of 200 lux, 8 hours/day, 5 days/week would be experienced by the painting after 3 - 6 years.

Some considerations which still need to be addressed are whether any fading of the pigmented paint "islands" would occur if the entire painting were to be light bleached, whether bleaching by fluorescent light would cause degradation of the canvas cellulose, and whether the bleached condition is stable, or if reversion is likely to occur.

If you know of any Robert Goodnough paintings, whether discolored or not, or know of other color field paintings where acrylic dispersions have been used to size bare canvas, we would very much like to hear from you.

Margaret Contompasis and James Hamm

A Wet Polishing Approach for a Stubborn Cleaning Problem

One of the casualties of the October 17, 1989 Loma Prieta Earthquake was damage to contemporary artworks on permanent display at the San Francisco International Airport. The large canvas triptych *Untitled* by Sam Francis, acrylic paint on white acrylic ground, was heavily soiled and stained when the adjacent suspended ceiling faulted and the automatic sprinklers went off, spraying sooty black liquid across the painting surface. Extensive study of the paint revealed that the deposit was extremely tenacious, and that a certain amount was lodged in the surface of the semi-porous ground, a large component of the overall design. The paint and ground films could withstand prolonged contact with water, however aqueous cleaning alone, even with elevated pH, could not remove the residual staining. Due to the large quantity of ground exposed, it was concluded that inpainting (or overpainting) of the stains, no matter how careful, would produce an unacceptable result that would be disturbing-ly obvious under the unforgiving airport illumination conditions.

To clean the ground effectively and with minimal alteration to the original, a wet polishing system was developed. Dilute aqueous detergents (Triton X-100, mixed with Super 10 detergent or traces of NH4OH), were mixed with a fine grade of polishing silica (obtained from a plastics fabricating firm). Methyl cellulose and carboxymethyl cellulose gums (2 to 4% solutions) were added for thickening and moisture retention. The resulting liquid paste could be applied with stiff bristle brushes (brights or toothbrushes) and worked to swell and release the stubborn carbon deposits. Recalling that the dentist cleans and polishes teeth with a similar wet abrasive paste applied with a circulating rubber tip, I thought, why not apply this technology to the Francis painting? The Koh-I-Noor Rapidiograph Cordless Erasing Machine, #2850 C, was found to be ideal for the job. It has a continuously variable speed motor, it is easy to maneuver (the unit may be used with or without a cord, and sits on its own recharging stand when not in use), and will work with over a dozen different types of 1/4" diameter eraser refills, manufactured by Koh-I-Noor, Eberhard-Faber ("Magic Rub"), and others.

For better accuracy, the 1/4 cylindrical eraser rods are first sharpened to a point in an electric pencil sharpener (this is a little tricky since the rods are somewhat limp). The cleaning mixture is applied to the stain to be cleaned, which is then carefully wet polished with the rotating rubber nib of the Koh-I-Noor. The pointed tip enables great control so that one can reach into dirt laden interstices or avoid selected paint boundaries. If continuing to work on a particularly stubborn spot, the area needs to be rewet regularly to minimize friction. After cleaning, residual detergent paste is rinsed away with deionized water.

The controlled, wet rubbing/polishing action of the electric eraser machine produced a remarkably successful result that salvaged the painting without compromising the structure. Although slight ghosts of stains were still discernable after cleaning, no inpainting was necessary. Solvent cleaning of the stains would have been disastrous, dissolving the gesso, driving the carbon further into the structure and leaving the surface matte and leached. There are probably many other applications in the conservation studio where this instrument can come in handy (for instance, in the removal of pressure sensitive tape adhesives). The Cordless/Rechargeable Eraser No. 2850C lists for \$83. and may be found at major art or drafting supply stores; or contact Koh-I-Noor Rapidiograph, Inc., Bloomsbury, NJ 08804. Tel: (908) 479-4124.

James Bernstein

Casting BEVA® 371 Adhesive for Transfer

The following is a technique for casting sheet films of BEVA 371[®], or other heat-activated adhesive, into sheets for preparation of lining canvases or other applications.

A solution of liquid BEVA® 371 (diluted 1:1, stock in xylenes), is carefully heated to 50° C and then brushed onto the silicone prepared surface of a silicone coated paper cut to the size of the lining canvas. When the Beva coating is dry (about 50 minutes later), place the BEVA covered paper face down onto the lining canvas and iron the silicone coated paper from the back. Let it cool. Once the surface is cool, peel off the silicone paper from the canvas and the BEVA film will be transfered to the lining canvas. The results are best when BEVA® 371 is brushed rather than rolled or flocked on the silicone coated paper.

The following advantages are noted:

This method does not saturate the fibers of the lining canvas and offers a "raw" aspect to the back of the relined canvas. It is less expensive than using the pre-prepared BEVA film. It also allows the conservator to play with different thicknesses rather than using the proprietary films which come in a given thickness. It also provides an alternative to flocking when no spray and exhasut facilities are available. Martine Barras.

[Ed. note: Due to the solvent toxicity and clean-up factors present when using quantities of liquid Beva® 371 or other solvent-based adhesives, many conservators will find the possible higher cost of the proprietary films worth the expenditure. The uniformly cast films come attached to release paper in rolls 27" wide by 20' long. Individual sheets may be abutted to form larger expanses; more than one thickness of the film may be ironed onto the support (one layer at a time) to produce thicker films if desired. BEVA 371® film is available from Conservator's Products Co., P.O. Box 411, Chatham, N.J. 07928. (201) 927-4855.]

Don't forget: "Share a Tip ... Save a Painting"

We hope the above Studio Tips are helpful and that interest is high for STUDIO TIPS III, to take place in Albuquerque, New Mexico. Colleagues are encouraged to participate and to contact James Bernstein (415) 285-1658 or Steven Prins (505) 983-2528 with possible tips for the June 1991 program.

THE TREATMENT OF A WATER-DAMAGED PAINTING William P. Brown, Assistant Paintings Conservator North Carolina Museum of Art 2110 Blue Ridge Blvd., Raleigh, N.C. 27607

This presentation details the treatment chronology of a severely water-damaged painting in the collection of the North Carolina Museum of Art. The affected work, a landscaped entitled Mount Washington, Conway Valley, N.H., was painted in oil on canvas by William C. A. Frerichs in the late nineteenth century. The painting was treated in 1988-89 during my conservation internship at the North Carolina Museum of Art under the supervision of David Goist, chief conservator. The water damage occurred while the painting was on loan to a historic building. Water leaking from an air conditioning system ran down the back of the painting and was absorbed by the support structure. Subsequent shrinkage of the canvas caused severe cleavage of the paint film and partial delamination of the lining. Prior to the water damage the painting was in stable condition. The painting had been glue/paste-lined onto linen in 1972, before its accessioning by the North Carolina Museum of Art. The museum's treatment involved the use of controlled, elevated humidity and lateral tension to remedy the severely tented cleavage and to retain the previously stable lining.

The damage to the painting was extensive. All layers of the painting's structure were damaged at each site of water contact. Water had run down the back of the lining canvas in a vertical band, collecting in the space between the bottom stretcher member and the lining support. The space acted as a reservoir for the water, slowing its evaporation and eventually causing the glue/paste adhesive bond to swell and lose adhesive and cohesive Subsequently, the painting canvas detached from the strength. lining canvas in a three-inch band across the bottom. Since the original tacking edge had been removed in the 1972 lining, the bottom edge of the painting was unrestrained and severe vertical shrinkage of the canvas resulted, along the warp. The shrinkage caused waves of tented cleavage and blind cleavage primarily in the horizontal direction. In the sky and the midground foliage there was also swelling of the canvas and glue layers and localized contraction of the painting support. The contraction of the canvas in the midground and sky caused severe localized vertical tented cleavage and a corresponding bulge in the lining support.

Apparently the shrinkage was primarily in the original support and not in the lining canvas, as thread counts of the latter in damaged and undamaged areas were the same. Possibly the glue/paste counteracted the tendency of the water-saturated yarns of the lining canvas to contract. Also, the lining canvas was restrained by its attachment to the stretcher. The shrinkage of the painting's support along the bottom edge probably occurred rapidly once it was detached from the lining. Notably, in the sky where the paint has a high lead white content there is localized buckling, but not the severe tenting seen below. Possibly the tougher, thicker layer of lead white was able to restrain the contracting canvas without rupture, whereas the more thinly painted area below could not. To make matters worse, water that had run down the face of the painting caused a narrow band of blanching.

Several variables contributed to the severity of the damage. Obviously the large amount water was a major factor. The painting's tightly woven canvas is prone to shrinkage. Also the glue/paste-lining provided a thick hygroscopic layer which, although it may have reduced the shrinkage of the lining support, acted as a moisture poultice against the painting canvas, exacerbating the problem. The bottom half of the painting was especially vulnerable to cleavage due to a thin, brittle, preprimed ground and the artist's technique of thinly painted transparent shadow areas.

Treatment of the painting began in 1988, three years after the damage occurred. The canvas layers, where affected by moisture in the sky and midground, were well adhered, but some distortion remained. The bottom of the painting remained detached from the lining support, and had curled up. The paint layer was very fragile and the blanching remained.

The primary treatment objective was to stabilize the paint, ground, and support layers. This required setting down the severely tented cleavage, a difficult task due to the canvas shrinkage and fragile paint condition. Also, we needed to either replace the lining or retain it; both choices presented potential hazards. Because the lining was relatively new, the adhesion between canvas layers was still very strong. Separating the two would jeopardize the fragile paint layer and removing the lining adhesive would weaken the fabric support. The lining canvas, except where detached at the bottom, was in good condition. Therefore if possible, we hoped to retain the lining and reattach it. In considering the cleavage problem, testing with Stoddards solvent indicated that infusion with wax, such as would be done in a "burnt finger" technique, might alter the tonal balance of The artist had used a thinly applied dark umber the painting. underpainting on a thin white ground to produce a luminous effect in the foliage and middle ground. Because of the complexity of the situation it was necessary to pursue an open-ended course of treatment.

Our proposed treatment called for the painting to be placed under lateral tension and in elevated humidification in an attempt to partially regain the shrinkage and distortion in the support canvases, thereby providing enough space for the tented cleavage to be set back into plane. Then we would reattach the lining canvas at the bottom. The extent of reversible shrinkage of the original canvas was unknown. Also unknown was the response of the lining canvas and adhesive to the proposed treatment. All subsequent treatment steps would require that the painting be kept face up due to the fragility of the tented paint. A facing was avoided to allow for manipulation of the cleavage with a tacking iron and also so we could observe the tenting and surface of the painting for any movement or change.

The treatment involved first a local application of BEVA 371 diluted with petroleum benzine to areas of cleavage. Where possible the cleavage was set down with a tacking iron, used with the aid of a binocular microscope. BEVA 371 was also brushed onto the inside surface of the lining canvas where detached at the bottom in preparation for reattachment at a later stage. sheet of silicon-coated Mylar was placed between the canvases to prevent premature adhesion of the two. Next the stretcher was removed from the painting, again with the paint face up, and then the tacking edges of the lining support were flattened. The glue/paste-infused tacking edges were very responsive to heat and moisture, becoming pliable without contracting. Examination of the painting canvas indicated some penetration of glue/paste adhesive into the fabric. The painting canvas was tested for its reaction to high humidity by holding a damp blotter next to the The canvas became flexible, but did not contract. canvas.

For moisture treatments at the North Carolina Museum of Art we generally use a relative humidity not exceeding 75% at 110°F. Due to the complex structure of the painting, and our uncertainty about how it would react to elevated humidity, we decided to first equilibrate the structure to a lower humidity in the 65% RH range at room temperature. A prolonged exposure time would be necessary for the humidity to uniformly permeate all the layers of the painting, after which we could assess the results before proceeding.

In the first stage of the humidification treatment the painting was put under tension in a double stretcher set-up and placed inside a humidity chamber. The chamber was constructed of plastic-coated Fome-Cor sides with a Mylar top. Beakers of water placed in the corners of the chamber were sufficient to maintain a relative humidity of approximately 65% at room temperature.

The double stretcher set-up provided tension to both the lining canvas and the painting canvas where it was detached at the bottom. A Terytex #39 polyester woven fabric strip lining was sewn to the tacking margins of the lining canvas with cotton thread and then secured to the outer Lascaux stretcher. A Hollytex 3261 strip was adhered with BEVA 371 film to the bottom flap of the painting canvas and then secured to the bottom member of the inner Lascaux stretcher. Terytex #39 and Hollytex 3261 were chosen for their strength and unresponsiveness to moisture. In this system the two stretchers could be keyed out independently as needed. The canvases were stretched finger tight.

After two days 65% RH was reached and maintained. The painting and lining canvases became flexible and slack as the glue size and glue/paste swelled. The slackening was keyed out in small increments for both the lining support and the bottom flap of the painting. The gentle expansion of the stretcher was continued once a day or as slack developed until a constant tension was maintained. This required nine days. Most of the expansion gained in the humidification step apparently went to reducing planar distortions such as flattening the tacking edges of the lining canvas and reducing planar distortions overall in the painting and in the detached flap. Most significantly, the vertical area of tented cleavage did appear to have lowered. Additional manipulation with the heated spatula was effective in setting down more of the cleavage. At this stage our options were still open.

This initial success encouraged us to continue with additional treatment. After the prolonged humidity step was completed the Fome-Cor enclosure was removed. The painting was placed onto the vacuum hot table and the Nascor-Versa Vac control box set-up to provide a controlled elevated humidity environment. Dartek cast nylon film was used to contain the humidity pumped in by the Versa Vac in an air bubble above the painting. The temperature was raised to 110°F and the humidity maintained at approximately 75% RH. We hoped, the additional heat and higher humidity would further relax the painting. Additional plasticity in the paint film and support would allow for increased mobility and slippage within the yarns of the canvas. After one hour and forty-five minutes additional slack in the canvas was taken up by gentle expansion of the stretcher. The medium-rich paint layers were markedly softened by the high humidity and the cleavage could be gently coaxed down with a heated spatula. After two hours the humidity was turned off and a vacuum was drawn to In order to reattach the lining canvas and evacuate moisture. painting canvas at the bottom, the hot table temperature was increased to 150°F to achieve a nap bond. After an initial vacuum of two inches H_2O was drawn, the vacuum was increased to ten inches H_2O . While the painting was under low vacuum, additional manipulation of the cleavage with the heated spatula further reduced the cleavage. The hot table temperature was reduced to room temperature under vacuum. The painting, still attached by its Terytex #39 strip lining to the Lascaux stretcher, was set aside to equilibrate to room temperature and humidity.

The overall results of the humidity treatment were acceptable. The vertical area of tented cleavage was not completely set down into plane, but the tenting was significantly reduced and the bulge in the lining support opposite the tenting was eliminated. Some minimal overlap remained in a few spots where there had been horizontal bands of cleavage, but most of the cleavage set down nicely. The bulging area in the sky caused by the swollen glue/paste was almost completely removed, possibly indicating that the glue/paste had reformed.

The narrow band of blanching was diminished after varnish

removal, but remained especially disfiguring in the sky and mountains. The blanching was eliminated in the landscape by several local applications of Acryloid B-72, 10% in toluene plus a small percentage of dimethylformamide. The varnish was applied with a small brush to the band of blanching only, allowed to dry, and then the excess was removed from the surface with toluene. Saturation of the blanching in the sky required several local applications of Laropol K-80, 5% in a solvent mixture of 40% xylene, 50% petroleum benzine, and 10% dimethylformamide. An overall isolating coat of Acryloid B-72 was applied before inpainting.

The open-ended treatment approach outlined in this presentation was largely successful in stabilizing a very serious condition. By using controlled, elevated humidity an infusion of the canvas with additional adhesive was avoided and a previously stable lining system retained, leaving treatment option open for the future.

I would like to thank the staff of the North Carolina Museum of Art, Conservation Department for their support.

Selected Bibliography

- Berger, G. A., and W. H. Russell. "Investigations into the Reactions of Plastic Materials to Environmental Changes. Part I. The Mechanics of the Decay of Paint Films." Studies in Conservation 31 (1986): 49-64.
- Bressee, R. Randall. "General Effects of Ageing on Textiles." Journal of the American Institute for Conservation 25 (1986): 39-48.
- Hedley, Gerry. "Relative Humidity and the Stress/Strain Response of Canvas Paintings: Uniaxial Measurements of Naturally Aged Samples." <u>Studies in Conservation</u> 33 (1988): 133-148.
- Mecklenberg, Marion F. "Some Aspects of the Mechanical Behavior of Fabric Supported Paintings." Report to the Smithsonian Institution (1982).
- Wilmot, Robert. "A Severe Case of Tenting on a Water Damaged Painting at the Australian War Memorial, Canberra: an Investigation and Treatment." ICCM Bulletin (Sept.-Dec. 1981): 16-35.

Condition, Change, and Complexity: The Media of Albert Pinkham Ryder

David Erhardt, David von Endt and Jia-sun Tsang, Conservation Analytical Laboratory, Smithsonian Institution

The painter Albert Pinkham Ryder, active in the late nineteenth and early twentieth centuries, played a major role in the development of American painting and has been the subject of much controversy and discussion. This paper is concerned primarily with the types of materials he used in his paintings. At the turn of the century most artists primarily used commercially available products. Ryder, however, was not typical. His living and working habits were unusual. During the last period of his career, he felt that he had lost the inspiration necessary to start any new works, and instead continually reworked his existing paintings. The general impression is that his eccentricities extended to his choice of materials, and the present deteriorated condition of many of his paintings is usually attributed to a combination of both unorthodox techniques and materials. Ryder's own writings, first-hand accounts of his work, and previous studies of his paintings all support this view to some extent. For instance, Ryder is known to have worked wet into wet, often laying down and admixing numerous layers of paint without letting any of them dry properly. This mixing of layers of differing degrees of dryness and ratios of pigment to oil might alone account for the problems seen in his paintings. He is also reported to have used fast drying mixtures, possibly including gums or glue, to coat still wet oil paint layers so that he could paint over them. Other reports of his techniques may be less reliable. For instance, Ryder is commonly thought to have used bitumen in his painting. This is because many of his paintings have darkened, flowed, or contain extremely thick areas which consist of a cracked upper surface over a much softer lower layer. Ryder's work was often forged even during his lifetime. It is thought that forgers of Ryder's time attributed the look of his paintings to the use of bitumen and may have used it in their forgeries, contributing to the confusion. Basic questions which might be answered by a study of the materials of his paintings are: Did Ryder use unorthodox materials? If so, did the use of these materials contribute to the present condition of his paintings? If not, what did cause these problems?

The analysis for bitumen is not simple, but is possible¹. One of the complicating factors is that not all bitumens are the same. Bitumen is an asphaltic material which can vary just as any other petroleum deposit². Figure 1 presents gas chromatographic separations of the methylene chloride soluble portions of samples of three historic commercial bitumen pigments from the collections of the Freer Gallery. The pigments are from the suppliers Weber, Roberson, and Winsor & Newton. As can be seen in the Figure, the chromatographic pattern of each one is distinct, and in fact we would be able to distinguish among the pigments if they were found in a painting. Despite the differences, though, they do have in common a number of compounds in the region labelled "Hopanes" in Figure 1. A

number of peaks in this region are due to derivatives of hopane, which are microbial alteration products of triterpenes found in many plant resins. This class of compounds, the hopanes, is in fact diagnostic for bitumen. If bitumen is present in a paint sample in any reasonable quantity, such as a pigment would be, then these peaks should appear in the analysis of an extract of the paint sample. Figure 2 is the gas chromatographic analysis of the solvent extract of a paint sample from a brown area of Ryder's "Moonlight". There is no indication of bitumen, as there are no peaks at all in the area where the hopanes would appear. This is true even when using the more sensitive technique of combined gas chromatography/mass spectrometry and looking specifically for masses characteristic of the hopanes¹. The sample size and sensitivity of the method are not limiting factors, because free fatty acids which have been extracted from the paint sample are easily detected. Normally, free fatty acids constitute no more than a few percent of the total paint sample, much less than any pigment would. If bitumen were present, it would have given rise in the area labelled "Hopanes" to peaks of at least detectible size. The same result, the absence of bitumen, was found for many samples from numerous brown areas from several different paintings of Ryder's. Lighter, yellow areas also were analyzed with the same results.

The question of whether Ryder added organic materials other than bitumen to the drying oils of his paints has been dealt with before. For instance, Svoboda and van Vooren used microchemical techniques, including fluorescent staining of crosssections, to identify layers containing protein, wax, resin, and non-drying oils in Ryder's paintings (they also reported finding no bitumen)³. In this work, we have used infrared analysis, high pressure liquid chromatography (HPLC), gas chromatography, and gas chromatography/mass spectrometry to study bulk samples of Ryder's paintings. While bulk analysis does not indicate which layers contain which materials, it does provide a better indication of the relative amounts of materials used. Any additives other than drying oils would have had to have been present in reasonable and detectable quantities to have caused the severe problems seen in Ryder's works.

HPLC analysis demonstrated the presence of minor amounts of glue in some samples, though always in paintings which had been glue lined. Figure 3 presents the results of infrared analyses of several samples from the painting "Desdemona", which had <u>not</u> been lined. Comparison of the infrared spectra of the paint samples with the infrared spectrum of egg white points out the absence in the paint samples of amide peaks at around 1650, 1630, and 1540cm⁻¹ which have been shown, even in aged samples, to be diagnostic for protein mixed in oil media⁴. If there is protein in these samples, it is either in an extremely thin layer or very dilute compared to the oil which is responsible for the peaks which are present.

Beeswax was identified in samples from some paintings, although when found it seemed to be associated with those which had been wax lined. For instance, media from the painting "Moonlight" does not seem to contain wax. The chromatogram
in Figure 2 contains no indication of the series of hydrocarbons normally found in beeswax which would appear in the same area as the hopanes.

Also, our analyses indicated that there were only small, if any, amounts of di- or triterpenoid resins such as damar or mastic in the media. Thus, if Ryder indeed used "resins" in his media as was rumored they may have been volatile essential oils rather than the higher molecular weight varnish type resins. Our analyses revealed the presence of an oil- rather than resin-based varnish on the painting "Woman with a Staghound". If this is original, then it may indicate that Ryder's use of resins was limited even in surface coatings.

Figure 4 is the result of gas chromatographic analysis of the total fatty acids in a sample from Ryder's "In the Stable". This chromatogram demonstrates that Ryder used drying oils, because of the presence of both residual unsaturated fatty acids and azelaic acid, which is an oxidative degradation product of the unsaturated acids. The amount of azelaic acid is less than in many older paintings. This is probably due not only to the relatively young age of the painting but also to the protective thickness of the paint film. The exact type of oil used in a paint medium normally would be determined by the ratio of palmitic acid to stearic acid.⁵ In the case of samples from Ryder's paintings which we have analyzed, the type of oil used usually is not certain. In paintings which were wax lined, the normal presence of fatty acids in the wax (beeswax) interferes with the determination. In most of the other samples which were analyzed, the ratio of palmitic acid to stearic acid (p:s) was in the range 2.0 to 2.9. In Figure 4, it is 2.8. Of the oils classically used for artists' paints, this is outside the range of linseed oil (1.2 to 1.9), and more in the range typical of walnut oil $(2.0 \text{ to } 3.0)^5$. It is unlikely, however, that so many, if any at all, of Ryder's paints were made from walnut oil, which is more expensive and which if used is typically reserved for lighter colors. If Ryder's paints were of linseed oil, which is more likely, the fatty acid composition which was found may indicate the addition of another oil with a higher p:s ratio. The analysis of such a mixture would yield a p:s ratio which would be a weighted average of that for the two oils. For instance, the addition of an oil such as olive oil, which has a higher p:s ratio and is non-drying, would raise the overall p:s ratio. The ratios higher than those typical of linseed oil argue against the addition of some other materials Ryder is reported to have used, such as tallow or stearin wax. Such materials have low p:s ratios and would have lowered, rather than raised, the p:s ratio of the mix. In a few samples, however, p:s ratios as low as 1.1:1 were found, which would argue for the addition of animal fats such as tallow or stearin wax, which is used in cheap candles. (Ryder is reported to have added candle wax to his paints.) There seemed to be no correlation, however, between the analytical results and the condition of the painting or section of painting which had been sampled.

In general, then, these analyses coupled with previous findings³ indicate that while Ryder did use nonorthodox materials and may have mixed in other materials with his paints, the amounts of these other materials were in general small enough to make them hard to detect by bulk analysis. Where detectable amounts were found, as in the possible addition of non-drying oils, they did not necessarily correlate with the condition of the painting. Much of the blame for the condition of Ryder's paintings, therefore, must be put on the way he used his materials rather than what he used. For instance, the darkening of his paintings is most likely due to the application of numerous layers of oil glazes. Working wet into wet, layering paints which contain different proportions of pigment, using layers of fast-drying materials, and overpainting paint layers which have not properly dried are other practices which are discouraged precisely because they can result in the types of cracking and degradation seen in Ryder's paintings. Ryder was obsessive at these practices, often overpainting and reworking paintings over periods of years. In conclusion, the present condition of Ryder's paintings is more the result of his techniques than of his materials.

References

- 1. Raymond White, "Brown and black organic glazes, pigments and paints", <u>National Gallery Technical Bulletin</u> 10(1986), pp. 58-71.
- 2. A. G. Douglas and P. J. Grantham, "Fingerprint gas chromatography in the analysis of some native bitumens, asphalts, and related substances", in: <u>Advances in Organic Geochemistry 1973</u>, B. Tissot and F. Bienner, eds., Editions Technip, Paris 1974, pp. 261-276.
- 3. Shelley A. Svoboda and Camilla J. van Vooren, "An investigation of Albert Pinkham Ryder's painting materials and techniques with additional research on forgeries", <u>Postprints of Papers Presented at the Seventeenth Annual</u> <u>Meeting, Cincinnati, Ohio, May 31-June 4, 1989</u>, Paintings Specialty Group, American Institute for Conservation, pp. 36-50.
- 4. Raymond J. Meilunas, James G. Bentsen, and Arthur Steinberg, "Analysis of aged paint binders by FTIR spectroscopy", <u>Studies in Conservation</u> <u>35</u>(1990), pp. 33-51.
- 5. John S. Mills, "The gas chromatographic examination of paint media. Part I. Fatty acid composition and identification of dried oil films", <u>Studies in</u> <u>Conservation</u>, <u>11</u>(1966), pp. 92-107.

Figure 1.

Gas chromatographic separation of three commercial bitumen pigments

Weber bitumen Hopanes ſ ala la da m Roberson bitumen Winsor & Newton bitumen



Figure 3.

Comparison of infrared spectra of egg yolk. and of samples from Ryder's "Desdemona"



Figure 4.





MAERTEN VAN HEEMSKERCK'S PANORAMIC LANDSCAPE WITH THE RAPE OF HELEN: PRELIMINARY REPORT ON THE ANALYSIS AND TREATMENT

E. Melanie Gifford*

Maerten van Heemskerck's <u>Panoramic Landscape with the</u> <u>Rape of Helen</u> (fig. 1), is unusual for the work of a northern artist of this period, both for its large format and its canvas support. The attribution of this atypical work was established in 1943 by the discovery that the work was dated 1535 and inscribed with both Heemskerck's signature and monogram. A technical examination of the painting that was undertaken in preparation for further conservation treatment gave new insights into this work's place in Heemskerck's oeuvre_and into the development of canvas painting in the north.²

Painted in Italy, the huge painting evokes the painter's trip to Rome early in his career between 1532 and 1536. The classical subject and the wealth of archaeological detail record Heemskerck's fascination with antiquity and the discoveries of Renaissance excavations. Technical examination has revealed that the painting also recorded Heemskerck's explorations into the use of Italian painting materials and techniques.

Early Netherlandish canvas paintings are rare. Paintings on canvas were not unknown before the 16th century both in Italy and the North, but canvas was frequently used for ephemeral decorations such as banners. While there seems to be some documentary evidence for the use of an oil medium on canvas in the North, 15th century guild regulations in the Netherlands reflected a policy of setting limits on canvas painters, including attempts to reserve the use of oil medium exclusively to panel painters. Virtually every surviving Netherlandish canvas painting of the 15th and early 16th centuries is a <u>tüchlein</u>: painted in glue distemper directly on a sized fine-weave fabric with no ground.

Italian painters, however, seem to have abandoned the $\frac{\text{tüchlein}}{\text{known}}$ technique by around 1500.⁵ Not only in Venice, well known for the early use of oil on canvas, but in Rome as well

Senior Conservator of Paintings, The Walters Art Gallery, 600 N. Charles St., Baltimore, MD 21201.

artists of the early 16th century turned to oil for canvas paintings. Though panels were still common as a painting support in Rome, the evidence of technical studies suggests that by the time Heemskerck reached Rome oil painting on canvas was not unusual, with some major works such as Raphael's Sistine Madonna executed in the technique.

Though Heemskerck's landscape is a canvas painting by a northern painter, in its technique it is more typical of Rome, where it was painted, than of the north. Instead of the fine canvas typical of a tüchlein, three sections of coarsely woven fabric were seamed together to make the support. While a tüchlein commonly has no ground, ' this fabric was prepared with a creamy-colored true gesso of gypsum toned with a small amount of earth color and bound with glue. This in turn was covered by an imprimatura of white lead also slightly toned with earth pigments. The handling of the paint ranges from thin washes to a moderate impasto typical of oil paint, and the palette is typical of an oil painting of the period. Analysis by gas chromatography/mass spectroscopy revealed that the paint medium is walnut oil, with a copper resinate used in green passages. A few details are reminiscent of tüchlein technique and may be features that Heemskerck, as a Northerner, routinely included in a canvas painting. The scalloped tacking edges of the canvas are intact and lie flat, suggesting that the canvas was originally laced into a strainer, and the edges of the image are delimited by a painted black line.

Very few canvas paintings by Heemskerck are known; since none but the Panoramic Landscape have been analyzed, no definite statement can be made on developments in his canvas painting technique. But he does seem to have used canvas predominately during his Italian sojourn. The three surviving canvas paintings date from his Italian stay,⁹ and documentary evidence confirms that he painted on canvas during these years. Karel van Mander recounts an episode in which an Italian acquaintance stole into Heemskerck's room and "cut two canvases out of their frames", ¹⁰ but later in his biography of Heemskerck van Mander refers only to panels. His choice of technique may have been influenced by the differing expectations of his patrons; by 1535 Italians may have perceived canvas as a support worthy of major commissions, while Netherlandish patrons may still have seen it as an inferior production.

The identification of the painting as a traditional oil painting rather than a <u>tüchlein</u> had important implications for the conservation treatment. A <u>tüchlein</u> has a characteristically matte texture that must be preserved during conservation treatment. Lining with a penetrating adhesive can irreparably darken the paint and stain the canvas, which is visible through the thin paint layers. A <u>tüchlein</u> should remain unvarnished, since a varnish also will saturate and severely darken the colors. As an oil painting the <u>Panoramic Landscape</u> did require some saturation of the colors, but since the absorbent ground was visible in thin passages throughout the painting, a penetrating lining adhesive was considered unsuitable. A discolored mastic varnish, older varnish residues, and repaint were removed with solvents. After the degraded paste lining was removed mechanically, the painting was lined to an acrylic fabric with Beva 371. It was lightly varnished with B72 in diethylbezene to even the color saturation, without obscuring the painting's characteristic texture.

Maerten van Heemskerck's <u>Panoramic Landscape with the</u> <u>Rape of Helen</u> appears to be the earliest Netherlandish canvas painting to date in which the use of an oil medium has been securely established. That Heemskerck used a coarse canvas primed with a gypsum gesso and painted in walnut oil suggests that the artist embraced not only the visual repertoire of Roman painting, but its materials as well. The varied handling of the paint from thin scumbles to rich copper resinate passages exploits the possibilities of oil paint on a textured support in a sophisticated way that is new to 16th century Dutch painting.

Notes

The Walters Art Gallery, Baltimore, MD, no. 37.656.
The Walters Art Gallery, Baltimore, MD, no. 37.656.

2. A limited number of paint cross sections were taken from the edges of existing paint losses and mounted for microscopic examination. The pigments were identified through polarized light examination of dispersed paint samples and through energy dispersive x-ray analysis using a Jeol electron microprobe. Myron Eugene Taylor, Director of the Electron Microscope Central Facility of the University of Maryland at College Park and Helaleh Maghsoudlou, Graduate Research Assistant, were, as always, most generous with their assistance in this analysis. Preliminary identification of the paint medium using visible light and ultravioletfluorescent biological stains was confirmed by gas chromatography/mass spectroscopy at the National Gallery, London. I am most grateful to Raymond White, Principal Scientific Officer for analyzing the samples and for his thoughtful interpretation of the results.

3. Diane Wolfthal, <u>The Beginnings of Netherlandish Canvas</u> Painting: 1400-1530, Cambridge, 1989: 26.

4. In Wolfthal, <u>Netherlandish Canvas Painting</u>, an oil medium seems even plausible in only a handful of the 111 paintings catalogued. Oil has not been identified by analysis in any of the paintings catalogued, and some earlier references in the literature to oil medium might represent the assumption that a canvas painting is always painted in oil.

5. Emil D. Bosshard, "Tüchleinmalerei - eine billige Ersatztechnik?" Zeitschrift für Kunstgeschichte 45 (1982): 31.

6. Karl Heinz Weber, "Die Sixtinische Madonna," <u>Maltechnik</u> Restauro 90, no. 4 (1984): 9.

7. Bosshard, 33. Wolfthal's remarks on grounds (Wolfthal: 25) are ambiguous, using the terms "sizing", "ground", and "preparatory layer" interchangeably. Several cited references to dark red grounds in early canvas paintings probably are mistaken readings of the appearance of the somewhat darkened canvas seen in paint losses.

8. The pigments identified include white lead, azurite, lead tin yellow, yellow lake, earths, vermilion, copper resinate green, charcoal black.

9. Besides the <u>Panoramic Landscape</u>, the <u>Venus and Mars</u> and the <u>Venus and Mars in the Forge of Vulcan</u>, both of 1536, are on canvas (see Rainald Grosshans, <u>Maerten van Heemskerck: die</u> <u>Gemälde</u>, Berlin [1980]: 119-124, plates 21-23).

Only two canvas paintings, both now lost, may date before Heemskerck's Italian trip. A <u>Man of Sorrows</u> on canvas, present location unknown, is recorded as being inscribed with an incomplete date that could be read as anything from 1525 to 1529, that is, before Heemskerck's Italian trip (see Ilja M. Veldman, <u>Maarten van Heemskerck and</u> <u>Dutch Humanism in the sixteenth century</u>, <u>Maarssen</u>, 1977: 26-27). A <u>Judah and Tamar</u> on canvas dated 1532, the year Heemskerck went to Rome, has been missing since 1945 (see Grosshans, <u>Maerten van Heemskerck</u>, Berlin [1980]: 105-6, plate 14).

10. Karel van Mander, <u>Het Schilder-Boeck</u>, Haarlem, 1604, translated in part in Wolfgang Stechow, <u>Northern Renaissance</u> <u>Art 1400-1600</u>, Evanston, Illinois, 1966: 46. Fig. 1 Maerten van Heemskerck, Panoramic Landscape with the Rape of Helen, signed and dated 1535. After treatment. The Walters Art Gallery, Baltimore, MD, no. 37.656.



TO CLEAN OF NOT TO CLEAN: THE ANALYSIS AND TREATMENT OF AN EARLY 20th-CENTURY PAINTING

By Susan Lake and Jia-sun Tsang*

In 1988 the Hirshhorn Museum and Sculpture Garden acquired a painting entitled <u>Capriccio Musicale (The Circus)</u> from the collection of Leigh Block of Chicago. Measuring almost four by five feet, it came to the museum with an attribution to the Italian genre painter Romano Rossini. Examination of the stylized signature and a portion of a buried inscribed label on the reverse eventually lead to the firm reattribution of the painting to Daniel Vladimir Baranoff-Rossiné.

Ukranian-born artist Baranoff-Rossiné (1888-1944) belonged to the generation of European avant-garde artists who pioneered in the development of abstract art.1 Originally trained as a painter in Tsarist Russia, he moved in 1910, at the age of 22, to Paris where he joined the vanguard Orphist circle of painters and poets led by Robert and Sonia Delaunay. In response to the stimulus of the Parisian art world, he developed a personal style of Cubo-Futurist painting.

After the February Revolution of 1917, Baranoff-Rossiné returned to his native Russia where he took part in the exuberent climate of artistic experimentation of the post-revolutionary Soviet Union, both exhibiting in progressive shows and serving as a faculty member for the Vkhutemus group in Moscow. In 1925, Baranoff-Rossiné left the Soviet Union to settle permanently in Paris. Much of his subsequent career was devoted to continued activity in painting and sculpture. He is believed to have been executed by the Gestapo sometime in 1944 during the German occupation of Paris.

While his paintings are relatively unknown, Baranoff-Rossiné has been recognized for his highly experimental constructed sculptural work, including such mixed-media pieces as <u>Symphonie</u> <u>No. 1</u>, 1913 (painted wood, cardboard, eggshells; collection of the Museum of Modern Art, New York). He is also known for his research on the correspondence between color and sound (also known as synaesthesia). As a result of this fascination, he designed in 1915 a "Piano Optophonique," which consisted of painted glass discs attached to a projector. The colored light projections were accompanied by musical performances on two electric pianos. <u>Capriccio Musicale</u> is dated 1912 and is a prime example of the Cubo-Futurist style of Baranoff-Rossiné's first Paris period of 1910-1917. In this work the artist has used a dynamic composition of faceted, Cubist planes and swirling colors, to capture the rhythmic movement of aerial trapeze artists who perform under spotlights to music. In style and composition, the painting had marked affinities with another major Cubo-Futurist painting by the artist entitled <u>La Forge</u>, 1911, which is in the Musee National d'Art Moderne, Paris.

European avant-garde artists of the early 20th century were very experimental in both their selection of materials and their use of techniques to achieve desired aesthetic effects. Little technical analysis has been done at the Hirshhorn on paintings of this period. The arrival of <u>Capriccio Musicale</u>, which was unlined and unvarnished, presented us with the opportunity to explore the techniques and identify the materials in an early 20th-century European painting that was in a relatively untouched state.

Initial examination suggested a rather unconventional painting technique. Solubility tests revealed some of the areas of paint to be soluble only in polar organic solvents. Other areas are very water soluble. Still others are so friable that rolling a dry swab over them brings up pigment particles.

Analysis of the painting layer structure confirmed that the painting is of mixed media.2 Over a lithopone and glue ground and a graphite underdrawing, the artist laid down thinly applied blocks of glue or gelatin bound paint. Superimposed over this initial design are more thickly elaborated alternating passages in oil and what may be gouache. Finally, over this design is a subtle pattern of spray-applied paint.

Cross-sections taken from water-soluble passages were stained with fluorochrome dyes and showed weak evidence of a protein binder.3 Analysis of microtomed sections with the Fourier-Transform Infrared (FT-IR) spectrometer produced an IR spectrum that confirmed the presence of a protein such as would be found in a glue or gelatin media.4

Curiously, not all the water soluble paint passages appear to have a protein binder. Analysis with gas-chromatography and mass spectrometry (GC-MS) indicated that some of these layers may have a gum binder such as would be found in gouache. However, due to the leaness of the paint, the peaks are very weak and the results are inconclusive. Cross-sections from the non water-soluble areas stained with a general lipid fluorochrome indicated the presence of a fatty acid such as would be found in an oil binding media. Analysis of a similar section on the GC-MS showed the palmitic/stearic acid ratio to lie between the expected figures for linseed oil.

The painting had initially entered the Conservation Lab for the repair of two small tears and for the removal of what was described as a heavy layer of surface dirt and grime. Analysis of this grime showed it to be, in addition to surface dirt, two distinct spray-applied layers. One, a fine evenly divided layer made up of small pigment particles. Where more heavily concentrated, these particles take the subtle shape of discs, rings, lines, and grids.

Over this layer is spattered aggregates of what looks like resinous beads. These beads are very water soluble and, while adhering to the lower layers, can be dislodged relatively easily with a dry brush. Examination with the polarized microscope of the particles that make up the beads showed them to be a mixture of opaque black and earth pigments. Staining of the binding media suggested a protein. Analysis with the GC-MS showed weak peaks for a gum, sugar-type material. Both results are really inconclusive due to the leaness of the paint and the small size of the samples.

While technical experimentation is characteristic of much vanguard art produced during the 20th century, the use of a spray technique before WWII is exceedingly rare. The most well known instance of an early spray technique in painting is a series of aerographs or air brush paintings completed between 1917 and 1919 by Man Ray.5 Baranoff-Rossiné's use of the spray technique, while not explored as fully, precedes Man Ray's by five years.

Analysis had confirmed what was suspected initially. The painting could not be safely cleaned. Analysis also supported what is generally acknowledged in treatment of modern and contemporary art. That is, that these paintings must be approached cautiously as they are often made with nontraditional materials or with traditional materials used unconventionally.

*Paintings Conservators, Hirshhorn Museum and Sculpture Garden and Conservation Analytical Laboratory, Smithsonian Institution, Washington, D.C.

NOTES

1. There is limited literature available on the artist. Dr. Judith Zilczer, Associate Curator of Paintings at the Hirshhorn, provided the information on the artist presented here.

2. All instrumental analysis of the paint samples was done at the Smithsonian Institution Conservation Analytical Laboratory.

3. The fluorescent staining technique used was that developed by Richard Wolbers, Associate Professor, Art Conservation Training Program, University of Delaware.

4. Meilunas, Raymond, James Bensten, and Arthur Steinberg, "Analysis of Aged Paint Binders by FTIR Spectroscopy," <u>Studies in</u> Conservation, vol. 35 (1990): pp. 33-51.

5. Foresta, Merry, et. al., <u>Perpetual Motif: The Art of Man</u> <u>Ray</u> (Washington, D.C.: National Museum of American Art, Smithsonian; New York: Abbeville Press, 1988).

The Extractable Components of Oil Paint Films

Jia-sun Tsang and David Erhardt, Conservation Analytical Laboratory, Smithsonian Institution

Introduction

It has been thirty years since the publication of <u>On Picture Varnishes and Their</u> <u>Solvents</u> by Robert Feller, Nathan Stolow, and Elizabeth H. Jones¹. Since then, there have been many papers and reports on solvent cleaning and its effects on oil paint films, but <u>On Picture Varnishes</u> remains the single best attempt at examining and explaining the various factors and effects of the solvent cleaning of oil paintings.

We have begun a project to examine the effects of solvents on oil films. The study includes measurements of many aspects of the chemistry, optics, and physical properties of paint films, and the changes induced by solvents. Leaching and changes in physical properties such as color, gloss, thickness, weight, and stressstrain relationships will be studied. Any changes will be correlated with the pigment, type of oil, age of the film, solvent, and method of exposure. The currently used guidelines for the choice of solvents used to clean paintings were developed to minimize drastic changes such as the swelling and dissolution of the paint film. We hope that data from the present project can be used to modify the guidelines so that effects such as changes in color, texture, and physical properties also can be minimized.

These studies will be conducted on both available aged samples and on samples which currently are being prepared. The new samples include paints prepared from various combinations of 44 historic pigments and eight types of oil. The oils include cold-pressed linseed oil, both as is and processed with acid, alkali, lead driers, and by heating. This set of samples prepared from a common set of starting ingredients will allow us to separate effects due to differences in pigment, and the type of oil and its processing. Until the freshly prepared samples are ready, we are conducting our initial studies on available five, ten, and fifty year old samples. These include films with lead white, vermilion, and raw sienna as pigments. One of the five year old samples contains a synthetic vermilion consisting of an azo dye with calcium carbonate filler.

Results

Initial studies of the types and amounts of material leached from paint films by soaking in various solvents have produced results which confirm Stolow's work and also demonstrate the effects of pigments and age. Free fatty acids and their degradation products were found in the extracts, and the amounts varied with the solvent, pigment, age of the film, and length and nature of solvent exposure. Films containing lead white, which catalyzes the polymerization of drying oils, generally yielded the smallest amount of extractable material, while the raw sienna films yielded the most. The effects of age were not clear, since the films of differing ages were not prepared identically. Four solvents, hexane, toluene, acetone, and ethanol, were used in these initial experiments. Of these four, acetone and toluene generally had the greatest effect.

Materials other than oil components also were extracted from the paint samples. Residues of turpentine which had originally been used to thin the fifty year old paint were detected. Materials such as paraffin wax and a synthetic dye adulterant which was present in a commercial pigment were extracted from other samples. The ease of extraction of such materials may make it particularly hard to choose suitable solvent cleaning systems for paint films which contain soluble additives. Such paints would include those which have wax or resin added to the oil, or the many modern paints which contain soluble synthetic dyes.

The changes in physical properties generally tended to correlate with the amounts of material which were extracted. Changes in thickness and weight generally were smallest in the lead white films and greatest in the raw sienna films. Changes in optical properties were less predictable. Lead white films were less bright after solvent exposure, vermilion films changed little, and raw sienna films were brighter. The loss of gloss was greatest in lead white films and least in raw sienna films. In general, changes in optical properties were much less sensitive to the type of solvent than other physical properties.

Paintings are exposed to solvents at times other than during cleaning. In fact, the most prolonged exposure of a painting to solvents may be during the application and drying of varnish films. Solvents in the varnish solution diffuse into the paint layers as well as evaporate from the surface of the varnish. Solvents which diffuse into the paint film may dissolve soluble components, diffuse back into the varnish layer, and leave the soluble components behind in the varnish as the solvent eventually reaches the surface of the varnish and evaporates. In essence, the applied varnish acts as a poultice in preventing the quick evaporation of the solvent and in providing a medium into which the solvent/solute mixture migrates and in which the solutes are left behind. This possibility is illustrated in Figure 1. Figure 1a is a gas chromatogram of scrapings from the very top of a varnish layer on a nineteenth(?) century landscape by an unknown artist. The chromatogram is typical for damar. Figure 1b is a chromatogram of the complete varnish layer, and 1c is of the entire varnish layer plus some paint removed by swabbing. Figure 1c obviously contains some extra peaks. These are due to free fatty acids in the paint film. What is interesting is that these extra peaks also are present to some extent in the lower varnish layer, but not at its surface. This can be seen more clearly in Figure 2, where the portions of the chromatograms where the fatty acids appear are expanded. There are no fatty acids detectable in the surface of the varnish layer (2a), indicating that the varnish contained only resin. Fatty acids are present in the sample which contained paint (2c). Fatty acids also are present in the sample of the entire varnish layer which did not contain paint (2b). The probable

explanation for this is as explained above. Varnish solvent diffused into the paint, dissolved fatty acids, and diffused back into the varnish layer with the dissolved acids. The fatty acids were carried only part way into the varnish and left behind as the solvent eventually diffused out of the varnish and evaporated.

We measured the physical changes in our sample paint films 72 hours after solvent exposures of 6 to 24 hours. Other experiments in our laboratory conducted by Marion Mecklenburg have addressed the dynamic changes that occur during solvent exposure. Figure 3 shows the changes in stress occurring in a stretched aged paint film as it is swabbed with solvent. We had expected to see a drop in the stress as the solvent softened the film and allowed it to relax. Instead, there is an almost instantaneous increase in stress, followed by a sharp drop and gradual return to pre-exposure levels. This sharp increase occurred with all solvents which were tested, and obviously occurred too quickly to be a phenomenon dependent on diffusion of the solvent into the paint layer. Temperature data collected in later experiments explained the phenomenon. In Figure 4, the surface temperature of the film is plotted along with the stress in the film. It can be seen that evaporative cooling of the solvent causes the restrained film to cool and to try to shrink, causing an increase in stress which mirrors the film's drop in temperature. Further experiments are planned to determine if the large increases in stress may damage paint films. Stress-strain measurements at low temperatures may show that the strength of paint films increases enough as the temperature drops to prevents damage to the film. Nevertheless, it appears that the evaporation rate of solvents may be a factor to consider when choosing solvents to clean paintings.

Conclusions

The results of these initial experiments indicate that it should be possible to improve the guidelines for the choice of solvent cleaning systems by considering factors other than just the swelling and dissolution of the film to be cleaned. These factors include the type of pigment and effects such as changes in optical properties. Other less obvious factors such as the evaporation rate of the solvent may play a larger role than thought previously. In addition, these experiments show that it is important to minimize the effects of exposure of the paint film to solvents during the application of varnish as well as during cleaning, and that the choice of solvents used to apply varnish films may be as critical as the choice of solvents used in cleaning.

Reference

1. Feller, Robert L., Stolow, Nathan, and Jones, Elizabeth H., On Picture Varnishes and Their Solvents, Intermuseum Conservation Association, Oberlin, Ohio (1959).

Figure 1. Gas chromatographic separation of components at three levels of varnish removal



Figure 2. Expansion of the sections where fatty acids appear in the chromatograms in Figure 1





Figure 3. Changes in stress in a restrained oil paint film caused by acetone swabbing

Figure 4. Changes in stress and temperature in a restrained oil paint film caused by acetone swabbing



When Trees in Blossom Becomes Winter:

Problems in Treating a Reworked Painting by Ernest Lawson

Serena Urry, Assistant Paintings Conservator, Conservation Services Lab, Detroit Institute of Arts, 5200 Woodward Avenue, Detroit, MI 48202

Good morning.

<u>Winter</u>, a large oil on canvas landscape by American painter, Ernest Lawson (1873-1939), was removed from storage at the Detroit Institute of Arts and sent to the Conservation Services Laboratory in order to prepare it for exhibition. Curatorial and conservation records noted that the painting had been purchased from the artist in 1923 and that it had been treated only once, in 1966, when it had been surfacecleaned and varnished with Rembrandt Picture Varnish. It now presented a grimy surface mottled grey and yellow. In spite of several areas of deep drying crackle, the painting was structurally sound. It seemed that the picture need only to be cleaned of its grime and discolored varnish in order to be installed. This assumption lasted only until the moment the painting was unframed.

The exposed edge of the stretcher revealed that the composition had been extensively reworked by the artist, while the painting was in a frame. Only the two patches of sky had not been altered. A sharply-defined strip of the paint around the painting's edges, one to two centimeters in width, such as might be covered by a rabbet, was noticeably thinner than the adjacent paint and matched it in neither color nor texture. The overlying brushstrokes were for the most part the violets, blues and whites of the sun-dappled snow in the scene. A suggestion of the colors in the painting before it was reworked could be seen through the overlying strokes, most noticeably in the trees and foreground landscape. These areas were warm light greens and, in the foliage, warm pinks, while the shadows were cool blue-violets.

Additional evidence that the painting had been reworked came with the discovery of a remnant of an exhibition label from the Carnegie Institute in Pittsburgh on the verso of the frame. On it were noted that the title of the painting was <u>Trees in Blossom</u> and that the owner was the artist, Ernest Lawson. The Carnegie Institute confirmed that a painting by Lawson entitled <u>Trees in Blossom</u> had been exhibited at the 14th Annual Exhibition of Painting in Pittsburgh in 1920. Another label on the verso of the frame was from the Daniel Gallery in New York and lists the title as <u>Winter</u>. The label is undated and does not note the owner. Though the price, \$3500, is the amount quoted by Lawson's dealer, Charles Daniel, when he wrote to the DIA in May 1923 while the painting was on view there in the Ninth Annual Exhibition of American Artists.

<u>Winter</u> is signed in thin green paint at the lower left. <u>Trees in Blossom</u> is also signed. At the lower right a second signature appears in violet under the snow. It's partially obscured.

Everything suggested that Lawson painted a picture he called <u>Trees in Blossom</u> sometime prior to 1920. (The Phillips Collection in Washington owns a painting of the same scene, entitled <u>May in Mountains</u>, with a signature and date of 1919. And indeed this is thought to be a view of Cornish, NH, where Lawson spent the summers of 1919 and 1920.) The fact that he signed <u>Trees in Blossom</u> suggests that he considered the composition finished, at least finished enough to send to the exhibit in Pittsburgh. Then, sometime during the next three years, when the painting was back in his studio, he changed the scene from spring to winter by applying the cool tones of <u>Winter</u> on top of Trees in Blossom.

There was a natural resin varnish on <u>Trees in Blossom</u>, which had become brittle and yellow. It had been applied rather unevenly. Some areas appeared to be more discolored than others, a difference which seemed to be due to the thickness of the varnish. The discolored varnish also showed through gaps and pits in the reworking. In many cases the reworking was comprised of microscopically thin brushstrokes lying on top of a deep puddle of discolored varnish. In a few areas the discolored varnish was a milky yellow-green as if some sort of wax, which had since discolored, had been added. Lawson was obliged, in one area at the lower right, to fill a loss with waxy putty before reworking. The fill had discolored and was clearly visible under the reworking. There was no evidence of a natural resin varnish on top of the reworking, though there did turn out to be some sort of coating, which I'll discuss later on.

Had the DIA not bought the painting directly from the 1923 show, it's possible that <u>Winter</u> might have undergone yet another transformation back in Lawson's studio. Lawson described his philosophy in an interview in 1932:

Color is my specialty in art. That's my special technique; experiment with color. I did it from the beginning...It affects me like music affects some persons - emotionally. I like to play with colors like a composer playing with counterpoint in music. It's sort of rhythmic proportion. You try one color scheme in a sort of contrapuntal fashion, and you get one effect. We don't actually copy nature in art. Nature merely suggests something to us, to which we add our own ideas. Impressions from nature are merely jumping off points for artistic creations.

In other words, while Lawson may have painted <u>Trees in Blossom</u> outdoors, in the springtime, he decided to experiment with the cool colors of snow on top of his vernal palette, "jumping off" from nature in the confines of his studio.

<u>Winter</u> is characterized by thick impasto everywhere. In raking light, the texture generally follows the forms in the composition, ranging from a smooth buttery surface to rough spikes of paint. For the most part it's the result of many thin layers of paint which make up both <u>Trees in Blossom</u> and <u>Winter</u>. Some of the brushstrokes appear to have been smoothed by hand, while small dabs of paint in the trees suggest the texture of the foliage. In the center mountain the paint has a stringy texture, as if Lawson had scraped the paint before reworking. Lawson described his technique during an account of studying under Alfred Sisley in Paris in the early 1890s: "I try

to get my whole canvas covered quickly before I put in any detail...All [Sisley] said was, after looking over the canvas and then taking in my appearance, 'Put more paint on your canvas and less on yourself.' He would not say that now for I occasionally overload and have to scrape some paint off."

As a result of Lawson's manipulation of paint in the reworking, not to mention the uneven application of varnish beneath, the boundaries between paint and varnish were virtually indistinguishable, even on a microscopic level. Equally apparent was the fact that we would not be able to thin the discolored natural resin varnish, using traditional solvent systems, without disturbing the reworking.

At this point of our examination we consulted with the curatorial department to discuss the treatment.

We decided to begin by removing the Rembrandt varnish from 1966, hoping that much of the mottling, which we believed at that time to be surface grime, would be removed as well. This mottling ranged from light to dark grey and appeared most often in the lower areas of the impasto. It effectively flattened the image and made the forms difficult to read.

The Rembrandt varnish was removed with xylene. It had yellowed slightly. And though a perceptible amount of surface grime was removed with it, unfortunately none of the dirt was in any way associated with the mottling. (In fact, these slides were taken after removal of the Rembrandt varnish.) Further testing of the mottling revealed that it was soluble in neither water nor organic solvents. Under the microscope it didn't appear as grime lying on the surface of the paint. It seemed more a part of the paint layer itself. We then thought it might be the result of staining from below, since Lawson also appeared to have used either varnish and/or some resinous medium in the execution of <u>Trees in Blossom</u>. Through drying cracks in the unreworked sky were visible small discrete threads of what appeared to be discolored varnish under several layers of paint. Elsewhere in the painting, this same discolored resin had bubbled to the surface through cracks and had beaded on top of the reworking. Many of the cracks indicated interlayer movement along a concealed varnish layer. A small loss in the foliage revealed at least one of these resinous layers. The exposed layer was beneath several layers of paint, which were in turn beneath the varnish on Trees in Blossom.

At this point in the treatment we took several cross sections of Winter in order to investigate the several anomalies in the painting, namely the mottling, the concealed varnish layer(s), and the possibility that still other additives were present. The sections proved difficult to take precisely because of the underlying varnish: the samples tended to break at a resinous layer. We were only able to take one entire section, from surface to canvas. (On the left is a schematic of this complete section and on the right, the top portion.) The section contained more than twenty layers. There were two distinct varnish layers, visible near the top of the first and second portions. Richard Wolbers has stained these sections and has found that the lower of these two layers was in fact three contemporaneous layers of resin, then oil-resin, and then resin varnish. There were also two pigmented resin layers, one with orange particles and one with green. Richard has also found that some of the paint layers test positive for both oil and protein, and has concluded that they are emulsions of oil and commercial tempera paint. Another cross-section of the reworking proved useful in investigating the mottling. (On the left is the section in normal light, and on the right, in ultraviolet.) In this section the mottling was revealed as a very thin discrete layer on top of the snow (the thick light blue layer). We thought that this layer, now discolored to irregular tones of grey, was some sort of protein coating, which Lawson applied to his reworking. Since that time, Richard's work has shown that while the surface of the snow tests positive for protein, the mottled layer is itself inorganic and does not fluoresce under UV. We're now working on the theory that the coating is some sort of inorganic drier, such as cobalt, that Lawson wiped on the surface of the painting. This theory is in keeping with the idea that Lawson was preparing his reworked composition for exhibit in Detroit and needed the fresh paint to appear as dry as the paint of <u>Trees in Blossom</u>.

The information we obtained from the cross-sections proved useful insofar as we began to understand that Lawson's "contrapuntal" approach to painting resulted in extensive layering of pigment, medium and varnish. The purpose and original effect of his technique were still a bit unclear.

Two other paintings by Lawson were examined at this time. Each were found to possess some of the same anomalies found in <u>Winter</u>. One was a small landscape entitled <u>Spuyten Divil</u>, in the DIA's collection. It had been wax-lined to a solid support and the impasto was flattened as a result. Nevertheless, photomicrographs of the drying cracks showed the same beads of varnish on the surface of the painting that were found in <u>Winter</u>. In addition, the broken edges of the original canvas provided a cross-section view of some parts of the painting. The layering technique was almost identical. <u>Harlem River</u> was from a private collection. It had been paste-lined and again, the impasto was rather flat as a result. Photomicrographs of <u>Harlem River</u> showed the same bi-level drying cracks as <u>Winter</u>, indicators of interlayer movement of the paint, perhaps along a varnish layer. <u>Harlem River</u> had been reworked on top of the varnish in at least one area, in the skyline. The photomicrograph was remarkably similar to one taken of Winter.

As interesting as the research into Lawson's technique had been, it provided no answers to cleaning <u>Winter</u>. Neither of the two other paintings examined appeared to have a similar coating, mottled or otherwise. Neither appeared to have the same thick pools of discolored natural resin varnish. Nor did either appear to have been cleaned to any noticeable degree. Likewise, neither the cross-section view of <u>Spuyten Divil</u> nor the cross-sections of <u>Winter</u> itself revealed a predictable pattern to Lawson's technique. 56

After removal of the surface grime and synthetic varnish <u>Winter</u> showed only marginal improvement. We decided to attempt to thin the natural resin varnish on the sky with a 5 to 4 to 1 solution of benzine, acetone and ethanol, in the hopes that by lightening the sky the painting would have more depth and legibility. The solution did thin the varnish, but proved difficult to control. At the sky-mountain interfaces it was particularly difficult to avoid interfering with the varnish under the reworking on the mountains. The solution also flowed into drying cracks in the sky and seemed to be reacting with the concealed resinous layers. At this point we decided to test cleaning the sky with resin soaps, rather than solvent systems, in the hope that the soaps would be more controllable.

We began cleaning under the microscope, in order to see exactly what effect the soap had. We also did extensive photo-documentation of each area as it was cleaned, shooting both regular details and photomicrographs of each section. I'll be showing these in pairs, with the "before" on the left and the "after" on the right.

After testing several of the soaps we decided to clean with Richard Wolbers' abietic acid and diethanolamine recipe. The pH was measured at 8.5. The soap was cleared off the surface of the painting first with saliva, then with Stoddard Solvent. The working properties of the soap were excellent. Its movement over the area to be cleaned was easily controlled. It also appeared to attack the varnish alone; it never leeched the paint and it ceased cleaning whenever an emulsion or other additive was encountered. After cleaning, the sky was noticeably brighter and the depth in the painting had increased.

We decided to attempt cleaning the reworked areas of the painting with the same resin soap, still using a microscope. A test cleaning strip (at the lower right) immediately showed that the soap removed the mottled coating. It worked more quickly on the coating than it had on the varnish in the sky, which meant that we could clean with no visible effect on the varnish exposed through the brushstrokes of the reworking. The resin soap was working admirably on all our test spots until we reached areas in the reworking where Lawson had used water-soluble paints. These were the deep violet, blue, red and green pigments and were susceptible to the soap only when they were present in pure form. Since the use of pure pigments was limited to only certain discrete brushstrokes, which we could clean very quickly or not at all, we decided to proceed with the resin soap.

The painting was placed on an easel and cleaned without magnification. This is a "during cleaning" shot of <u>Winter</u> as the mottled coating was being removed. Now I'm going to flash "before-and-after" slides of the cleaning. I have both details, and photo-micrographs. The overall effect of the cleaning was excellent. With the removal of the mottled coating, the image sharpened and became legible. The colors cooled and intensified, and the sense of depth in the composition increased. Though much of the discolored varnish remains visible, particularly in the mountains, it is far less visually disruptive, given the overall brightening of the scene.

After cleaning, only one area of discolored varnish intruded: a triangle of waxy yellow green at the upper left edge, in the mountains, had not been affected by the cleaning. In consultation with the curatorial department, we decided to tone this area down with watercolor because it was now so noticeable.

The rest of the treatment of <u>Winter</u> was fairly straightforward, with the losses being filled and inpainted. Since the reworked areas of the cleaned painting were now unprotected by a coating, we consulted the curatorial department and reached the decision to varnish <u>Winter</u> with a dilute, matte, methacrylate varnish. This thin brushcoat saturated the paint, and will protect the water-soluble pigments from future surface cleaning. And this is Winter after treatment.

In conclusion, the treatment of <u>Winter</u>, a.k.a. <u>Trees in Blossom</u>, presented many problems. Given the difficult factors of extensive reworking, a complicated (to say the least) layer structure, and the mottled coating, traditional solvent systems could not have been used to clean the painting. Thus we were presented with a good candidate for cleaning with resin soap. As the <u>copious</u> photo-documentation demonstrates, the soap was successful in rendering the painting suitable for exhibition. Without it, <u>Winter</u> would have remained in much the same condition in which it was removed from storage, a mottled, discolored, flat, and rather dull, landscape.

I'd like to thank my colleagues at the DIA: Barbara Heller, Alfred Ackerman and Kenneth Katz, for walking me through this treatment during my internship; and Leon Stodulski, for preparing the cross-sections. And I'd like to thank Richard Wolbers for his help staining and analyzing the cross-sections. Thank you.

A Radioisotopic Assay for the Direct Measurement of Residual Detersive Materials on a Paint Film

Richard C. Wolbers

Introduction

The use of organic solvents to "clean" paintings, that is, to remove aged, deteriorated coatings or other accumulated materials from their surfaces is a time honored traditional method in the restoration of such works of art. To a limited extent, even certain aqueous preparations have found usage in this regard as well. But while solvents eventually leave the surfaces that they are applied to by virtue of their volatile nature, the amounts of residual materials left behind from aqueous preparations -- the soaps, detergents and the like that they contain, have never been directly measured on these kinds of surfaces. Apart from questions of relative efficacy, or for that matter methods of clearance, the more fundamental questions of how much? and, under what conditions? need to be answered. Presumably critical solution parameters such as detergent concentration and type, ionic strength, pH, type of counter ion, and so on will affect to some degree the adsorption process; but so too will the condition of the painting surface. While we may never fully characterize or understand completely the surface of an aged, varnished, grime-laden paint film, we can characterize, and even define, the types of materials we put on them. The limiting factor may well be though our ability to experimentally measure the small amounts of residual materials left behind on such surfaces, even under closely defined conditions.

In the present study use was made of radioisotopically labeled detergents to help trace and measure the residual amounts of these types of materials on the surface of an actual test painting. The use of such radioactively labeled materials to follow the deposition and clearance from an organic sustrate by a detergent is not new. Shebs (1) presents a concise overview of the use of radioisotopically labeled detergents in terms of evaluating their deposition and removal from textile substrates, as well as a review of radioactive materials, their detection, and safe handling. Isotopically labeled compounds, that is, where one atom within a molecule has been replaced with a radioactive form of the same element, are ideal for these kinds of tracer studies. Extremely small amounts of labeled materials can be detected and quantitatively measured by taking advantage of the fact that, for the isotopic forms of normal carbon or hydrogen, that is, C14 and Tritium, both are beta emitters. That is, either is capable of, as they radioactively decay, giving up high speed electrons to the surrounding environment. In doing so, if a "scintillator" is close by, that is, an organic molecule whose electronic structure is capable of being excited by the emitted beta particle, light will be emitted by the scintillator through fluorescence. These scintillators are usually dissolved in aromatic

solvents such as xylene or toluene (2). The resultant fluorescence from a beta particle collision with the scintillator can be measured photoelectrically, and the amount of fluorescence, and hence the number of beta particles being emitted per unit time by a radioactive source, can be directly measured. The incorporation of a C14 or Tritium label within a molecule usually doesn't change the chemistry of the molecule, it simply tags it with a distinct radioactive "signal".

In the present study three detergents, all commercially available with such internal labels, were used to follow and measure residual amounts of them that were left behind on an actual easel painting surface. Two of the three, Deoxycholic acid and Triton X-100, have been used in practice by this author for the removal of accumulated grime, or deteriorated natural resin coatings on the surface of easel paintings (3). The third, Palmitic acid, represents a rather ubiquitous soap common to a number of animal or vegetable triglycerides.

A fragment of a badly vandalized painting (4), a portrait of an unknown sitter, estimated to be oil on fabric, and signed and dated by the artist, "Frank Linton, 1915, was used as the test material in this study. The painting was badly torn, and a large section of the sitter was missing. Apart from the vandalized area, the painting appeared not to have been restored in its life time. A microscopic examination of a small sample removed from the painting, revealed a lamellar type of structure; light colored ground, dark brown paint (in the area used for this study), and at least two surface coatings or varnishes. Fluorescent dyes were used to characterize the paint and ground layers as possibly oil bound materials (5); the surface coatings were characterized by FTIR as possibly natural resin types of varnishes (6).

Materials and Metods

The assay system for the measurement in situ of residual detergent materials was as follows: A fragment of the vandalized painting was further sectioned into rectangular pieces approximately 5.5×3 inches in dimension. Each painting piece was then overlayed with an identically sized sheet of .050" thick dental baseplate wax (Neowax, Polysciences Inc., Warrington PA) to effect a mask or template over the painting rectangle. The wax mask was lightly affixed to the surface of the painting piece by warming in the stream of a hot air gun, and then quickly pressing it in place on the painting surface. Test "wells" were then created through the wax mask by heating, again in the stream of air from a hot air gun, a 6" length of copper tubing, O.D. .5", and pressing it through the wax dam to the paintings surface. This in effect created a uniformly defined test area on the painting's surface, sealed the edges of the annular, punched out test area, and facilitated the removal of the wax disc created within the test area. Each rectangular piece of painting overlayed with the baseplate wax was "punched" with a uniform array (3x6) of such wells or test areas. The 5.5x3"size, 18 well test sheet, thus prepared proved to be a convenient format to handle, and on which to perform a maximal number of tests on the smallest amount of substrate.

All assays were done on test sheets prepared as described above; the assays were done on a standard lab benchtop overlayed with absorbent paper in case of spillage. Additionally, a 6x8" piece of glassine paper was layed under each test sheet when the assays were actually being performed as an additional precautionary measure. All assays were performed in triplicate, in the test wells adjacent to one another along the shorter dimension of the array. Both radiolabeled detergent mixtures and subsequent water rinses were delivered by automatic pipettors (Eppendorf), fitted with disposable plastic tips. Generally, unless otherwise noted, 50 ul volumes of each were delivered to the test wells; this volume proved to be a convenient amount to both cover the test area (and volume) defined by the punched out wax template (.5" diameter) with detergent solution, but also provide enough liquid to rinse the same defined area as well. Typically, an "assay" would proceed as follows: 50 ul of a radiolabeled detergent solution would be placed in a test well, and left to sit for 1 minute approximately. A machinemade cotton swab (Citimed Corp., #22-9612, 6 inch cotton tip applicator, pre-sterilized) would then be used to both roll around and roll up the excess detergent on the painting surface. The top 1.5" of the cotton swab (including the cotton tip) would then be broken off and placed in a scintillation vial (Sargent-Welch, S-83235, screw cap, borosilicate). The test area would then receive 50 ul of

deionized water, and again, after about a minute, be rolled around and up onto a dry cotton swab. Again, the top 1.5" of the water rinse swab would be broken off, and loaded into a scintillation vial. The test well thus treated was then cut or punched out with the aid of a .5" I.D. standard laboratory cork borer: the test sheet, with glassine underneath it was placed on a block of wood, and the cork borer pushed into the test well to punch out the treated area of painting defined The resulting .5" diameter piece of by the test well. treated painting was then loaded into a scintillation vial. All materials to be counted were mixed with 10ml of a preprepared scintillation fluid (Scintiverse II, Fisher Scientific) designed as a "cocktail" type of scintillator, capable of emulsifying and counting aqueous samples, as well as hydrophobic materials. All samples were counted on a Beckman LS-100 liquid scintillation system, on a combined Tritium and Carbon 14 window, for 5 minute intervals, or to a preset error level of .2%. Each assay, thus, included (in triplicate for each) the total number of counts applied (50 ul of labeled detergent solution only), the initial swab, the water rinse swab, and finally the section of painting treated. Controls included, a blank (scintillation fluid only), painting sample, swab only, wax baseplate material only, painting and wax material combined, and a filter paper disc "wipe" of the work area benchtop.

The detergents selected for this study were all commercially available as radio-isotopically labeled materials. They were: Deoxycholic acid (carboxyl - C^{14} , from ICN radiochemicals, Irvine, California, cat. no. 12273, lot no. 2837132, 58.2 mCi\ mmole, 50 uCi in Ethanol), Triton X-100 (phenyl - H³, from New England Nuclear, DuPont, Wilmington DE, NEN 556, lot no. 2481-229, 1.0 mCi\ml, 250 uCi in Ethanol:water, 2:8), and Palmitic acid $(1-, C^{14}, also New$ England Nuclear, NEC-075, lot no. 2635-050, .1 mCi\ml, 2.8 $mg \mid ml$, 50uCi in Ethanol). Both the Deoxycholic acid and Palmitic acid stock solutions were used neat; the Trition X-100 was diluted prior to use, 1:5 with an Ethanol:water (2:8). This was to assure that in a 10 ul volume of each radiolabeled detergent preparation a target amount of 1 uCi (approx. 2x10⁶ CPM) could be delivered in a minimal volume to a working stock solution of "cold" or unlabeled material. Working "cold" stock solutions were prepared as described below; 1ml of each was aliquoted and mixed with 10 ul of the appropriate stock solution of labeled material. Given the nature of the counting efficiency of each isotope, the 50 ul of the labeled, aliquoted material used for each test should have theoretically contained approximately 100k CPM.

"Cold" working stocks of detergent preparations were made using materials purchased from Sigma Chemical Co., St Louis, MO., (Deoxycholic Acid, Sodium Deoxycholate, cat. nos.D2510, D6750: Triton X-100, no. X-100, and Palmitic acid, Sodium Palmitate, nos. P5917, P9767). These materials were 99% or purer in grade; Reagent grades of Triethanolamine, Diethanolamine, Ethanolamine (also Sigma) were used. "C12" refers to an ethoxylated form of Laurylamine produced by Akzo Chemie, Chicago, Illinois under the tradename "Ethomeen C-12".

Working Stocks of each of the three detergents were prepared where concentration, relative to the Critical Micelle Concentration (CMC) for each, was varied. Thus, a 50x CMC solution of each detergent was prepared, and diluted incrementally with distilled water as; 50x, 40x, 30x, 20x, 10x, 5x, 2x, 1x, .5x, and .1x the CMC for each. The literature values for the CMC's of the three detergents were: Deoxycholic acid, .005M, Triton X-100, .00024M, and Palmitate, .0021M (7) (8). All dilutions were done with distilled water. The Deoxycholate stock (50x CMC) was prepared by adding 9.82g of Deoxycholic acid to 100ml distilled water; adding 1.6ml of a 50% solution of NaOH and stirring on a magnetic stirrer (pH, 12.5). These concentrations represent a 10:1 molar excess of the base to free acid; they also insure that the stock is at a pH well above the pK for Deoxycholic acid, therby putting essentially all of it into solution. This stock was unbuffered; the pH was allowed to drop through the course of the dilution series.

A 50x CMC stock of Triton X-100 was prepared by adding .75ml of the detergent to 100ml of distilled water, along with enough 50% NaOH to raise the initial pH to 12.5. Again, the pH was allowed to drop with the dilution series.

A 50x CMC stock solution of Sodium Palmitate was prepared by dissolving 2.69g of the salt in 100ml of distilled water; the pH was brought to 12.5 with the addition of a small amount of 50% NaOH. This method was used rather than dissolving the free acid directly into a basic solution because of the marginal solubility of the free acid in water; its self emulsification tendency made its solubilization by this method difficult at best. The Sodium salt, as a pre-prepared material was much easier to put into solution, and the addition of an excess of the base to bring its pH close to that in the other two dilution series facilitated making a comparable material. Again, the pH was allowed to drop as result of the dilution with distilled water.

A second series of working stock solutions for each detergent was prepared whereby the concentration of each was kept constant, and the pH was varied. In this case, the concentration was fixed at 2x the CMC for each detergent, while the pH was adjusted from 12.5 down to 8.0 with the addition of HCl. In all cases 1% NaH₂PO₄ was used as the buffering agent; the initial ionic strength was measured and adjusted with the addition of NaCl where needed to make the three series isotonically comparable.

A third series of materials were prepared based on a 5x CMC concentration of Deoxycholate in solution. The pH was held constant at 9.0 with the addition of 1% of the dibasic phosphate, and enough HCl to adjust the pH to that point. The "counterion" was varied however in this experiment; Deoxycholic acid was mixed with an excess (10:1 molar ratio) of the following bases; NaOH (as a 50% solution of NaOH), NH4OH (as a 50% solution of NH4OH), Triethanolamine. Diethanolamine, Ethanolamine, and C12, to produce the a series of six detergent solutions that were essentially similar except for the counterion present.

A final, albeit limited series of detergent solutions were produced based on Deoxycholate, 5xCMC, pH 9.0, but with the viscosity increased from 0 to 100 cps with the addition of Methyl cellulose as the thickener. Prepared essentially as described above in the "counterion" series, a Triethanolamine\Deoxycholate solution was made, which included as a final ingredient 2% Methyl cellulose (Sigma Chem Co., nos.M7140, M6385, and M0262 (diluted)) in various grades to produce the desired viscosity. It was found that, while higher viscosity producing Methyl celluloses were available, above about 100cps and the solutions were too viscous to allow for ease of pipetting or efficient mixing.
Results

Results have been expressed in graphic form; each data point represents the arithmetic mean of three replicates for each condition. While the assay system as devised seemed to work quite well, one problem which was apparent early on was the irreversible absorption of labeled materials into the test painting structure. It was assumed that any residual, labeled material left behind on the paintings surface after application and rinsing would be resolubilized by the scintillation cocktail and therefore be counted, and directly reflect the amount of deposition. There were, however, in all cases or conditions a certain amount of counts left behind that were apparently absorbed in the painting structure that were not readily resolubilized by the scintillation cocktail. This became apparent because the "book-keeping" didn't add up; the total number of counts applied in any one situation didn't equal the sum of the counts picked up on either of the swabs or the treated test area of painting. An additional series of controls were done which showed that the cotton swabs did not interfere with the counting; nearly all of the counts (89.9%) applied to a glass slide, and then readsorbed onto a swab were counted by the cocktail; only 12.7% of the counts applied to a painting test sample under the same conditions were resolubilzed by the scintillation fluid. It was possible however to dissolve the sample paint film with DMF and "release" the hidden counts; at least 64.3% of the counts prevolusly unaccounted for, could then been recovered. While the absolute mechanism of adsorption remains to be elucidated (see discussion below), it was possible to recover them directly through a pre-treatment of the painting sample with DMF prior to counting, or to estimate the irreversibly adsorbed counts by adding up those accounted for on the swabs and in the scintillation fluid, and subtracting them from the total applied. Generally, the latter method was used. For ease of display, the following graphs (figs.1,2,3, and 4,5,6) are plots of the total number of counts applied in a given situation, the "solubilized" counts (i.e., the sum of the counts that were recorded for both swabs and the counts resolubilized in the scintillation fluid), and by difference, the counts irreversibly absorbed in the painting sample.

With all three detergents it is apparent that, at least at a pH of 12.5, (figs. 1,2, and 3), the relative amount of residually deposited material remains proportional to the amount applied, when the concentration varies from a high concentration (50xCMC) to a low one (<10xCMC). As the concentration of the detergent approaches that of the CMC, the amount of deposition seems to change, in some cases quite dramatically. In the case of Sodium Deoxycholate, fig. 1, at or near the CMC, the solubilized counts rise rapidly, and concomitantly the absorbed counts rapidly decrease. Above the CMC and detergency is manifested by a surfactant; below it, and the surfactant acts more like a simple solute, and apparently tends to remain in solution. The surprising aspect of figure 1 is the amount of deposition; fully 50% of the applied detergent apparently remains behind on the surface under these conditions (high pH, high concentration).

A similar pattern can be seen in fig.2, as the concentration of Triton X-100 is varied; here, however, the amount of absorbed material appears quite high (80%), relative to the amount being applied, at most concentrations greater than about 10x the CMC. Again, a distinct change in the solution properties of the detergent occurs below it's CMC, and the drop in absorption at this point seems to be a manifestation of this.

Sodium palmitate follows a similar pattern to the other two detergents, in that a 'break' occurs in the deposition rate as one approaches the CMC; above this critical concentration and the amount of deposition relative to the applied amount of material appears to be fairly constant, on the order of 30-35%. One additional note in regard to the Palmitate series; it was found that at the pH that this experiment was run (12.5), if the labeled mixture was counted, in the Scintiverse II cocktail, a low counting efficiency was observed. At lower pH's (below the pK of Palmitic acid, 9.5) no such problem was observed. It was assumed that at the higher pH's, and fully ionized, Palmitate ion was either not being solubilized by the cocktail or was quenched to some extent by it; in any case a simple neutralization step by the addition of 250ul of 2N HCl prior to the addition of the cocktail eliminated the problem.

In terms of the actual amounts of materials (weight ug\unit area) being left behind on the test areas of painting surface (based on the CMC for each of the detergents), figs. 1a, 2a, and 3a can be used to illustrate the experimental results in a slightly different way. The actual weight of detergent left behind in the case of Triton X-100 (fig 2a) is quite low when compared to that of the other two detergents, because its CMC is the lowest of the three detergents tested. The plot of residual weight versus concentration is rather linear; again, the amount left behind is proportional to the amount applied. The range is about 300ug (at 50xCMC), to around 5.4 ug at the CMC. In figures 1a and 3a similar plots are presented, and both reflect the same kind of linear relationship between the amount of material applied, and the residual material left behind. In the case of Sodium Deoxycholate (fig 1a) the range over the tested concentrations was about 2.5 mg (at 50xCMC) to about 35ug at the CMC; for Sodium Palmitate, 13.45mg (at 50xCMC) to about 270 ug at its CMC.

Figures 1b, 2b, and 3b are plots of the percent of the

applied material absorbed on the test painting surface as a function of concentration; again for all three detergents the amount deposited appears constant for concentrations above about 10x the CMC for each detergent. As the concentration approaches the CMC, the rate of absorption decreases sharply for both Deoxycholate and Triton; the rate of absorption actually seems to increase for Palmitate close to its CMC. Presumably, this is because of the relatively more soluble character of Deoxycholic acid and Triton in aqueous environments, over that of Palmitic acid, which is essentially insoluble in water.

When the concentration is held constant for the detergents (2xCMC), and pH is incrementally changed, slight decreases in the absorbed counts, and concomitant rises in counts remaining soluble were noted. In figures 4 and 5, at least, this trend was true; for Deoxycholate, the most counts were absorbed at a pH of 12 (38%), and the least at a pH of 8.5 (8%). Since the amount applied in every case was theoretically the same (2xCMC, or 196ug), the plots of percent residual counts and the absolute weights of residual material left behind yield similar curves (figs. 4a, 4b). Triton X-100 seems to behave in a similar manner (fig.5); although there is a less steep decline in the number of residual counts over the same pH range. The most counts (and the most material, weight-wise) is deposited at a pH of 12.5 (60%), the least, at a pH of 8 (42%), (figs. 5a, 5b). The series where the Sodium Palmitate concentration is kept constant (2xCMC) and the pH is varied (fig 6) was limited to the 9.5 to 12.5 range; this was simply because the pK for Palmitic acid is about 9.5, and little if any Palmitate remains in solution below this point. There appears to be a slight decline in absorbed counts throughout the range from 12.5 to 9.5, but the least amount of deposition occurs at a pH of 11 (figs. 6a, 6b), and the most at the pK. Again, as with the series where the concentration of Palmitate was varied, a neutralization step was required just prior to the addition of the scintillation cocktail.

The experiment where Deoxycholate (5xCMC) was prepared at a pH of 9.0, with a series of different counter ions present is partially displayed in figure 7. While there appeared to be some correlation between counter ion and the number of absorbed counts, the most striking feature was that as the TEA, DEA, or Ethanolamine salt, Deoxycholate seemed to be retained significantly more than either the Na or NH4 salts (light bars). But when compared to the number of counts that were retained, but resolubilized by the scintillation fluid, TEA was, for instance, one of the more easily washed off of the painting surface (solid bars). It may be possible that a counter ion such as TEA may impart both an increased resolubility to a residual salt, as well as an increased solvency fot the substrate.

The final experiment (fig 8), ostensibly was designed to see whether or not building the viscosity of a detergent solution would either enhance or hinder the removal of residual material on the painting surface by decreasing the diffusion of the detergent into the substrate. A 5xCMC Deoxycholate\TEA solution was prepared (pH 9.0) and was aliquoted. The viscosity was increased in each aliquot with the addition of 2% Methyl cellulose of varying viscosity grades. As stated previously in the materials and methods section, viscosities of greater than 100 cps made it virtually impossible to insure proper mixing and pipetting of small volumes of more viscous preparations. None-the-less, over the range from 0 to 100 cps a slight decrease in absorbed counts was noted, along with a concomitant rise in resolubilized counts, suggesting that, indeed raising the viscosity, if only slightly, did allow either more material to remain on the painting surface, or to slow the penetration rate into the substrate.

Discussion

The goal of the foregoing set of experiments, at least from the outset, was simply to arrive at some sense of the amount of residual surfactant that might remain on a paintings surface after it came in contact with an aqueous detergent solution. While admittedly limited in scope, such critical solution parameters such as pH, concentration and type of surfactant, and even counter ion, where appropriate, were thought to play some role in the adsorption and desorption process to a real painting surface. The substrate for the present study was purposely selected as a fragment of a real painting. And while a naturally aged, grime-laden painting may, in some ways, represent a kind of "black box"; that is, a complex surface on which to make or take measurements, it is very much like the object of everyday scrutiny by the paintings conservator. And surprisingly, for as much of a "black box" as it represents, some of the results do suggest that predictable relationships can exist between concentration and pH, for instance, and residual materials.

Appreciable amounts of applied materials were retained, and tenaciously so, when the pH of the cleaning solution was elevated. At a pH of 12.5 the surface of an oil film is undoubtedly rapidly swollen; perhaps the large amount of residual material is simply physically trapped in the swollen and then reformed surface upon drying. With all of the detergents tested this effect was lessened, to one degree or another, as the pH was lowered. Certainly, as the pH is lowered less swelling can be suspected in an oil layer. An alternative hypothesis though, might be that, since a good portion of a paint film is pigment, that some of the adsorption occurs on the inorganic material within the paint film; lowering the pH in effect desorbs more material by ion Regardless of the nature of the adsorption, the exchange. lesson seems clear; high pH and concentrated amounts of detergent seem to, regardless of detergent type leave appreciable amounts of detergent behind.

Less alkaline conditions seem to cause less deposition; this was true at least in the case of Deoxycholate and Triton X-100; but this must certainly be mollified by the example of Palmitic acid. Below its pK this particular anion no longer remains in solution; worse, the residual material seemed to increase on the test surface as the pK was approached. To work effectively, the pH may have to be so high in some cases so as to rapidly swell the surface of an oil film. The judicious choice of detergent may well be in the interest of the practitioner if he is working on a film that may be sensitive to alkaline conditions. It might be added as well, that since some residual material was evident with all three of the detergents, working at a concentration at, or just above the CMC for a particular may at least minmize the amount of material prone to be left behind.

Finally, although clearance per se was not examined in the present study, there were some features of the experiments which do suggest some of the problems that might be encountered in trying to remove residual materials from a painting surface. It should be pointed out that, even though every assay performed included a water rinse after a detergent was applied, few if any counts ever came back up in the water rinses. Water alone may not be an ideal clearing agent for a variety of reasons. At a pH of 7.0 (or less), water may simply precipitate further weakly anionic and dilute materials on a hydrophobic surface by neutralizing them; a much better strategy might include rinses with a slightly elevated pH to maintain them as charged species in solution and to effect their eventual dilution. The use of viscous media to slow diffusion into films shows promise and should be explored further. Varying the counter ion in solution with the detergent also shows promise; if the Deoxycholate\TEA system in the last experiment was followed by, say, a solvent rinse rather than a water rinse, more residual material might have been solubilzed. The advantage of using organic ions rather than inorganic ones as the counter ion may lie in their ability, as complexed salts, to be soluble in a range of polar solvents, in addition to water.

Acknowledgement

The author gratefully wishes to thank Dr D.W. Smith of the Health Sciences Department of the University of Delaware for his guidance, expertise, and lab space for the foregoing work.

Footnotes

1. Cutler, G. and Kissa, E. (Eds), <u>Detergency: Theory and</u> <u>Technology</u>, Chapter 3, "Radioisotope Techniques in Detergency ", By Shebs, Wm., pp 125-195, Marcel Dekker, NY, 1987.

2. pp 137 -141, op.cit.

3. Preprints, 1988 AIC meeting, New Orleans, "Aspects of the Treatment of Two Late 18th Century Portraits by William and Richard Jennys" by Richard Wolbers

4. The portrait fragment was a donation to the jointly sponsored Graduate Training Program between the Winterthur Museum and the University of Delaware.

5. Preprints, 1987 AIC meeting, Vancouver B.C., "The Use of Direct Reactive Fluorescent Dyes for the Characterization of Binding Media in Cross Sectional Examinations" by Richard Wolbers and Gregory Landrey.

6. See Appendix A for spectrum.

7. Womack, M.D., etal., Biochim. Biophys. Acta, 733, 210, 1983. Also: Matson, R.S. and Goheen, S.C., LC-GC, 4, 624, 1986

8. Osipow, L., <u>Surface</u> <u>Chemistry</u>, Reinhold Publishing Co., NY, 1962, p.166.



Figure 1a. Sodium Deoxycholate, pH 12.5. Residual or absorbed material, expressed in terms of ug\ unit area as a function of concentration.



Figure 1. Sodium Deoxycholate, pH 12.5. Residual counts (\Box — \Box), solubilized counts (Δ — Δ), and total counts applied (\circ — \circ), as a function of concentration, expressed in terms of the CMC for Deoxycholate (.005M, or .1963g\dl)



Figure 2. Triton X-100, pH 12.5 (NaOH). Residual counts (\Box -- \Box), solubilized counts (Δ -- Δ), and total counts applied (σ -- σ), as a function of concentration, expressed in terms of the CMC for Triton X-100 (.00024M or .015 g\dl)



Figure 1b. Sodium Deoxycholate, pH 12.5. Residual or absorbed counts, expressed as % total applied counts, as a function of concentration.



Figure 2b. Triton X-100, pH 12.5 (NaOH). Residual or absorbed counts, expressed as % total applied counts, as a function of concentration.



Figure 2a. Triton X-100, pH 12.5 (NaOH). Residual or absorbed material, expressed in terms of $ug\$ unit area as a function of concentration.



Figure 3a. Sodium Palmitate, pH 12.5. Residual or absorbed material, expressed in terms of ug\ unit area as a function of concentration.



Figure 3. Sodium Palmitate, pH 12.5. Residual counts $(\Box - \Box)$, solubilized counts $(\Delta - \Delta)$, and total counts applied (O - O), as a function of concentration, expressed in terms of the CMC for Palmitate (.0021M or .0539 g\dl)

76



Figure 4. Sodium Deoxycholate (2xCMC). Total counts applied (\bigcirc), residual counts (\square), and solubilized counts (\triangle), as a function of pH.



Figure 3b. Sodium Palmitate, pH 12.5. Residual or absorbed counts, expressed as % total applied counts, as a function of concentration.



Figure 4b. Sodium Deoxycholate (2xCMC). Residual or absorbed counts, expressed as % of total counts applied, as a function of pH.



Figure 4a. Sodium Deoxycholate (2xCMC). Residual or absorbed weight expressed in terms of ug\unit area, as a function of pH.



Figure 5a. Triton X-100 (2xCMC). Residual or absorbed weight expressed in terms of ug\unit area, as a function of pH.



Figure 5. Triton X-100 (2xCMC). Total counts applied (0----O), residual counts (\Box ---- \Box), and solubilized counts (Δ --- Δ), as a function of pH.



Figure 6. Sodium Palmitate (2xCMC). Total counts applied (O—O), residual counts (\Box — \Box), and solubilized counts (Δ — Δ), as a function of pH.



Figure 5b. Triton X-100 (2xCMC). Residual or absorbed counts, expressed as % of total counts applied, as a function of pH.



Figure 6b. Sodium Palmitate (2xCMC). Residual or absorbed counts, expressed as % of total counts applied, as a function of pH.



Figure 6a. Sodium Palmitate (2xCMC). Residual or absorbed weight expressed in terms of ug\unit area, as a function of pH.



Figure 8. TEA Deoxycholate (5xCMC), pH 9.0. Total counts (0-0), residual counts (0-0), and solubilized counts ($\Delta - \Delta$), as a function of viscosity (cps).



Figure 7. Deoxycholate (5xCMC), pH 9.0. with varying counter ions, as labeled. the solid bars represent the counts resolubilized from the painting surface, and the light colored bars the counts absorbed on the painting surface; both are expressed in terms of % of total counts applied.



O