1993

AIC PAINTING SPECIALTY GROUP POSTPRINTS

Denver, Colorado • Saturday, 5 June 1993

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A.I.C. PAINTINGS SPECIALTY GROUP POSTPRINTS

Papers presented at
the Twenty-First Annual
Meeting of the American Institute for Conservation
of Historic and Artistic Works

Denver, Colorado
Saturday, 5 June 1993

Compiled by J. William Shank

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Uncovering the Working Methods of Thomas Cole: An Ongoing Study

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According to his biographer,Louis Legrand Noble, Thomas Cole's first employment, shortly after his arrival in Philadelphia in 1818, was as a wood engraver for a man who supplied woodcuts to printers. When his family moved on to Steubenville, Ohio towards the end of 1818, he stayed on in Philadelphia, boarding with Quakers, and as a member of that family recalls "working on a pine table in the back room of our old Second Street house."

He made illustrations for books such as John Bunyan's Holy War. During this period, which also included a trip to the St. Eustatia in the Caribbean, from which he made topograhical studies of the island, Cole spent his creative energy on drawings in crayon and pencil. When he rejoined his family in Steubenville, he remained at home in the service of his father who has opened a paper hanging factory. He helped his father by "combining colors, drawing and designing patterns and engravings, as usual, on wood." Although, as he later wrote to the writer and fellow artist, William Dunlap, "there is too little art and too much manual labor for one of an imaginative mind." Often overlooked is the fact that Cole taught watercolor painting and drawing in 1820 to supplement the family income. Between the period of 1820 and 1823, Cole learned the use of oil paints from the itinerant painter, John Stein. He became a traveling portraitist for a short period and studied from time to time at the Pennsylvania Academy of Fine Arts.

An important crossroads in Cole's graphic style came about in the Spring of 1825 when Cole got his hands on a copy of William Oram's Precepts and Observations on the Art of Colouring in Landscape Painting published in 1810. Cole began sketching extracts from the Precepts in his notebook. This little book by Oram, a royal officer and amateur landscapist who died in 1777, appears to have very much affected Cole's development of landscape painting techniques. Oram's Precepts provided Cole with a model - a way of ordering his observations and translating them into paint. Cole made careful selections from Oram's recommendations and ended up with a sound advice "On Painting Skies", "For the Clouds" "For Colouring Leaves" and "Colouring the Sea". Cole carefully copied out selections from Oram's manual. So it is not surprising to find Cole's pencil drawings in this stage of his career to follow what can be found in Oram's illustrations - crisply rendered outlines with a few notations written in as reminders of what colors to choose and degree of chiaroscuro actually observed at the moment the drawing was done. We find the same schematic formula that Oram used, being adopted by Cole.

For proof that Cole thoroughly absorbed Oram's lessons, one doesn't have to look far. His South View from Featherson Park, Duanesburg, New York was executed near the end of 1825 or the beginning of 1826. It comes very close to Oram's own From Hampstead Heath. This technique of quick note taking suited Cole's artistic personality perfectly and he adopted it on his trip up the Hudson into the Catskills in 1825. The method anchored him in topographical accuracy that he so sought after. It's apparent that the view from Featherston was first drawn in pencil then some of the outlines were retraced or reinscribed in ink. The visual effect of the black ink against the white paper is a visible reminder of Oram's plate but the connection is made stronger by Cole's inscribing "shadow", "light" "wood" "shade" and foreground light as well as the longer note "The most distant mountains very faint made of ochre vermillion and blue - having a smoky appearance as in all the distance as it recedes. The woods are lighted with a reddish tint throwing shadows - the sky of a greenish appearance rather redder and darker on the horizon."

This method of notation suited Cole's style as well as the rapid sketching in his notebook as he strolled through the scenic Hudson River Valley. This method of sketching and note-taking dominated his style from the mid 1820s until his death in 1848. Even while adopting this quick style in pencil, he did not abandon detailed nature studies that stand alone and these show up in his sketch book of 1825-26. Cole made 3 trips to the White Mountains of New Hampshire. In 1827 he made the journey, at the urging of his patron Daniel Wadsworth. In 1828 and 1839, he returned in the company of fellow artists, Henry Pratt and on the final trip, Asher B. Durand.

The 1828 sketchbook encompasses the full range of Cole's drawing techniques from delicate penciled drawings, to fully worked up detailed topographical studies of rocks and mountain peaks. Two examples from that sketchbook are White Notch Mountain. Pencil heightened with pen and black ink and numerous notations. Notice how detailed the drawing is. Every curve and notch has been carefully rendered. Cole also made copious notes on the mood of the site and the grandeur of the setting that touched him deeply. Another drawing View from Chocorua Peak with Mount Washington in the Distance also exemplifies the neat and carefully executed drawing he concentrated on producing during this period. A continuous line of pen and brown ink has been used over pencil in several areas.

While it was common for Cole to use his drawings to create paintings in his studio, none can be specifically linked to the 1828 sketchbook. Interestingly, when he reached the top of Mt. Chocorua, he commented on the intended purpose of his trip and accompanying sketchbook. "The view was sublime but not a scene for the canvass - too much like a map - It was not for pictures I ascended the mountain but for ideas of grandeur, for conceptions- and for these, this was the region." It is not know exactly how Cole transcribed his pictorial notes on paper to canvas for painting. It has been suggested that Cole was familiar with Bouvier Merrimée instructions to artist, Handbook of Young Artists and Amateurs in Oil Painting, published by Laughton Osborne in 1845. Although Osborne's book comes near the end of Cole's life, it's likely, as Joyce Zucker suggests, that it has far reaching effects much earlier. Chapter IV in Osborne's book, "In What Way the Design is transferred to the canvas or other subjectile, and then rectified, and made out more distinctly, with the hair-pencil," offers interesting insights into how artists may have underdrawn their paintings at the time.

The chapter begins with, " A practised artist usually prefers to make his design directly on the canvas, because the feeling with which he is inspired communicates itself more surely in this manner to his outlines." He states that the advantage of working out the drawing on paper is that the surface is "not worried by going over and over again, line after line, erasing, restoring and re-erasing the contours of his subjects. He recommends designing and correcting directly on the paper. He describes using a pounced method of drawing transfer, transfer by tracing and outlining with reddish-brown pigments and a little drying oil. The treatise goes on to say, "Moreover, with the point of your pencil, do as in drawing, enforce certain traits that are more strongly characterized and more energetically expressed than the rest. These strong and broad touches, made in the proper places and without dryness, and a great deal of expression to the contour, and enable you to establish the shades with less distrust and hesitation." What stands out with relation to Cole is the recommendation of using a sure and strong hand with a delicate touch when using pencil to lay in the drawing on the canvas.

The basis of Cole's landscape painting were outdoor sketches. He would counsel young painters on the importance of solitary walking and sketching in the open. However, invariably the paintings were done in his studio based partially on his sketches and in part on old master compositions that were available through engravings. In looking at Cole's drawings, it is important to make a distinction between those that were preparatory compositions and those stand-alone drawings.

A particularly successful two-canvas series, The Departure and The Return came after Cole's trip to Europe in 1832 where he became immersed in the landscape of ancient ruins and cultures. Both paintings are in the Corcoran Gallery of Art and are dated 1837. These very sentimental paintings show the legend of the hero who goes out to battle and returns as a corpse at night.

Of the 21 paintings examined thus far by infrared reflectography, 10 revealed underdrawing.

The Departure demonstrates the principal underdrawings elements found. A very thin graphite line can be found to follow the mountain contour. A very free and lyrical line delineates the mountain to the right of the castle. The castle itself has a ruled underdrawing with some indication of pentimenti. Squiggly lines appear time and again in Cole's underdrawing. The immediacy and alla prima nature of this pencil line is juxtaposed to the thoughtful outlining of the mountain so reminiscent of the same treatment in Cole's drawings on paper. The castle was originally conceived to be lower and longer into the hillside. Some very quick and sketchy lines were used by the artist. Squiggly lines seem to indicate position of clouds and are not related to the shape of the clouds. These lines turn up in other paintings.

The Gothic church in The Return has a grid. The horizontal and vertical lines are probably used here to achieve geometric balance in the arches and strict architectural elements of the church. The base of the column has been carefully rule-drawn with a rather thick line. Some minor adjustments in these lines are visible. The tower in the Return from the Tournament has freely drawn lines to indicate the arches. Some pentimenti are visible. One vertical line for the center of the tower is crossed by a horizontal line. Windows in the upper portion of the tower were originally larger. The tower is the only apparent underdrawn area in the painting. Although, the possibility that underdrawing exists under the foliage cannot be excluded.

The Wadsworth Atheneum in Hartford, Connecticut is home to some of Cole's most important paintings. Daniel Wadsworth, friend and patron to Cole, bequeathed 6 paintings by Cole to the museum. The museum has a total of 14 paintings by Cole. They span the career of the artist from the early St. John in the Wilderness and Scene from "The Last of the Mohicans", Cora Kneeling at the Feet of Tamenund, both painted in 1827, and View of Monte Video, the Seat of Daniel Wadsworth painted in 1828 to the later Mount Etna from Taormina painted in 1843, five years before the artist's death.

All of these paintings were examined by infrared reflectography, with the exception of Mount Etna from Taormina which was travelling at the time in the exhibit, "The Lure of Italy". No underdrawing was found to be present in these paintings. It is certainly possible that underdrawings are present and are not being detected because of a thick paint film or the impenetrability of certain pigments, but even in light, apparently thinly painted areas in the sky, no underdrawing was found. There are hundreds of extant drawings on paper by Cole. Apparently his important commissions were first worked out on paper and only summarized on the canvas. It was enough for the artist to delineate a thin mountain profile or horizon line to find the proper placement of forms in a two dimensional space. The small paintings examined tell another story. Landscape with Round Temple is a small painting believed to have been painted in the 1840s and possibly a sketch for an eventual larger painting. It is not identified with any particular painting by Cole. Although the image of the reflectogram is not very clear, a grid and quite of bit of pentimenti can be observed.

Three small panels, also in the Wadsworth Atheneum, are from doors in the home of Luman Reed, the New York patron for whom Cole painted the compelling series Course of Empire in the mid 1830s. Cole most likely worked directly on the panels without preparatory sketches on paper. Balloon Ascension shows that he positioned the balloon in several places before deciding on right of center. Positioned at one time in the center the artist opted for the final location to offset it against the lone tree in the lower left area of the painting. Mullian Stalks shows minor shifts in the placement of the stalks. A grid was uncovered in the small panel Ruined Castle as well as a curious compass-drawn line. It's purpose is not fully understood especially since there are no curvilinear elements to this painting. Dan Kushel brought to my attention the fact that similar curved lines were found in the Voyage of Life series at the Munson-William-Proctor Institute in Utica. It might be a positioning device much in the way the horizontal lines are used in other works such as Schroon Mountain in the collection of the Cleveland Museum of Art as noted by Christina Currie. The infrared study by Currie of this large painting dated 1838, revealed three major horizontal guidelines. The tip of the mountain lies directly on the uppermost line. Although all the lines are ruled it seems that the last few inches are hand drawn. Curious, vertical lines are in the right sky. There purpose is not fully known but could relate to indicating the direction of shafts of light and cloud formation in that area.

Two small oil sketches from the National Museum of American Art reveal some underdrawing. These oil sketches are a part of numerous works in preparation for Cole's series of narrative landscapes which had been fermenting in the artist's mind for some time. The study for the Pilgrim of the Cross at the End of his Journey is dated 1846-47. The underdrawing shows a larger cross in the sky and that the rim of lyrical cloud formation once closed in further on the cross. There is not underdrawing for the figure, as expected. Pilgrim of the World at the End of his Journey, is dated 1847 and a monochromatic brown. The only underdrawing here are directional lines in the cylinder in the lower right. No outlining of the large rocks is detectable although this could be masked by the pigment the artist used.

From this very preliminary study of some of Cole's paintings certain observations can be made. It appears that he primarily used pencil for underdrawing. Robert Gilmor, the art collector from Baltimore and patron of Cole, once wrote in a letter to Cole " your pencilling is really admirable and faithful imitation of nature in the form, color and disposition of your rocks, the variety in the shrubbery, grasses and moss, would alone constitute this a fine picture." He enjoyed walking through the mountains and sketching in a notebook. These ideas he took back with him to his studio where he would compose and work his ideas into paintings. Drawings on paper were used as preparatory sketches and were also works that could stand alone. The preparatory pictorial notations he used in his underdrawing were: a grid, with the idea of an eventual transfer of the idea into a larger work; a thin contour line tracing the outline of a mountain, for example, squiggly lines to indicate the position of clouds and streams of light; and horizontal lines, in order to line up trees, mountain peaks in his compositions.

It appears that his large paintings were probably well worked out on paper before he touched the canvas. Then he would transpose only the essential lines, often directional lines, that would assist in composition and perspectival arrangement. Interestingly, it seems that the works most underdrawn are small oil sketches or paintings that would conceivably be large, complete works in the future. The compositions of these works was arranged and rearranged directly on the canvas.

With the sure hand of the accomplished draftsman that he was, and the countless drawings on paper attest to this, he was able to limit his underdrawing to just capturing the essential lines in a composition and did not feel it necessary to create a detailed underdrawing. In a letter he wrote to Daniel Wadsworth on April 23rd, 1828, he said, "It is always my intention to introduce nothing in a picture for which I cannot give a good reason."

Acknowledgements

I would like to thank Stefano Scafetta and Quentin Rankin at the National Museum of American Art for their assistance and enthusiasm with the study of the three paintings there. I am also grateful Steven Kornhauser and Patricia Garland, conservators at the Wadsworth Atheneum and Betsy Kornhauser, Curator of American Paintings and Sculpture for their expertise and help during the examination of the paintings in Hartford. I would also like to thank Christina Currie, a fellow at the Cleveland Museum of Art for sharing with me her findings from the investigation of Schroon Mountain and View of Florence. I would like to thank Tim Vitale of CAL who examined with me the paintings at NMAA and the Corcorcan Gallery where Dare Hartwell's help was so valuable and Dan Kushel at Buffalo State Conservation Dept. for sharing his study of the series The Voyage of Life. Joyce Zucker at the New York State Bureau of Historic Sites, Peebles Island, was most helpful with information on 19th century painting techniques particularly in the work of Church and Cole.

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BOLIVIA - A CONSERVATOR'S EXPERIENCE

M. Randall Ash, Paintings Conservator

A Fulbright Scholarship provided an exceptional opportunity, and experience, to live and work in Bolivia as a visiting conservator for five months. The adventure began when the plane landed in La Paz, Bolivia's capitol, which rises well over 12,000 feet above sea level. Bolivia, close to the center of South America, combines a rich cultural heritage with traditional native life. This is a land of copious art and architecture, Incas, and cocoa.

The majority of my time in Bolivia was spent in La Paz at the Labatorio Central in the Instituto Boliviano de Cultura (IBC). I was fortunate to work on projects with Carlos Rua, the Director and Head Conservator of this central laboratory, and his staff. There were opportunities, continually extended, to visit sites and projects overseen by the IBC and Carlos. These excursions throughout La Paz and environs were always an education. On one such trip we inspected the status of a church being rebuilt on the "Alto Plano", at an altitude above 14,000 feet, and economically limited. I learned firsthand about the use of traditional building materials and techniques and the inventiveness of the people. Not all the visits were so rewarding. Carlos, I, and the police were involved in investigating a theft whereby paintings were cut from their frames in an Alto Plano church. Sadly, this is a too common incident in the remote areas of Bolivia.

Through the United States Information Services (USIS), I was asked to visit cultural institutions and lecture in Sucre, the "White City", and judicial capital of Bolivia, as well as Potosi, one of Bolivia's mining centers and home of one of the major museums of the area, Casa Nacional de Moneda. The chance to see the vast cultural wealth of this country and the hurdles faced daily by museum officials, made my respect for this country and the people grow constantly.

When I arrived, Carlos said that it couldn't have been at a better time, for the Lab had been given a major project to examine and conserve paintings that were to be loaned for an international art exhibit, **"America, Bride of the Sun"**, in Antwerp, Belgium. This exhibit included art from all the South American countries and Cuba. Bolivia's representation was larger that most of the other countries. My appearance was opportune as an extra professional was gratefully needed meet with exhibit deadlines. I, too, was fortunate to have the chance to work on major paintings from the National Museum of Art's collection, and the prospect of exchanging my knowledge of new methods and materials with both their traditional and innovative techniques. This made for a mutually beneficial and professionally enriching experience.

I helped with many of the paintings that were being lent, but my main project was the conservation of one of the principal paintings in the National Museum's collection. The painting is Descanso a la Huida a Egipto, also known as La Virgen Lavanerra by Melchor Perez Holguin (1660? - 1733?). It measures H 125 cm (49.25") x W 104 cm (40.98"), (fig. 1). The advice of and interaction with Carlos Rua was invaluable.

CONDITION

The painting was executed on hemp fabric, plain basket weave, natural color, and comprised of three pieces, sewn together. The hemp was of a finely woven quality. Hemp was not unusual for this period or the fact that the large canvas was comprised of multiple pieces sewn together. The perimeters of the canvas were glued directly to the strainer. This was a common practice as canvas was too costly and scarce to extend the edges around onto the sides of the strainer. Uncharacteristically, the top horizontal was turned over and tacked to the side of the strainer but not glued to it. This "tacking edge" had original paint and ground. The visual examination of the support and the painted images began to raise suspicion as to whether this painting had once been larger. The right vertical edge had two strips of painted canvas, of approximately 2" in width, which were joined short end to short end, and glued directly to an addition to the strainer. These strip additions were suspicious. As treatment progressed we decided they were probably from this painting but in it's larger scale. Six patches were visible on the reverse (fig. 1). Two were obviously modern repairs using a sticky contact adhesive and linen fabric. The four remaining patches were cotton fabric attached with a water-based, ocher colored gesso. The age and technique of the four older patches gave rise to the possibility that the artist had done them in an attempt to smooth out some of the irregularities in the fabric. The overall flexible condition and strength of the fabric was quite remarkable, indicating that the painting had been in a consistent climate most of its life. Humidity in La Paz is always very low and generally consistent. The fabric was quite buckled and extensively undulated. The more recently patched areas caused a slight puckering of the original fabric. The older patches were not obvious from the front.

The strainer was constructed of six members: two vertical with the horizontal members butted in between the verticals. A horizontal cross-bar was positioned three quarters up or just above the center. It was notched into the sides of the strainer. The sixth member was attached to the right vertical and extended the width of the painting approximately 2" (fig. 2).

The canvas was glue sized followed by the even application of a thin, red earth-colored, oil-based gesso.

The paint was of a vehicular consistency typical of oil. Application was wet into wet with varying densities of opaque paint. Scattered areas of overpaint and indications of general abrasion were visible. The overpaint was obvious in the grey robe of the Christ figure, the sky, and scattered in the skin tones of the figures. An earlier restoration was thought to be responsible for the overpainted damages and, certainly, the abrasions.

A heavy layer of accumulated grime, and a yellowed natural resin varnish had obscured much of the subtleties of the image and artist intent. Carlos Rua felt that the varnish was most likely a copal resin which was commonly in use during this period and certainly in Bolivia, and the region surrounding it. Copal was also more accessible than dammar in South America.

TREATMENT

The treatment was intended to improve the structural and aesthetic quality of the painting by cleaning, consolidation, plane improvement, and retouching of losses.

The painting was removed from the strainer. The fabric was released from the strainer simply by removing the tacks from the top horizontal. The remaining three sides required an altogether different approach. Areas on the edges, that appeared to be fragile, were faced with wet-strength tissue using "colapez" as the adhesive. The colapez was a gelatin soaked in water until it gelled. It was diluted slightly but generally kept quite gelatinous. The canvas was then mechanically separated from the strainer using knives and spatulas.

The painting was placed face down on a protected surface, in order to address the glue residue and patches on the reverse. The two more modern patches were easily detached and the adhesive residue removed with petroleum distillates. Of the four remaining patches, still thought to be original, the bottom patch was the most suspicious, as it was a large lump of material that would not have been consistent with the craftsmanship of this artist. We then suspected this was applied at the time this painting had been reduced or cut from the larger painting. Closer examination of the remaining three patches revealed them to be of a similar fabric and adhesive as the first. The cotton fabric used for the patches was removed, the gesso adhesive softened with water, and reduced as much as possible. The areas of the patches were placed under blotters and weights to reduce planar distortion. These areas of canvas insecurity were reinforced with a minimum patch of tan, fine weight, nylon fabric attached using Beva 371 film and low heat.

The reverse had a heavy accumulation of dirt and general glue residue. It was lightly sanded, scraped, and thoroughly vacuumed. Areas of excessive glue were covered with a carboxy methyl cellulose gel (CMC) and scraped after the glue became soft. A perimeter, about 3" to 4", was scraped to establish an edge for a future strip lining. At this same time, the vertical, secondary edge strips from the right were removed, the reverse cleaned, humidified, and blotters and weights placed on top until dry.

The planar distortions in the canvas were addressed with a humidification treatment. Dampened filter paper was placed on the reverse and the entire painting covered with plastic sheeting. The painting was monitored closely for 30 minutes. Small plastic hygrometers, which I had brought to Bolivia, were used to monitor the Rh. The humidity never reached 80% (certainly an aspect of an environment with extremely low Rh). After 30 minutes the filter paper was removed and folded newsprint was placed over the entire reverse. Care was taken to butt the newsprint up against the seams of the fabric to reduce potential flattening of these seams. Plastic sheeting, boards, and weights were placed over the newsprint and left over night to dry gradually. The next morning the painting was examined. Although in much better plane, further reduction of the undulations of the canvas was desired. It was decided to treat the front before any further humidification treatment.

The facing paper and any adhesive residue was removed with water. Areas of insecurity were consolidated with an infusion of a warmed 20% solution of Beva 371 (ethylene vinyl acetate copolymer - Conservation Products Co.) in gasolina (a product somewhat similar to mineral spirits). Once all the diluent had evaporated, the areas of insecurity were returned to plane with the use of a warm tacking iron and gentle pressure.

It was decided to reattach the extension strips from the right vertical. Although they did not have a visual similarity to the edge, it was thought they were from this painting and, therefore, very important to have the strips remain with it. Encapsulating and putting them in the painting's file was not an option. The long pieces were aligned and reattached to the edge using wet-strength paper and a dilute CM-Bond M-4, (acrylic emulsion Conservation Materials, W. R. Grace, Co.).

Cleaning was carried out initially using a 5% solution of ammonium hydroxide (NH4OH) in water. This solution readily removed the heavy grime accumulation and reduced the copal varnish. The remaining varnish and overpaint could then be removed with either toluene or isopropyl alcohol depending on the areas to be cleaned.

A second attempt to minimize the planar distortions was made using the same method as before. This was more successful for the major undulations were removed and any other irregularities were acceptable.

The general good condition and flexibility of the canvas in combination with the lack of tacking edges made the painting a perfect candidate for strip lining. This was accomplished using linen strips of 8" width attached to the painting with Beva 371 film.

The painting was mounted onto a new stretcher of butt-end corners with mortise and tenon joints and secured with staples. Lascaux 360 HV (acrylic emulsion, A. K. Diethelm) was used to secure the back flaps of the lining to the stretcher. Wood keys were inserted and secured and the corners minimally expanded to put the painting into good plane and proper tension.

Losses in the painting were filled, before varnishing, to approximate the texture of the original paint using a traditional gesso material of calcium carbonate, dry pigment (in the red earth family), and cola tiza (gelatin). Fills were made using the warmed mixture. Excess was removed with water or saliva.

An isolating and saturating varnish of dammar resin diluted in gasolina, of approximately 15% dilution, was applied to the surface of the painting. The painting was so absorbent that repeated brushing was necessary to accomplish the even surface desired.

Losses and areas of abrasions were inpainted to match the surrounding original surface with dry pigments in PVA/AYAC (polyvinyl acetate resin, Union Carbide).

A beautiful surface finish was achieved and the inpainting integrated completely with the varnished surface. Thus it was decided to defer a final varnishing until the painting returned from exhibition. Carlos was hesitant about applying a brush coat of varnish over the inpainted areas even though I reassured him there would be no difficulty in applying a secondary varnish. There was no dependable spraying equipment available for a minimal varnishing and giving the inpainting an more than adequate period to temper was certainly an acceptable option. I was assured a final protective finish would be applied when the painting returned from exhibition in 8 months.

Many thanks are extended to the Fulbright Foundation, and to Kimberly King, the Cultural Affairs Officer for the United States Information Service at the U.S. Embassy in La Paz, Bolivia, who took the time and had the enthusiasm to expand my Fulbright experience to other parts of Bolivia. Thanks are also due to all the wonderful and helpful people at Instituto Boliviano de Cultura. A very special thanks to Carlos Rua, Chief Conservator, who set the example of an open exchange of ideas, and to his staff who were more than kind and generous with their time and genuine affection for a fellow colleague. We all learned from each other!!!

Figure 1

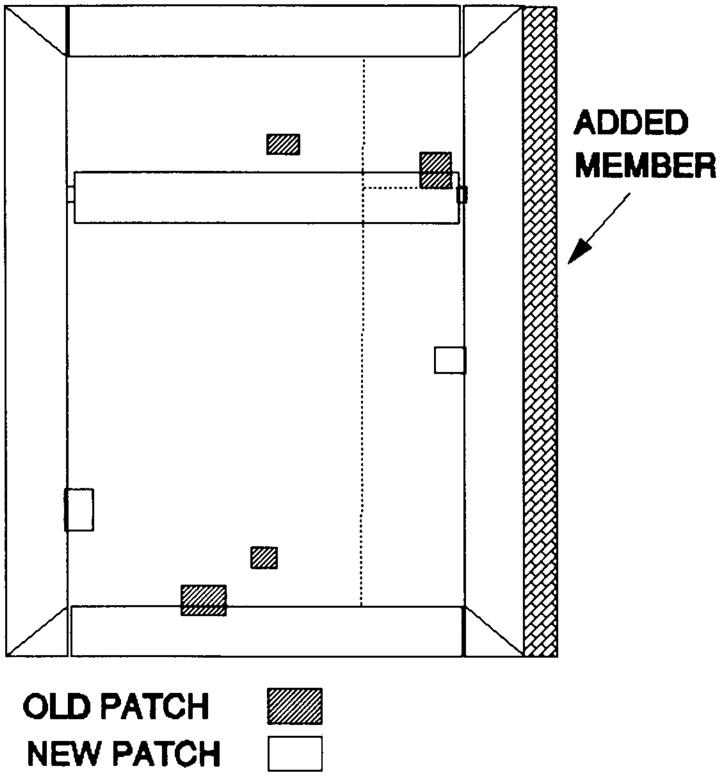

Figure 2

VANCE KIRKLAND: AN INNOVATOR OF ABSTRACT EXPRESSIONISM

(1904 - 1981)

Cynthia Kuniej Berry

INTRODUCTION

Vance Kirkland once said that "too many artists are bored with what they are doing, and it always shows."[1] In search of new ideas, Kirkland moved from the Midwest to Denver in 1929, to paint in the open spaces of the West, where he felt he could be free of all artistic influences. Having chosen the wilderness, rather than the feverish activity of the New York art scene, he was able to get in touch with his own imagination. Yet, aware of art history and current art movements, Kirkland wanted people everywhere to realize that art produced in the West could surpass the regionalism of cowboy and indian paintings. He also wanted people in the West to experience a more creative art. His pioneering spirit introduced Denver and the surrounding region to the 20th-century art world.

Kirkland produced nearly one thousand paintings, and half as many drawings, over a career spanning from 1927 to 1981. He spent the first half of his career working in watercolor or gouache. During this period, he produced a few works in casein, tempera, and oil. From 1954 on, however, he worked primarily in oil, experimenting briefly with acrylics and lithography. It was his mastery of the watercolor technique, in combination with the use of the oil painting medium, that eventually resulted in his unique creations. His work is shown in museums throughout Europe and the United States. Although he participated in as many as 159 exhibitions, only two known publications on the artist exist.[2] A recent documentary on Kirkland is in production, and will soon air on PBS. The film will undoubtedly introduce Kirkland to a wider audience.

The goal of this paper is to introduce Vance Kirkland to the conservation community through an overview of his work, his materials, and potential problems that may be encountered with his art. Vance Kirkland's painting technique developed over a period of more than fifty years, during which he passed from various realist modes to Surrealist and Abstract Expressionist styles, combining the use of oil paint and watercolor techniques. His style ultimately evolved into a unique series of "Dot Paintings" with oil and water floats as a ground. These paintings grew naturally out of the watercolors produced in the first half of his career.

DEVELOPMENT OF STYLE

Kirkland began his artistic training in a traditional academic manner at the Cleveland School of Art. He recalled that as a student he was expected to reproduce nature and the surroundings without imagination. Told that he put too much emphasis on the use of color, he recounted that his professors complained that he did not follow the rules, and had not solved the problems. Kirkland actually failed a watercolor class in his freshman year. Often he was told that one did not put certain colors together because they fight visually for attention.[3] Kirkland was unable to see why fighting with color was wrong. He found the fight stimulating. *Romantic Spring*, a watercolor of 1927 exemplifies his bold use of color. One of his teachers, who had been influenced by Hans Hoffman, supported and encouraged Kirkland's interest in using color theory as a means to express emotion.

Kirkland developed his own personalized watercolor technique during the late 1920s. He referred to his new way of looking at the natural world as "designed realism." These paintings became adaptations of, rather than reproductions of, the natural world. *Tulips and Rhubarb* for example, a 1931 oil painting, is a mysterious interpretation of color and rhythm. *Rhubarb Life & Death*, a 1936 watercolor, explores the passage of time visible in nature.

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During the 1930s, Kirkland began to look closely at other things in the Colorado landscape besides the mountains. The two watercolors, *Mountain Stream* of 1939, and *The Stream* of 1940, exemplify the more unrealistic imagery that characterized Kirkland's paintings of the 1940s.

Between 1940 and 1954, Surrealism became Kirkland's greatest vehicle for his expression with watercolor. Yet, he continued to experiment with casein, gouache, tempera, and occasionally oil. The intense solitude of painting in the mountains led him to produce paintings that focus on specific elements of the landscape. The paintings that resulted possessed mysterious and dramatic effects. In *Tree Form in the Mist,* a watercolor and gouache of 1944, a fallen tree is transformed into a ghostly form. The 1945 watercolor *Fantasy - Ten Million Years Ago* depicts a whole colony of people, intermingled with the decaying leaves inside the fallen tree. From this point on, his images continued to become even more abstracted.

Kirkland's works between 1947 and 1957 consist of his Abstractions from Nature, which fall into two major groups: the Timberline Abstractions, mostly executed in oil, and the non-objective Pure Abstractions. Although these groups of paintings overlap somewhat with the previous and following periods, and the delineation of styles is not always clear. *Fantasy Garden*, a 1945 casein, is a unique work that marks a transition into the Abstractions from Nature. The synchronistic energy of the 1952 watercolor *Colorado Quartet*, signals a transition into pure abstraction. It is considered the most pivotal work of Kirkland's career by Charles Stuckey, Curator of 20th Century Painting at the Art Institute of Chicago. The painting previsions the bursting energy, mysterious light, and amorphous forms of his later, fully developed most characteristic works.[4]

Trio, a watercolor of the following year, is Kirkland's first attempt at an oil and water resist on paper. Frustrated by attempts to control the movement of the materials within the drying period, he temporarily abandoned this technique. Kirkland continued trying to develop a way of translating his love for watercolor into using oil paint in a fluid way. He discovered that he could float tempera colors on a white gesso panel, although when the paint dried, its sharp edges created a static surface. Nor could he achieve the effects he wanted with casein, because of the short drying time. Even when he used a gessoed canvas, sanded smooth between the layers to emulate the quality of paper, and floated thinned oil color on the canvas, the paint still had a poured look that Kirkland did not like. This was the case with *Fantasy* of 1953, his first painting using oil and water on canvas.

But when he placed water on the canvas, and then added spots of oil paint, wonderful things happened. The Nebulae Series developed out of this technique. *Space Mysteries* of 1954 was Kirkland's first nebula painting using an oil and water float on canvas. The possibilities with this technique catapulted his vision away from earth, and toward space to explore the evolution of the universe. Simultaneously with the development of this series, he continued using oil and water to create pure abstractions with somewhat ambiguous titles, such as *Wrinkled White on Venetian Red* of 1954, which Richard Brettell, former Director of the Dallas Museum of Art, considered the best example of his break from watercolor to oil painting.[5]

Nebula Near Mars of 1959 demonstrates Kirkland's interest in the principal of dynamic symmetry.[6] He was concerned with balance, and the organization and movement of masses. The Explosions in Space Series became splashes, not of a brush, but of water and color erupting on the canvas, as in the 1960 *Creation of Space*. A year after this series began, he noticed the paintings resembled photographs of actual nebulae he discovered in current issues of *Time, Life,* and *Astronomy* magazines. Kirkland's abstractions of how he imagined space, began to look realistic. Avoiding comparison with the photographer's vision of space, he abandoned this idea temporarily.

In 1960 Kirkland went to Rome for an exhibition of his work at Galleria Schneider, where his paintings received considerable acclaim. He later visited villas in Pompeii, Naples, and Ostia Antica. These trips resulted in paintings influenced by the colors and textures of the excavated walls he observed there. *Villa dei Misteri,* and *Framenti di Villa Giulia* both incorporate oil and water floats that capture the essence of the Italian ruins.

Kirkland later traveled to India, Burma, Cambodia, and Viet Nam. There he found new color and movement in the decayed surfaces outdoors. The extraordinary patterns that contrasted with the colors of the Buddhist monks's robes are captured in *Memory of Cambodia* of 1961. These Asian paintings became larger than any he

Figure 1. *Memory of Burma*, 1963 no. 10, oil on canvas, 66 x 76 in. Photograph from *Vance Kirkland: Fifty Years*, exh. cat. (Denver: Denver Art Museum, 1978), p. 23.

had created before. *Floating Mysteries of Burma* measures 80" x 128", and is similar to the painting shown in Figure 1. In the former picture, the shapes are suggestive of three buddhas. The applied gold leaf, superimposed on vermillion, scarlet, and saffron reflects richness of Buddhist temples and the colors of the monks robes. The contrasting black and white relates to the to the decay of the once resplendent culture, and the shadowy encroaching jungle upon the ruins.[7] This period led Kirkland to the use of progressively stronger colors and larger canvases. These changes provided the tools necessary to explore space in his later paintings.

When he returned from his travels abroad, Kirkland's interest in the unexplored led back to outer space, but in a new way. He combined the expanded color and size he enjoyed in the paintings of the Orient, with the previous energy of the Nebulae, and Explosions in Space paintings. He revitalized the idea of using dots from his early watercolors, which were initially added merely as accents to break up the solid colored background. *Painting No. 2* of 1963 is the first painting of the Dot Series incorporating oil and water floats as a ground. *Painting No. 17* of 1964 succeeds in making the cool blue background advance on the red, by the kinetic movement of the speckled and applied dots.

In 1965 Kirkland abandoned the oil and water technique in *Blue on Blue Green*. The painting retains the amorphous nebulae forms through the gradual color transitions, and placement of dots to create shading, and a flow of movement in space. The dots started with irregular shapes and sizes. However, Kirkland eventually discovered that he could produce perfect dots using dowels. A dynamic energy is conveyed by the regularity of dots in *Vibrations of Yellow on Scarlet and Green* of 1968. During 1970 and 1971, the artist departed from such obvious geometric patterns, and used more color variation for the dots and backgrounds.

Kirkland became fascinated with the idea of combining the vibration of color with the idea of after images.[8] The after image becomes almost as strong as the actual image physically present in *Scarlet and Blue Forms* of 1972. Later that year, in *Painting No. 8*, he began using oil and water float backgrounds again to explore new themes. Diffusive matter and energy explosions interested Kirkland, and led him to produce free form, floating shapes that might be interpreted as the evolution of space.

Kirkland's latest paintings combine all the techniques of previous periods in a catalytic process generated by new concepts. These unique creations contain the energy of the previous Mysteries, and Explosions in Space Series, dominated by themes of universal time and evolution. They embody the directness of Designed Realism, the rhythms of Surrealism, the freedom of Abstraction, the floating forms of the Nebulae Series, the largeness and bold color of the Roman and Asian paintings, the color vibrations of Dot Series, and the dynamic expanding Energy in Space. All these previously explored concepts are combined in the culmination of Kirkland's artistic expression in his final period. *Scarlet, Yellow, and Blue Mysteries in Space* of 1973, continues the ideas of the Geometric Vibration Series. Dots completely cover the surface in *Conception of Space Mysteries* of 1974. The painting conveys what one might imagine seeing while looking at a cross-section of a gigantic nebula or galaxy.

The Scorpio Series of dot paintings developed with explosive, active, sprawling expanses of color. The background retains light and dark areas with floating forms, but splashes of oil and water have been added. A final abundance of dots is placed over such a background in *Unknown Energies of Scorpio* of 1977. Kirkland moved to explore the source of such energy in the stars and the suns. *Energy of Explosions 24 Billion Years BC* of 1978, uses intensely bright yellow, orange, and white radiating from two main centers of activity.

A more expansive example of such is seen in *The Energy of Explosions of the Sun 60 Billion Years BC* of 1978, which measures 75" x 100" with its trailing tails of dots, and is similar to the painting shown in Figure 2. Although the last paintings seem to approach scientific reality, Kirkland made no attempt to relate to scientific and astronomical observations. His first nebula painting of 1954, was created well before satellites were launched in space. Kirkland had established the Mysteries, and Energy of Space Series as the major forces of his career during the late 1950s and early 1960s, when images of space were not yet common to man. Space was merely a catalyst for his inspiration, but not a source for images. His artistic ideas were derived from interest in the microcosm of life, as well as the macrocosm of the universe. Kirkland once mentioned that his dots might also convey the idea of the multiplicity of cells and life forces.[9] This seems all the more evident in *Explosions on a Sun 70 Billion Light Years from Earth* of 1979. The viewer is drawn closer to the inside of the color explosion or life force, and is no longer observing from a distance.

Before his death in 1981, Kirkland completed his last work, *Forces of Energy from a Sun in the Open Star Cluster,* in his hospital room. *Forces of Energy from a Sun in the Great Star Cloud* had previously been started in his studio but remains unfinished, and provides a clue to the artist's working technique. It gives us the chance to study the way in which he built up a surface. Swelling currents have been laid down in the background, but the overlying washy wisps and veils of dots reveal less crispness due to the unsteadiness of his trembling hand.

MATERIALS AND TECHNIQUES

The Kirkland Studio remains today much as it did when the artist was alive, with many of his supplies still in stock.[10] Although the materials vary amongst the earlier works, the layers that constitute the last fourteen years of work are pretty consistent.

Kirkland used thick, specially reinforced stretchers and Belgian linen prepared with several layers of Liquitex gesso that was sanded between each coat. Only his earlier paintings were sized with rabbit skin glue. Inventory lists from his studio confirm that the artist's palette was diverse, including four brands of oil paint: Grumbacher, Liquitex, Shiva, and Winsor & Newton Permanent Pigments. He used as many as twenty-seven different reds, for example, but only lamp and mars black, and just titanium white. The paints were never used directly from the tube, but diluted with water, plus a mixture of turpentine and stand oil, or a just bit of linseed oil. Ron Babcock, an artist who worked with Kirkland during the last three years of his life, has claimed that Kirkland treated his paint like a dry martini: he would open the jar of stand oil close to the paint, but he never put a lot

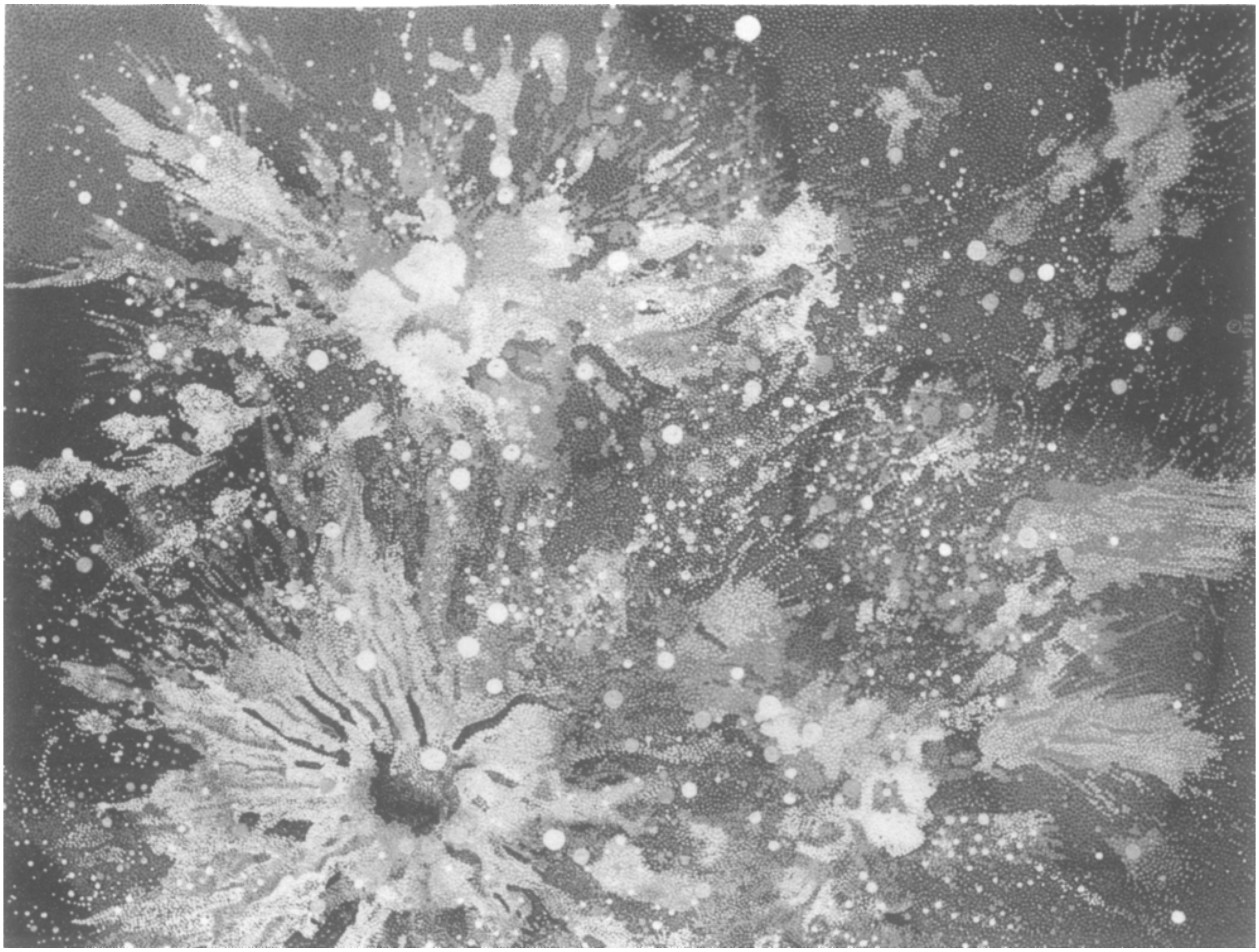

Figure 2. *The Energy of Explosions Twenty-Five Billion Years B. C.*, 1978, no. 4, oil on canvas, 75 x 75 in. Photograph from *Vance Kirkland: Fifty Years*, exh. cat. (Denver: Denver Art Museum, 1978), p. 32.

in. After awhile, Kirkland quit using stand oil altogether, and clearly had no set formula. How the paint was mixed depended on how Kirkland wanted the surface to appear.

Each of Kirkland's paintings required about a month to create. He worked on the paintings flat, painstakingly applying numerous layers of oil paint. Working from above, Kirkland moved constantly around the canvas. But he did not do this in the manner of Jackson Pollock, spattering paint on canvases on the floor.[11] Instead he worked flat on a table, where the painting could be closer to him. As his canvases increased in size over the years, it became difficult for Kirkland to reach the center of the pictures. When his hips began to give out, Kirkland became creative about his approach to technique. He had a mechanical pulley and harness designed so that he could be suspended over the table like a bird to reach the desired area.

Photographs of Kirkland at work illustrate part of the artist's oil and water painting technique. Over the smooth gesso, a background layer of flat forms was applied. This was usually one principal color varying in intensity and shade, and often in a gradation from one edge of the canvas to the other, or from the center outward. This process may have been repeated several times, and the area was sometimes heavily worked with broad brushes to achieve the desired effect.

In his second layer of floating forms Kirkland adapted the water color technique to the oil paints by floating or pouring them onto the canvas. Sometimes he used spoons to splash or splatter the paint on the surface. He controlled the movement of the floating form, directing the paint by pressing on the canvas. The water was immediately soaked off with paper tissues. Sometimes a paper towel was used to drag the paint and oil across the surface to a desired location. Kirkland also used tissues or paper towels for dabbing, to create a specific effect. Occasionally, he would place the towel down, and then pull on it in an upward direction to remove some of the water. This was similar to a technique he derived with the watercolor medium.

The final stage of his painting process appears as an abundance of dots of different sizes, colors, and textures, which were meticulously placed on the surface with wooden dowels. Some of the dots are quite sharp, while others are less defined, and appear to be floating. The dots were often applied between and around the forms, using dowels of various thicknesses. The majority of these dowels were actually old paint brushes with the ends cut off. To increase the size of the dots Kirkland cut branches from the tree in the yard behind his studio. Once completed, the paintings were allowed to dry flat for about three months, and they were coated with damar varnish after six months.

A few of the paintings that were produced between 1971 and 1972, when Kirkland was executing his Open Sun Series, have since exhibited a problem with adhesion of the dots. The dots began to delaminate and literally fall from the surface, revealing an oily film on the underlying paint. Not all of the paintings of the period, however, exhibit this characteristic. The artist discontinued using stand oil a short time later, but not necessarily because he knew about these problems. Although it is thought that Kirkland used similar materials throughout his career, there is no written record of how they varied. This problem remains to be investigated.

CONSERVATION TREATMENTS

Carmen Bria, of the Western Center for the Conservation of Fine Arts in Denver, recently treated Kirkland's *Il Muro a Ostia*. This oil painting exhibited planar distortion due to the slackness of the fine weave linen support, and the insufficient strength of the stretcher to support the weight of the paint layers. Reddish stains of an unknown origin, visible on the reverse, were unrelated to the cracked and flaking commercial ground and subsequent paint layers. Weak ground to canvas adhesion was obvious on the unpainted tack edges. Recently acquired from Ostia, the painting may have suffered from exposure to an uncontrolled Mediterranean environment, rather than problems induced by its construction. The unvarnished soiled surface was disfigured by crude attempts of a previous restorer to conceal the unfilled losses.

The treatment involved overall consolidation from the reverse with dilute BEVA 371$_{\circledR}$, an ethylene vinyl acetate copolymer (Conservator's Products Co.), activated on the vacuum hot table. The painting was restretched on the original stretcher, which had been modified with a cross-bar. Excess adhesive was removed from the surface with xylene. Grime was reduced using a dilute solution of Triethanolamine (Sigma Chemical Co.) in distilled water. The painting was sprayed with an acrylic varnish. Losses were filled with an acrylic/calcium carbonate compound. The most interesting aspect of the treatment involved cosmetic compensation. This was to be completed by the restorer at Kirkland Studio. Although not documented, according to Hugh Grant, the artist apparently did not want his pictures retouched with acrylic paint. Kirkland preferred this be done with materials and techniques similar to the original. Having worked with the artist for years, Kirkland's restorer was comfortable to reproduce the artist's palette and techniques.

Kirkland's painting *Friends* was also treated recently by Bria. Numerous dents, dings, punctures, and insecurities were accompanied by, an overall raised crack pattern, and extensive scattered loss of the ground and unvarnished paint layers.

Flaking paint was first locally consolidated with dilute BEVA 371. Planar distortions were relaxed with controlled moisture treatments. The tears were aligned and reinforced with CM Bond W-2$_{\circledR}$, a poly (vinyl acetate) emulsion (Conservation Materials, Ltd.). The painting was then infused overall from the reverse with BEVA 371. It was lined to glass fiber fabric prepared with Rhoplex AC 234$_{\circledR}$, an acrylic emulsion polymer (Rhom and Haas), and then lined to linen using BEVA 371 as an adhesive between each layer. The lined painting was restretched on the original stretcher. After being coated with Liquitex Soluvar Gloss Picture Varnish$_{\circledR}$, a mixture of butyl methacrylate resins in petroleum distillate (Binney & Smith, Inc.), losses were filled with an acrylic/calcium carbonate compound. Bria inpainted the losses with oil paints at the request of Hugh Grant. Bria determined this to be an acceptable solution, in this case, because Hugh Grant was adamant that Kirkland did not approve of acrylics for retouching his paintings. Bria was confidant that the oil paint would be applied only over reversible fill material, it could be safely removed if necessary, and it will remain detectible in ultra-violet light.

CONCLUSION

Vance Kirkland was an eminent artist whose work is gaining recognition. His mature Abstract Expressionist style explores the dynamism of space using innovative oil and water emulsions. Conservators should be aware of the complicated surfaces that resulted. Kirkland's unique mixtures and his wishes concerning conservation warrant consideration when one is confronted with the treatment of these paintings. Information that might contribute to research on this subject is welcome.

ACKNOWLEDGEMENTS

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NOTES

[1] Grant, Hugh, *Vance Kirkland; Mysteries in Space*, (Denver: Hugh A. Grant and Paragon Productions, 1978), p. 53.

[2] Only two known publications on Vance Kirkland exist. One is Hugh Grant's catalogue based on an exhibition at Genesis Galleries, Ltd. in New York, and on a documentary survey centered on discussions with the artist about his work. The other is *Vance Kirkland: Fifty Years*, an exhibition catalogue (Denver: Denver Art Museum, 1978).

[3] Ibid., Grant, p. 4.

[4] Unpublished manuscript transcribed from interviews conducted between 1991 and 1993 for a documentary on Vance Kirkland produced by Hugh Grant for PBS. Those interviewed include: Richard Brettell, Dallas Museum of Art; Peter Briggs, Museum of Art of the University of Arizona; Elizabeth Broun, National Museum of American Art; Lewis Sharp, Denver Art Museum; Charles Stuckey, The Art Institute of Chicago; and Diane Vanderlip, Denver Art Museum.

[5] Ibid., Brettell.

[6] Grant (Note 1), p. 70.

[7] Ibid., p. 67.

[8] Ibid., p. 68.

[9] Ibid., p.72.

[10] The author's visits at the Vance Kirkland Studio to interview Hugh Grant, curator and lifelong friend of the artist, and Ron Babcock, an artist who worked with Kirkland during the last three years of his life, provided information on his choice of materials and techniques.

[11] Brettell (Note 4).

CAUTIONS FOR CONSERVING CHINESE WALL PAINTINGS

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INTRODUCTION

Conservators at the Rocky Mountain Conservation Center have been responsible for conservation of a Ming Dynasty wall painting, *The Female Attendant*, from the collection of the Denver Art Museum. The fragment was showcased in the Museum's centennial exhibition, "Collecting, Preserving and Interpreting," with an accompanying film segment which demonstrated and discussed its conservation process. The painting is attributed to the Shaanxi Province of Northern China.[1] The materials and techniques employed in construction of the painting and the subsequent alteration and restoration, together with constraints on time and funding, required that particular caution be exercised in its conservation. This paper will present aspects of the examination, analysis and treatment of the painting.

DESCRIPTION

The painting fragment, which measures 162 cm high, 75.2 cm wide and 3.2 cm thick, depicts a nearly life-size female attendant in elegant, flowing robes, playing pipes. Attendants such as this usually flanked a central Buddhist figure. The fragment was part of a larger wall painting, probably from a temple setting. The palette consists of thinly painted passages of red, dark green, blue, gray, black, brown and ivory colored-paint. Details of the hair ornaments, collar, jewelry and edges of the costume worn by the woman are composed of relief decorations with yellow metal leaf.

Asian wall paintings were typically painted *a secco* on the prepared surface of a natural rock grotto or an architectural wall, perhaps in a temple. Preparation usually involved application of one or more rendering layers of clay or mud in a cohesive matrix of vegetable fibers,[2] followed by a smooth ground layer which might include kaolin, gypsum, calcium carbonate or other associated minerals. The paint medium was typically composed of inorganic pigments and organic lakes bound in a water-soluble glue or gum.[3]

EXAMINATION AND CONDITION

Treatment rationale was predicated on the findings of surface examination, testing and technical analysis.[4] Surface examination indicated that the wall painting fragment had undergone extensive alteration during removal from its original setting and subsequent restoration, including major fractures which have extended vertically through the rendering and lesser cracks which radiate perpendicularly from them. A fabric scrim was adhered to the reverse with animal glue, probably to hold the painting together after the transfer process. This scrim was, in turn, affixed to a plywood support with additional animal glue. Losses were either filled with plaster and inpainted or the rendering itself simply inpainted to visually minimize disfiguring losses in the paint layer. A plaster surround was applied to the perimeter of the fragment and painted a purplish-brown color. The rigid, inflexible nature of the surround and fills contributed to the weakness of the perimeter of the rendering layers.

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Attachment to the plywood support was evaluated by probing the interface from the edges, investigating strata exposed when two interior fills were removed, and by studying surface topography and deflection induced by gentle downward pressure on the surface. (An alternative examination technique developed in the aircraft industry, air-coupled ultrasound,[5] was explored for use in determining the presence of air pockets between the layers. For logistical reasons and associated cost, this technique was not pursued for this project.) It was determined that the rendering and scrim layers had locally detached from the plywood along its perimeter beneath the rendering no more than 7 cm from the edges. The perimeter of the rendering layers, exposed on removal of the plaster surround was found to be desiccated and friable, requiring consolidation.

⇧ The Female Attendant, unknown painter after conservation treatment.

Examination of the paint surface revealed a porous, friable surface which appeared dull and darkened.[6] Traces of bright color were exposed on removal of portions of the plaster surround, suggesting significant alteration of color had occurred, perhaps as a result of exposure to light and other environmental factors. It was obvious that some passages of color, as well as outlines, had been enhanced by a later hand. A coating was observed which appeared to have been selectively applied, being more prevalent in the blue and gray passages and absent from red, green and white passages. The coating displayed yellow-green autofluorescence under long-wave ultraviolet illumination, typically associated with aged triterpene natural resin films, and was presumably applied as a surface consolidant to arrest flaking and paint loss. The coating may have actually caused or aggravated this insecurity. Accumulated surface grime was observed overall, obscuring the selectively-applied coating and complicating its removal. The perceived color of the paint surface was altered as a result of accumulated grime and the degraded coating.

Initial tests for solubility of the grime layer, coating and paint film revealed that the paint surface, particularly the uncoated red and greens, was disrupted by aqueous systems which were partially effective in removing surface grime: distilled water, saliva and a 1% (w/v) solution of trisodium phosphate in distilled water. The paint surface was stable to application of petroleum benzine, xylenes, and ethanol, but these non-aqueous solvents were ineffectual in removing grime. All cleaning systems were readily absorbed by the porous paint, ground and exposed rendering.

TECHNICAL ANALYSIS

Analysis of two multi-layered fragments[7] by visible light microscopy and fluorescence microscopy[8] revealed the presence of two rendering layers, a single ground layer, underdrawing, single paint layers and metal leaf. The two rendering layers were found to be of similar composition, composed of dried earth material in a matrix of vegetable fibers; multi-layered particles were observed which appeared to derive from painted or decorated surfaces.[9] The layers were differentiated only by the higher proportion of fibers in the lower layer. Elemental analysis by scanning electron microscopy/energy-dispersive spectrometry (SEM/EDS)[10] revealed the layers to be rich in silicon (Si), calcium (Ca) and aluminum (Al) with minor presence of sulfur (S), potassium (K) and iron (Fe). A sample of the rendering was analyzed by Fourier-transform infrared microspectroscopy (FTIR),[11] and no organic binder was detected.

A single white ground layer was observed adjacent to the rendering layers. Particle analysis by polarized light microscopy (PLM),[12] SEM/EDS and FTIR revealed the presence of kaolinite.[13] FTIR also revealed the presence of weak amide bands at 1625.1 and 1544.0 cm^{-1}, indicating the presence of a small amount of protein , possibly a binder.

Each sample revealed a single thin underdrawing layer composed of finely-divided carbon black particles which conformed to the surface of the ground layer. Each sample contained a single thin paint layer varying in thickness from 2-26 micrometers. Poor resolution of the surface coating and accumulated grime along the deteriorated, porous surface of the cross-sectional samples did not allow identification of component materials or precise sequence of layers. Analysis of a gilt portion of the painting revealed a thin metal leaf layer secured to the paint surface by an unidentified autofluorescent mordant layer; qualitative SEM/EDS revealed the composition of the leaf as gold (Au) with trace amounts of copper (Cu) and possibly silver (Ag).

Pigment identification was performed by PLM and SEM/EDS on seven paint samples individually removed from the surface of the painting. (Budget constraints did not allow confirmation of pigment identification by x-ray diffraction.) The paint samples were found to contain vermilion, red lead, possible hematite, ultramarine blue, yellow ochre, carbon black, calcium carbonate, and calcined bone. Each sample also contained a significant quantity of quartz and other unidentified minerals, present as fillers, or as contaminants in sampling from the underlying ground layer. FTIR analysis of the vermilion sample revealed the minor presence of protein, possibly a binder.

TREATMENT

A central issue to the conservation of the painting was the structural insecurity which resulted from detachment of the rendering from the plywood support. Removal of the plywood support would allow general consolidation of the rendering layers from the reverse and replacement of the plywood with a more stable, inert support, but examination did not indicate that the condition warranted such invasive treatment. Consequently, a less invasive consolidation was performed.

Having determined the extent of detachment from the plywood support and the condition of the rendering layers, steps were taken to consolidate the perimeter of the rendering layers and re-establish adhesion between the rendering, scrim and plywood support. The literature on conservation of similar wall paintings cites a wide range of consolidants used in their conservation.[14] Several of these consolidants were tested on the exposed perimeter of the rendering and the results noted. Of the consolidants tested, a 2.5% (w/v) solution of methylcellulose, a cellulose ether, was selected for consolidation of the friable edges of the rendering layers because it imparted sufficiently high cohesion to the exposed edges while causing minimal alteration in the appearance of the rendering or adjacent ground and paint layers.

The next step was to choose an adhesive to secure the lifting portions of the rendering to its plywood backing which could be reversed mechanically or with heat. The physical properties and reversibility of several adhesives were evaluated on prepared test blocks,[15] and a 50% (w/v) solution of Acryloid B-72 in acetone bulked with an equal volume of glass microspheres was chosen to augment attachment between the rendering and plywood support as it could be easily injected beneath the lifting edges, provided both adhesive and bulking properties and could be reversed with a heated microspatula.

Compensation and replacement of the plaster surround and fills was discussed the Associate Curator of Asian Arts at the Denver Art Museum, and it was determined to replace the plaster surround and the two fills removed during examination, but not to reconstruct lost design. A variety of fill materials based on synthetic spackling compounds were tested. Pollyfilla, a mixture of calcium sulfate and cellulose fiber, was selected as the fill material. The exposed edges of the rendering were first isolated with a 5% (w/v) solution of Acryloid B-72 in acetone. The Pollyfilla was bulked with macerated blotting paper and toned with pigment to approximate the color of the rendering layers, and was applied using a microspatula, and toothbrush to simulate the surface texture of the rendering layers.

Removal of accumulated grime, degraded coatings and restoration was then considered in consultation with the museum's Director, Associate Curator of Asian Arts and Conservator. The issue of cleaning was particularly vexing from numerous standpoints: how the painting might have originally appeared, what alterations might have resulted on long-term exposure to light and other environmental factors, what alterations might have resulted due to human intervention, and how cleaning might be safely achieved.

Initial examination and technical analysis revealed the paint and preparatory layers to be porous and friable, water-soluble and subject to damage by abrasion -- especially since the paint layers were observed to be extremely thin and granular, conforming to the adjacent ground. The unvarnished red and green passages of the painting proved most sensitive to removal of accumulated grime as they were not protected by applied coatings.

Aqueous and non-aqueous cleaning systems quickly penetrated the surface due to its porosity. In order to restrict penetration of test solvents, some of which had proved effective in removing the accumulated grime and varnish, various solvent combinations were gelled with polyacrylic acid.[16] The resulting gels containing mineral spirits, xylenes, ethanol or acetone and a minor proportion of water could be applied to select coated surfaces of the painting without lateral flow or significant penetration through the paint surface. Tests indicated that the discontinuous coating could be safely reduced in thickness, but that, in practice, exposed unvarnished paint could not be cleared of non-volatile components of the gels without disrupting its surface. Additional aqueous cleaning systems were tested for removal of grime without success, including use of very dilute solutions of ammonium hydroxide and ammonium citrate, a chelating agent.

The Associate Curator for Asian Arts was consulted regarding the susceptibility of the paint surface to disruption from removal of residual grime and degraded coatings and the need for additional examination and analysis. Constraints on time and budget allowed neither additional analysis to investigate more fully the order and interaction between paint, grime and coating, nor more extensive testing of other cleaning systems. The desire to recover a balanced, even surface precluded selective removal of grime and varnish.[17] It was therefore decided to forego removal of the grime and coating until sufficient time and funding could be appropriated for a more thorough and systematic treatment.[18] A soft sable brush and micro-vacuum were used to remove airborne debris from the surface of the painting, leaving embedded or firmly attached grime, and the degraded coating intact.

CONCLUSION

In applying accepted standards of practice to provide appropriate conservation treatment of this Chinese wall painting fragment, we have gained a deep appreciation for the delicate surfaces and fragile nature of these objects, and the caution which must be exercised in their conservation. We have adopted a very conservative approach to the conservation of this painting in keeping with the level of research and time we have been permitted.

ACKNOWLEDGMENTS

In addition to the numerous colleagues who contributed to this project by sharing their knowledge and experience in conserving Chinese wall paintings, the authors thank Carl Patterson, Chris Stavroudis and Richard Wolbers; Pam Martoglio of Spectra-Tech, Inc. (Stamford, CT) for providing FTIR-microspectroscopy; Gary Hansen of E. Licht Co. (Englewood, CO) for use of their Wild MPS photomacrograph system; and Nancy Piatczyc and Williams College for use of the Cambridge Stereoscan SEM.

ENDNOTES

[1] Attribution was made by Julia White, Associate Curator of Asian Arts, Denver Art Museum, on the basis of historical and stylistic aspects of the wall painting fragment. The painting was acquired by the Denver Art

Museum in 1991 from a local art dealer. Background information on the painting is scant, with no documentation of its provenance, detachment, or subsequent restoration.

[2] Numerous sources describe materials and techniques used in these preparatory, or rendering, layers; however, few sources describe composition beyond general terminology such as clay, mud, mud plaster, etc.

[3] While binders such as fish glue, animal glue and various gums have been described in literature, analysis often fails to detect their presence, presumably due to initial use of very dilute concentrations or chemical alteration with time.

[4] Examination and treatment of the painting was undertaken at the Rocky Mountain Conservation Center by conservators Cynthia Kuniej Berry and Judy Greenfield. Technical analysis was performed at the Williamstown Regional Art Conservation Laboratory and Williams College by James Martin.

[5] The use of air-coupled ultrasound, a technique developed for aircraft technology, was considered as a means of determining the bond between the rendering and the wooden support. Chris Fortunko (National Institute of Standards, Boulder, CO) developed the technique with Alison Murray (Analytical Research Services, Canadian Conservation Institute) for examination of panel paintings; the technique is the subject of Murray's doctoral dissertation. Murray applied the technology to both actual and mock panel paintings to detect cracks and delaminations in, and between, the paint, ground and support layers. In air-coupled ultrasound, a signal is sent through the painting by a transducer and received by a second transducer. If the sound wave encounters a void in the structure, the signal is interrupted; the two-dimensional image produced is characteristic of a type of disruption, whether crack or delamination. Coupled with x-radiography, this technique has the potential for assessing unseen flaws in a variety of artifacts in a non-intrusive, non-destructive manner. A portable apparatus is under development.

[6] The possibility that some surface discoloration or darkening may have resulted from chemical alteration of pigment, especially vermilion, was considered. Definitive analysis to ascertain the presence of such alteration products was precluded by time constraints and was a factor in the decision not to clean the painting.

[7] Multi-layered fragments were embedded in slotted capsules using Bio-Plastic® resin (Ward's Natural Science Establishment Inc., Rochester, NY) which was prepared using ≈ 1.75 ml of MEK peroxide catalyst per 10 ml of casting resin and polymerized at 46C for two to three hours. Sectional planes were exposed for analysis using an American Optical 820 rotary microtome with steel knife; multiple sectional planes were exposed in each sample to assess consistency of layer number and arrangement.

[8] Sectional planes were examined using an Olympus BH-2 (BHSP) polarizing light microscope equipped for individual or simultaneous oblique visible, transmitted visible and epi-fluorescence illumination. Sectional planes were covered with Soltrol 130 and cover glass for examination. Epi-fluorescence illumination is provided by a 100 watt high-pressure mercury lamp and two filter/dichroic mirror cubes (ultraviolet cube, 365 nm maximum excitation/435 nm emission; violet cube, 435 nm maximum excitation/475 nm emission).

[9] These particles were not studied in detail, but appeared to be composed of multiple colored layers; the color and sequence of these layers contraindicated naturally-occurring metal corrosion layers. The particles did not derive from preparation of the samples. They probably are man-made in origin, present in the rendering layer as extraneous material, or perhaps inadvertently added as filler.

[10] Sectional samples for SEM/EDS were adhered to tapered capsule blocks mounted to aluminum stubs, carbon sputter-coated, and analyzed using a Cambridge Stereoscan 100 scanning electron microscope equipped for energy-dispersive spectrometry with a Tracor lithium-drifted silicon detector. Accelerating voltage was 15-20kV. Magnification, raster size and acquisition times varied by sample.

[11] Samples were analyzed by Pam Martoglio (Spectra-Tech, Inc., Stamford, CT) using a Spectra-Tech IRμS FTIR microspectroscopy system (15x objective, doubly apertured, narrow-band MCT detector). Transmission samples were compressed on a diamond cell with a small crystal of KBr. Transmission spectra were acquired from 600-4000 cm^{-1} using a triangular apodization function with a resolution of 8 cm^{-1}. 256 background and 256 sample scans were ratioed to obtain spectra. Attenuated total reflectance (ATR) spectra were acquired by contact with the ZnSe crystal of the ATR objective.

[12] Samples for PLM were prepared by dispersing several micrograms of randomly selected particles between glass slide and cover slip using Cargille meltmount 1.662 (refractive index 1.662 @ 25C; R.P. Cargille Laboratories, Inc., Cedar Grove, NJ).

[13] The ground layer also contained associated colored and colorless minerals of low refractive indices and varying degrees of birefringence; funding constraints did not allow for identification of these minerals.

[14] These consolidants included Acryloid B-72 (Bone, 1988), Beva D-8 (Gordon, personal communication, 1992), cellulose ethers (Malenka, personal communication, 1992), polyvinylbutyral (Miller et al, 1987), Primal AC 33 (Schwartzbaum et al, 1983), Rancanello E 55050 (Hanna et al, 1988), Rhoplex AC234 (Phillimore et al, 1984), Vinavil (Schwartzbaum et al, 1979), and Wacker Stone Strengthener (Schwartzbaum et al, 1979).

[15] Several adhesives were tested: Acryloid B-72 bulked with glass microspheres, PVA-AYAC, Lascaux 360HV and methylcellulose.

[16] Polyacrylic acid is a thickening agent which is commercially available from numerous vendors, including B.F. Goodrich (Cleveland, OH) under the tradename Carbopol®. The Carbopol® resins were dispersed in the solvents, and the dispersion thickened by addition of Armak® Ethomeen ethoxylated amines (Akzo Chemie America; Chicago, IL) according to discussions between Cynthia Kuniej Berry, Chris Stavroudis and Richard Wolbers. Dry cotton swabs were used to remove the bulk of gel; standing residue was removed using swabs saturated with the constituent solvent. Use of these gels was reconsidered following results of technical analysis.

[17] The decision to not undertake selective cleaning, or general cleaning without definitive analysis. is aptly underscored by the following quotation from Mora, Mora and Phillipot: "... the removal by cleaning of all non-original materials does not restore the work to its original state, i.e. the state in which it was left by the artist on completing the original work. It simply reveals the present state of the original materials."

[18] Additional research, which may permit further treatment of the painting, is being undertaken through a collaborative project with conservators at the Williamstown Regional Art Conservation Laboratory to present a joint paper at the conference "Conservation of Ancient Sites on the Silk Road" in Dunhuang, People's Republic of China in October 1994.

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THE SUCCESSFUL USE OF SOFT FACED MONOMESH AS THE LINING SUPPORT FOR A 14' x 17' MURAL

Susan S. Blakney, Paintings Conservator

In 1981 Margaret Sutton and I from West Lake Conservators Ltd. began a search for synthetic fabrics suitable for the lining of paintings. After two years of testing lining adhesive systems, with collected samples, in a variety of combinations, we presented our findings at the 1983 AIC Conference, in Baltimore. Our Poster Session was titled "A Sensual Lining Comparison". This resulted in the introduction of Terytex®, a 100% polyester multifilament plain weave, which has now been used as a lining support in many labs across the United States.

Another ideal support fabric we discovered was Monomesh, an unusual material which meets the desired characteristics for lining canvas murals or oversized paintings, and also has potential for numerous other conservation applications. Available in many styles, in widths up to 390" (32.5'), its stiff yet flexible and porous characteristic offers a semi-rigid support which lends itself to a variety of lining and installation techniques.

We selected Soft Faced Monomesh, style SE-8334 (Fig. 1) as an ideal support for the lining of oversized paintings. This two-ply weave (recently renamed Monotex) is composed of rectangular cross section polyester monofilament yarns in the machine or warp direction, and a combination of monofilament and spun acrylic yarns in the cross-machine or weft direction (Fig. 2). Both polyester and acrylic are chemically inert and have resistance to changes in temperature, relative humidity, moisture absorption, rot, microbial attack, and organic solvents.

The fabric ranges from 3.5 to 4.5 oz. per square foot. Its tensile strength is 1,100 lbs/inch to break, with elongation of 23% at break. Its permeability of 25 CFM is an advantage as an air conduit in vacuum applications, and for ease in reversing adhesives with direct application of solvents through the reverse. The spun yarns incorporated in the face of the fabric together with the special weaves employed, result in a very smooth and soft contact surface. The fuzzy nap offers strong adhesive attachment (Fig. 3).

Manufactured by an established international company, SCAPA Inc. (Forest Products Division, Waycross, Georgia) as a dryer fabric, Monomesh is used in the paper industry to create a non-marking surface in the drying of paper sheet. Monomesh belts run at high speeds (up to 50 mph), have excellent wear resistance and a high heat tolerance (285° F. acrylic and 300° F. polyester). The rectangular yarns give the fabric increased stability and resistance to bowing on the paper machine.

Also available are flawless Y-Pin seams, designed to be non-marking. This allows the fabric to become endless, and create a sharp angled bend. The fabric can be easily rolled for transit or storage. It can be cut with heavy scissors and the edges heat-sealed to prevent unraveling. Monomesh is woven on high tech looms to precise specifications, resulting in absolutely smooth dryer fabrics with a high degree of repeatability, which are designated with an "ISO 9001" International Quality Standard. SCAPA's "Total Quality Commitment Program" makes customer satisfaction a priority, and custom orders are welcome.

In 1986, our first proposed use of this fabric, to line a group of badly cupped, oversized oil on canvas paintings, did not materialize due to funding problems. We did, however, vacuum line with Beva 371® adhesive, a formerly cut out section of one painting, to be used for fundraising purposes, to demonstrate how the paintings could be stabilized and as a test for monitoring the corrected surface plane. No weave interference was detected, and the vignette remains stable seven years later, although displayed in a harsh uncontrolled environment. Excited by the prospects of Soft Faced Monomesh, Margaret Sutton and I presented the fabric at the 1986 AIC Conference in Chicago. We were too late for the abstract to be included in the Pre-Prints. This limited introduction was titled "Soft Faced Conserve Monomesh, A Possible Lining Support For Oversized Paintings". Due to the infrequency of treatments of this nature, it wasn't until several years later that we had the opportunity to employ Monomesh as proposed.

West Lake Conservators, Ltd., P.O.Box 45, Skaneateles, NY 13152

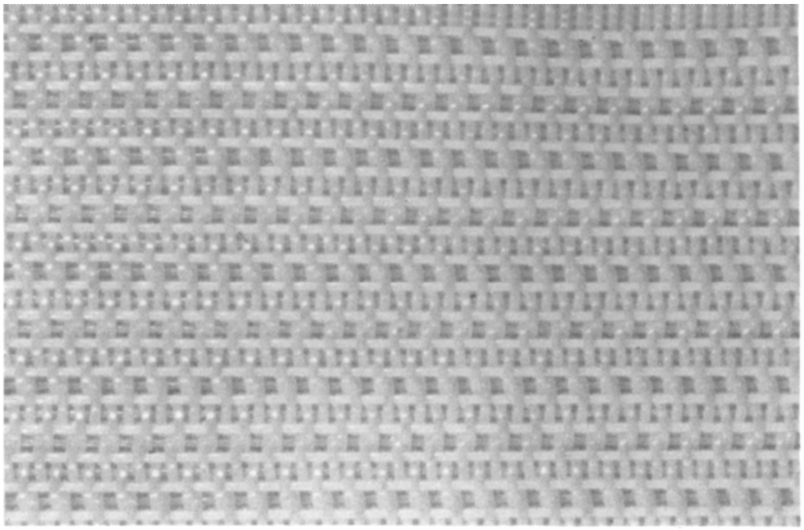


Figure 1

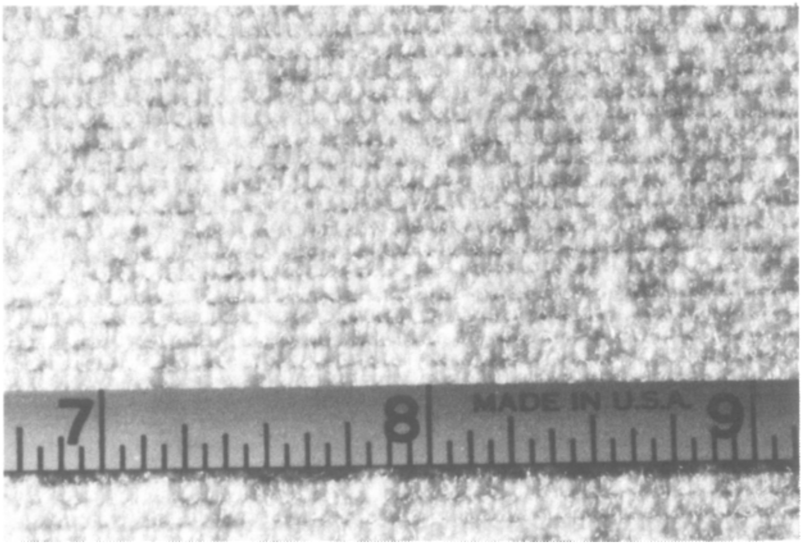
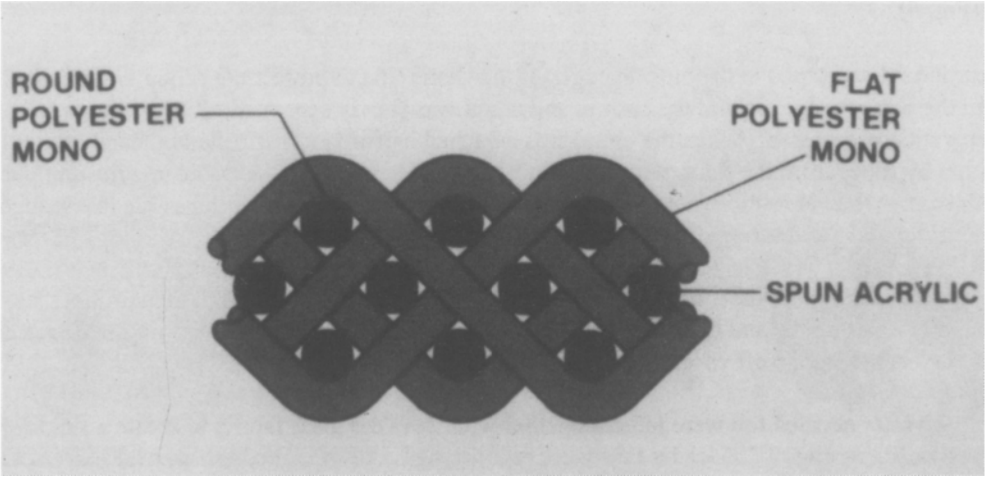


Figure 2

Figure 3



In March, 1990,West Lake Conservators were asked to save a 14' x 17' WPA-era mural, which was doomed to destruction by scheduled renovation. The mural was designed and painted by Virginia True in 1937. It depicts the mission of the College of Human Ecology, where it is located at Cornell University, Ithaca, NY. Our team was composed of associate conservators Margaret and John Sutton, apprentice Kennis Howard, and myself. With just over a month's lead time, we planned and completed its removal during the college's 5-day spring break.

The painting was executed in low profiled oils upon a heavy weight canvas with a thin oil ground. The canvas was glued tightly, to a plastered, concrete wall, with a water based adhesive. A simple strip molding covered and framed the outside edges. It was located 10' from the floor, above a black board, in a two-story amphitheater with very cramped floor space, and limited access through a narrow corridor, off of a hallway. This necessitated precise calculations and planning to accommodate equipment and the removal of the rolled mural (Fig 4).

Block and tackle, rented from our local sailboat shop, was secured by a Cornell maintenance crew to ceiling beams, approximately four feet from the wall, beyond the ends of the mural. The space age fiddle blocks (500 lb. test) with ball bearings and jam cleats, made relatively easy work of lifting and securing heavy weights. Electric Genie lifts proved the only means of accessing the mural repeatedly from top to bottom with ease, while allowing necessary clearance to roll the mural. Limiting toxic exposure was a major priority when selecting all of the materials. The possible effects of toxic vapors was thoroughly considered, both to ourselves and to others within the building. A protective working varnish of Soluvar was applied by brush from top to bottom. Next a paper facing of wet-strength tissue cut roughly in 16" squares, was applied with wheat starch paste.

Wide tabs of Beva® impregnated fiberglass cloth and Terytex®, were wrapped around an existing 1/2" diameter metal cable, which was stretched along the ceiling and top edge of the mural. These tabs were heatset onto the faced mural, with Beva® film adhesive and hand irons. This precautionary measure was taken to safeguard against the mural falling during separation. Simple tools of varying lengths were cut from scraps of G10 phenolic resin plate. Two layers were taped together quickly, with double sided tape, for increased rigidity of the handle section, and the tips were beveled with a file. These extended our reach, and facilitated separating the canvas from the wall.

Once the bottom 1/4 of the mural was separated, wide leader tabs of Beva® coated fiberglass and cotton duck were heatset in place, with Beva® film adhesive and hand irons. The other ends were stapled to the tube and covered with tape. These leaders allowed the mural to be rolled without crimping the painting, while lifting the mural away from the wall, thus creating space to continue the separation. A 20"-diameter Sonotube® on which the mural was to be rolled, was prepared by covering the outside with acid-free blotter secured with double-sided tape. Two layers of 3/4" thick plywood were cut into circles matching the inside diameter of the tube, glued and screwed together. Holes were drilled through the centers, and the prepared templates were inset 6" into each end of the tube, and screwed securely in place with flathead wood screws. A 3-section 2" galvanized pipe was run through the tube, and floor flanges were screwed onto the threaded ends. The tackle was tied to both ends of the pipe; the roller was lifted off the floor (Fig. 5).

Cushioning cardboard was taped to the outside edges of the Genie lifts to protect the rolled mural from contact. Working from the bottom edge, behind the canvas, the mural was slowly separated. Plaster debris fell clear of the roll as the separation progressed. When the mural was detached halfway, it was rolled by hand onto the tube, as it was lifted higher by ropes from the floor (Fig. 6). Again the Genies were indispensable in adjusting our working platforms with ease. When at last the mural was free, the tube was lifted to the ceiling as the last section was rolled on. We cut the safety tabs and lowered the tube to 4 x 4 standards resting on dollies.

After sawing excess ends off the tube, four men maneuvered the rolled mural through the corridor, into the hallway, through exterior doors, and back into a nearby auditorium. Here the mural was unrolled face down onto a sheet of polyethylene, to scrape off excess plaster and vacuum the reverse.

Wide strips of polyester needled felt were joined together with Beva'd® glass fabric, to create a single sheet of cushioning interleaf for storage. The leader tabs were repositioned, and the rolled felt was laid across a row of chairs behind the tube. Rolled strips of glassine were laid beneath it on the floor, and the ends of all layers were secured to the tube with staples and taped over. The mural was re-rolled onto the suspended tube with both

Figure 4

Figure 6

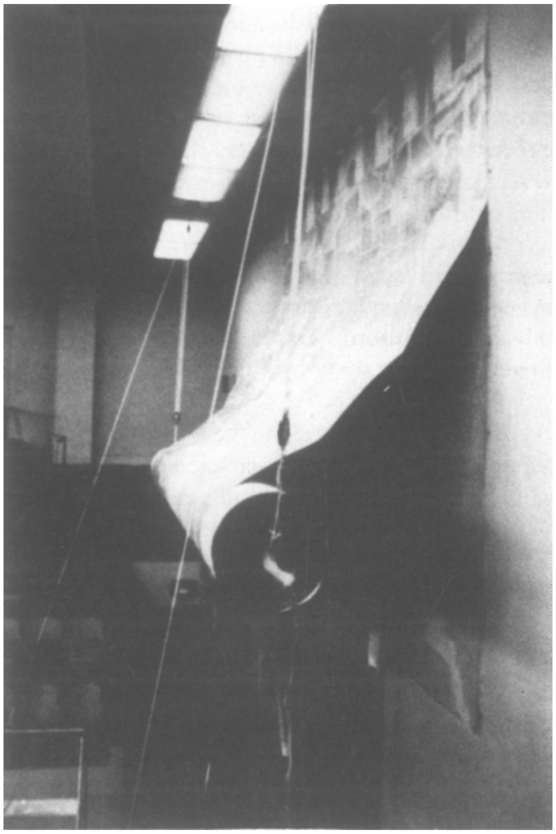
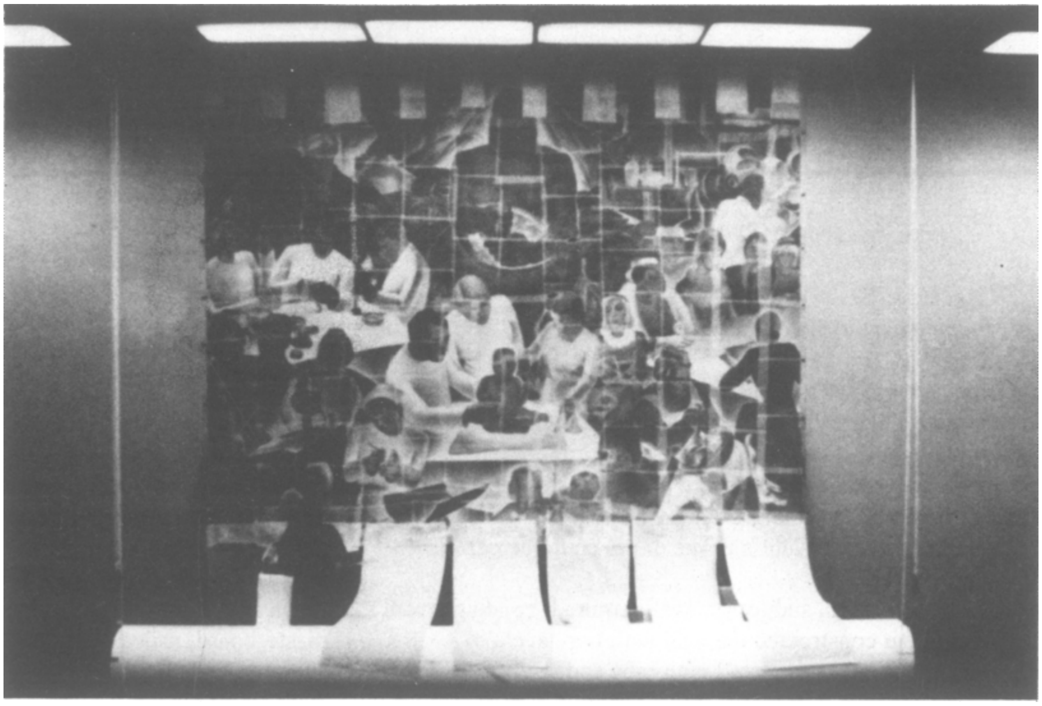


Figure 5



glassine and felt protecting the paint layer. Wide bands of Terytex® were taped in place to secure the roll, and it was covered with polyethylene for indefinite storage.

Three months later a new location was obtained for the mural, and we transported it to our lab for STAGE B consolidation, cleaning, lining and inpainting. Additional work space was rented within our building and the mural was unrolled face-down on a smooth floor covered with clean polyethylene. A low work platform was created, with two poly-covered 16' 2x12's, with ends resting atop dollies. This allowed easy access to all parts of the reverse, for removal of excess adhesive and irregularities, prior to lining. The reverse was consolidated with two separate penetrating applications of Beva 371® adhesive, diluted with VM&P Naphtha 1:4, applied with paint rollers on extension handles and dried before re-rolling and unrolling face up.

The protective facing was now carefully removed. No areas of paint were delaminated and the paint/ground layer was generally sound. Removal of the working varnish and excess Beva® was accomplished with VM&P Naphtha and Varsol-1 (Exxon). Traces of a slight grime layer were removed with a mild soap solution. We decided to line the painting in our studio, within a vacuum envelope, atop a modular lining table. The heated section was created by adjoining our two hot tables together, and adding a drop-leaf to one (Fig. 7). An overall extension was created by nailing a 2 x 4 ledge along the length of the tables, onto which the ends of foamboard sheets were stapled; their other ends laid atop the poly-covered platform planks, which rested on top of other studio furniture and books. Staples and tape easily secured this extension, creating a table 14' x 17'. A single sheet of polyethylene, larger than the surface was laid across the entire modular lining table (Fig. 8).

A 14' x 17' piece of Soft Faced Monomesh was custom ordered from SCAPA, with the warp or machine direction threads running vertically, to insure the fabric would hang flat naturally, uncurling from top to bottom. The fabric was unrolled onto the prepared modular table, soft side up, and rolls of Beva® film were manually heatset onto the fabric, butting the adhesive together to create a continuous film. The Monomesh fabric, due to its inherent stiffness and open weave, created an overall flat surface, ideal for a uniform vacuum. The rolled mural, suspended upon its standards, was positioned at the edge of the table, and the painting was easily unrolled onto the prepared lining fabric of soft faced Monomesh.

After diagonal measurements and squaring the mural upon the fabric, the release sheets were removed from the adhesive. A vacuum envelope was created, with Dartek nylon film as the top sheet, by sealing all joins of polyethylene and Dartek with an auto finishers heat-resistant masking tape, called Tuck Tape #139. The lining was heat-activated in two sections at a vacuum of 1" mercury. First the top half, then the envelope, was swiveled around, and the bottom half was heatset with the aid of space blankets which quickly brought the layers to temperature. This was monitored with paper thermometers, activated at 65° C. They were strategically positioned across the face of the mural, beneath the Dartek, and circled on top with marker for better visibility.

The lining results were excellent, and no weave interference was detectable. The outside margins were now trimmed with scissors to an even border of 2 1/2" all around the perimeter of the mural, and heat-sealed to prevent unraveling with a Vulcan Hot Edge Sealer tool borrowed from SCAPA. Perimeter holes were burnt through with a soldering iron at approximate 4" intervals, trimmed with a scalpel and set with brass grommets to finish (Fig. 9).

Small losses from screw holes and old perimeter repairs were filled and textured as necessary with Liquitex acrylic paste, and toned with Liquitex acrylic paint. Final retouch was completed with combinations of polyvinyl acetate AYAB, powdered pigments, and Maimeri Restauro colors. Inpaint was sealed locally with Soluvar varnish. The overall surface was dusted with a tack cloth and brushed with a Soluvar matte varnish to finish. The mural was rerolled with interleaves of felt and glassine as before, and transported to the college for three months' storage until their winter break, when reinstallation of the mural could be performed.

The only available space on an auditorium wall required building a wall to cover a sculptural frieze. The college maintenance department constructed the wall with two layers of 4 x 8 x 3/4" plasterboard, nailed to a 2 x 4 sub-frame. A smooth finish was created with tape and spackle. The rolled mural was positioned on its standards beneath the wall and another 2" diameter pipe was positioned atop the standards over the mural. The top edge of the mural was tied to the pipe with cords run through the grommets approximately every two feet. Block and tackle was

Figure 7

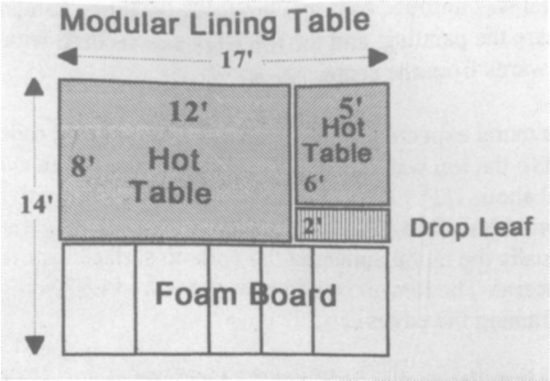


Figure 8

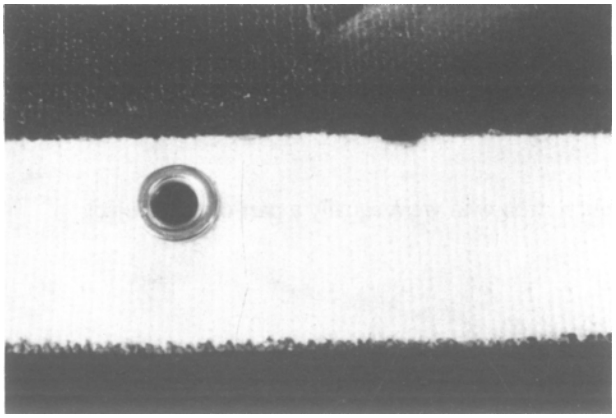


Figure 9

secured to two hoist arms atop two towers of scaffolding, and to the ends of the pipe attached to the mural. The mural was unrolled as it was lifted into position, hanging from the pipe (Fig. 10). Measurements were taken to square the painting, and the top edge was secured with flathead Phillip's screws with electric drivers, working outwards from the center.

The mural expectedly developed a curl from being rolled (Fig. 11). To flatten the surface, the pipe which had been tied to the top was retied to the bottom, creating an even downward weight. The center of the mural hung off the wall about 1/2". Manual smoothing failed to bring the mural into contact, so the sonotube was lifted and also rolled down the surface. When this failed to resolve the variance, it was determined that the wall may have been concave. Visually the mural appeared flat with no surface distortions and therefore we decided there was no cause for further concern. The remaining edges were secured with screws, and the college maintenance crew were left with the task of framing the edges (Fig. 12).

This installation was accomplished with relative ease in five hours. Two of these hours were spent waiting for the carpenters to locate and raise the scaffolding a section higher. This final photo was taken in June, 1993, two years after the installation. A simple perimeter frame finishes the edges (Fig. 13). There are no visible surface irregularities and the treatment remains a success (Fig. 14).

I highly recommend Soft Faced Monomesh as a lining support for oversized paintings due to the following advantages:
Available width - 390" (32.5');
Flexibility - Easily rolled for transit or storage;
Stiffness - Semi-rigid; capable of combatting the memory of tears and cupping;
Permeability - As a woven fabric, it serves as an air conduit, and simplifies reversing adhesives with direct application of solvents thryough the reverse;
Soft Face - Fuzzy mark-free surface, excellent for cling or nap bond applications;
Materials - Polyester and acrylic are chemically inert and have resistance to changes in temperature, relative humidity, moisture absorption, rot, microbiol attack and organic solvents;
High Heat Tolerance - Maximum safe operating temperature - 285° F (acrylic) / 300° F (polyester);
Y-Pin Seam - Angled canvasses and equipment, cycloramas, etc.;
Strength - Capable of carrying heavy load;
Ease of cutting - Edges heatseal.

Obviously other adhesive systems and numerous installation techniques can be employed with this fabric. It, or another style of monofilament fabric, could be used as a lining fabric, and then strip-lined and stretched onto an auxiliary support. In 1988 Toronto conservator Diane Falvey (who had worked with us during our 2-year lining support research project), used the Soft Faced Monomesh in a laminate with Terytex® as a lining support with an acrylic emulsion adhesive for a 4' x 12' stretched painting. We once used another style of Monomesh, as an air conduit, to increase the size of our negative pressure cold table, which facilitated the lining of a 5'x 13' painting, with an acrylic emulsion adhesive onto Terytex®. Another style of Monomesh was used as a surface fabric on a suction table by the Department of Conservation at the Royal Museum of Fine Arts in Copenhagen, and the Department of Conservation at the National Museum in Brede, Lyngby, Denmark. Numerous other conservation applications may include supporting the washing, drying or hanging of oversized paper and textiles such as carpets or tapestries.

This unusual fabric opens the possibility of saving many marouflage murals, allowing them to be lined, rolled for storage or transportation, and installed or removed with relative ease. Perhaps it will create avenues for the first traveling exhibition of WPA murals.

In closing, I wish to thank my partners, Margaret and John Sutton who were equally a part of this project.

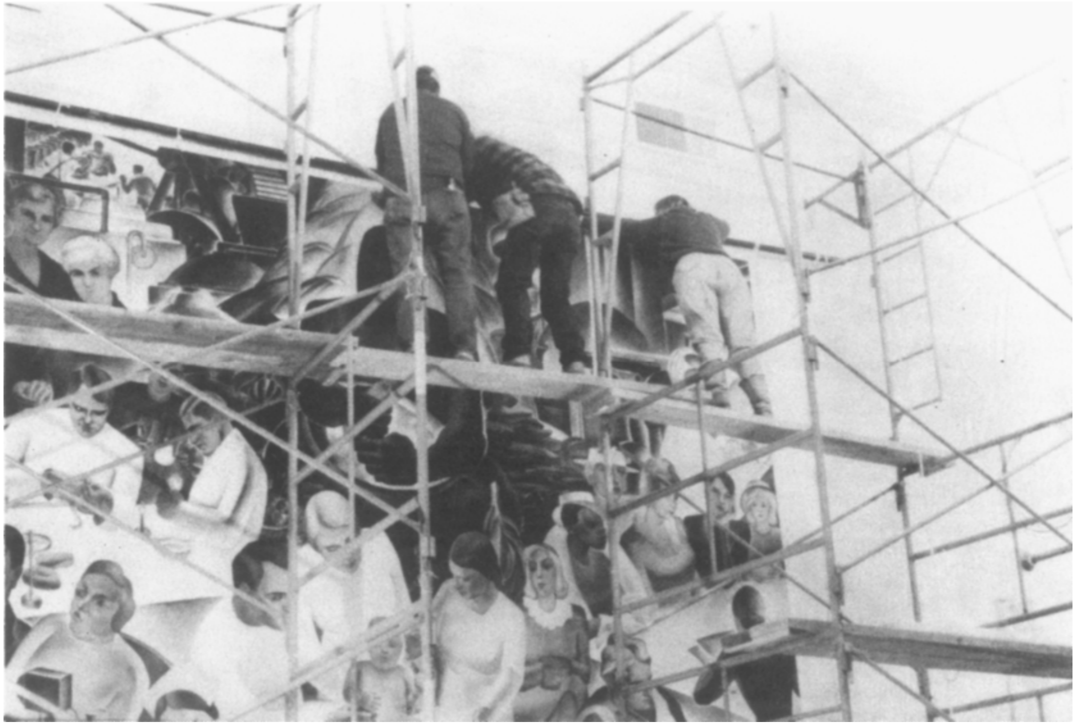


Figure 10

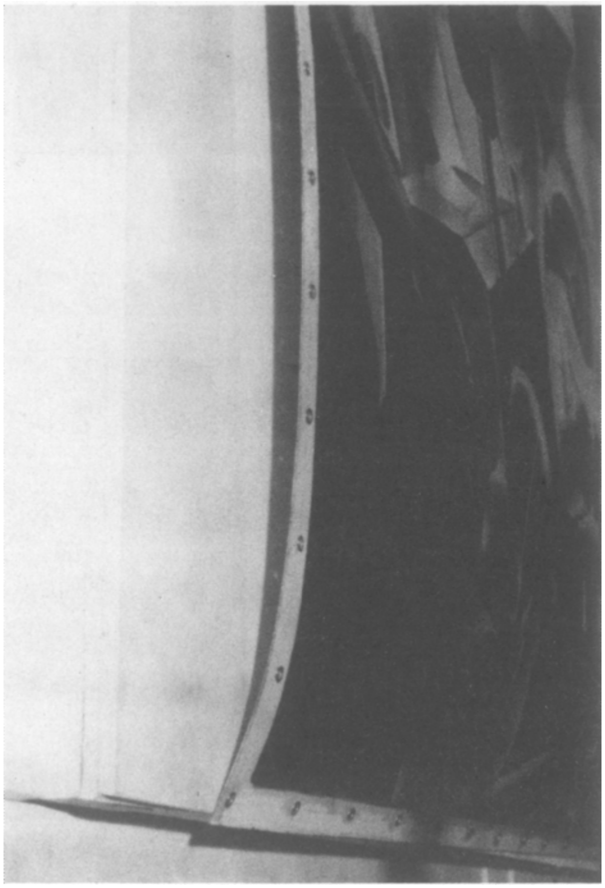


Figure 11

Figure 12

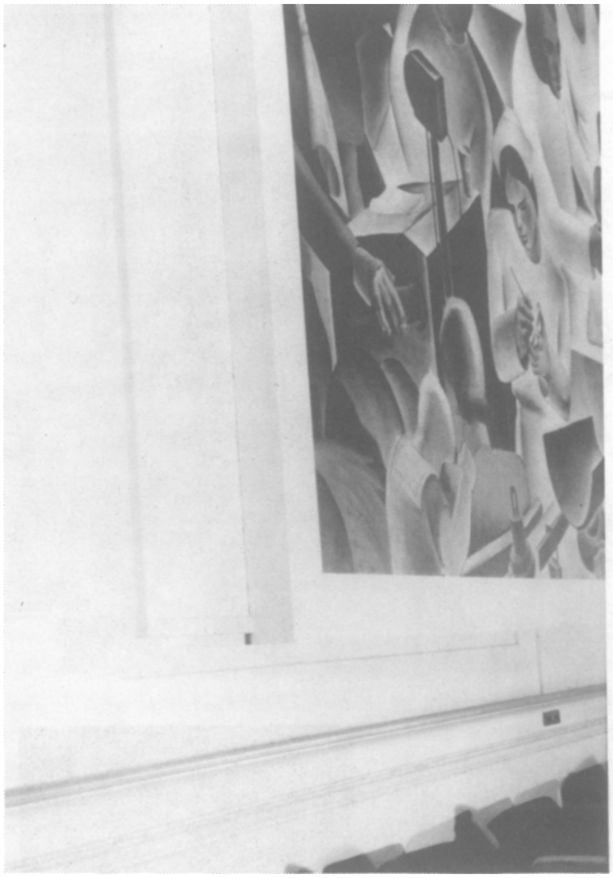


Figure 13

Figure 14

SOFT FACED MONOTEX [formerly Monomesh]- SPECIFICATIONS

(2'S + 2 ACRYLIC FACE)

WEAVE: #18
WARP YARNS: .014 X .021" (.35 X .53 MM)
WEFT YARN: SPUN ACRYLIC
WEFT CENTER YARN: 0.020" (50MM) POLYESTER MONOFILAMENT
WEFT BOTTOM YARN: 0.020" (50 MM) POLYESTER MONOFILAMENT
PERMEABILITY: 25 - 50 CFM (AS REQUIRED)
WEIGHT: 4.2 - 4.5 OZ/SQ FT
TENSILE STRENGTH: 1,100 LB. PER INCH TO BREAK
ELONGATION AT BREAK: 23%
PICKS PER INCH: 40 - 45 (DEPENDING ON PERMEABILITY REQUIRED)
ENDS PER INCH: 54

MATERIALS VENDOR LIST

SCAPA INC.	**SOFT FACED MONOTEX (formerly Monomesh)** POLYESTER/ACRYLIC	
FOREST PRODUCTS DIVISION	SE-8334 390" (32.5') WIDE	$8.75 SQ FT
P.O. BOX 1055	SMALL SAMPLES UP TO 3' X 3'	$5.00 SQ FT
WAYCROSS, GA 31502	OFF-CUT UP TO 100" MAX.	$6.50 SQ FT (IF AVAILABLE)
Bill Westhead, V.P., Gen. Manager	Many Styles of MONOMESH, Y PIN SEAMS AVAILABLE	
Tel. 800-221-2274, Fax 912-287-0091	Many Styles of SCAPEX	

CONSERVATOR'S PRODUCTS CO.	**BEVA® 371** - FILM -	$ 95 /ROLL
PO BOX 411	SOLUTION -	$ 70 /GAL.
CHATHAM, NJ 07928		

P & S FILTRATION	**TERYTEX®** - STYLE #39, 79/80" W	$11 /YD.
JORDAN RD.	STYLE #1666, 41" W	$18 /YD.
SKANEATELES FALLS, NY 13153	(FINE /DENSE)	
Tel. 315 685 3466	NEEDLED FELT, POLYESTER	
	AMT 30890 UNT, 78" W	$5.08 /YD.

ACCURATE PLASTICS, INC.	**G10** - ACCULAM G10/FR4, 36" X 48" :	
18 MORRIS PLACE		
GEES. .0153648N	015 THICKNESS (GEES .0153648N)	$21.32 (1-4 shts.)
YONKERS, NY 10705-1929		
Tel. 914-476-0700	020 THICKNESS (GEES .0203648N)	$22.57 (1-3 shts.)

HOW MUCH IS TOO MUCH? CONSERVATION versus RESTORATION

-- Dr. Duane R. Chartier & Susanne E. Friend --

AUTHORS' NOTE: This talk was originally presented in dialogue form to emphasize the dichotomy inherent in the treatment of works of art. There are also a number of novel techniques of interest besides the moral and ethical issues which are discussed. The main body of the text was delivered by Susanne Friend and the italicized interjections by Duane Chartier.

This talk presents the conservation and/or restoration of a WPA mural by Helen Lundeberg in the Fullerton, California Police Station as an example of the kind of conflicts and compromises that most conservators are forced to confront not only from a treatment perspective, but also from the point of view of client exigencies.

What do you mean -- is the work that you are presenting conservation or restoration?

If I can avoid interruptions from my egregious colleague, the discrimination will become apparent. But first let me give you a brief history of the mural itself and of the project.

The painting was executed as a federal Works Projects Administration work in 1938-39. The mural represents the history of the development of California and was carried out after the entire building, also a WPA project and originally the city hall, was finished. The painting covers three adjoining walls and is 900 square feet in area. It is executed in oil paint, applied very thinly in washes over a one inch thick "acoustic plaster" which is very porous, soft and highly textured. The artist and her assistants made their own oil paints and, with the exception of outlines of figures and most objects, the paint is extremely medium-poor.

The east wall, the historical beginning of the narrative, shows the landing of Cabrillo at San Diego Bay and the development of the missions. The south wall depicts the transition from Mexican to American rule and the gold rush. The west wall shows the development of the area to an agricultural and industrial region. The painting ends with a reference to the movie industry.

In 1963 the entire building was turned into the Police Station. The room with the mural, originally the Fullerton City Hall Council Chamber, was needed for additional office space and was divided into several offices and the ceiling was lowered to different levels. The most significant alteration was that the mural was painted over from the lowered ceiling down, leaving two thirds of the total surface area essentially intact but hidden by the dropped ceiling. Over the years the overpaint layers accumulated, differing in each office according to the whims of its occupant, to as many as nine layers of oil and acrylic housepaint. Portions of the walls were punctured to install air conditioning ducts and electrical fixtures.

In June of 1991 the City of Fullerton, after a five year renovation of the Police Station, finally turned its attention to the mural by Helen Lundeberg. The police, anxious to have what was to be their new briefing room, were champing at the bit. An RFP was circulated by the city Redevelopment Agency. We visited the site and upon cursory examination realized that the city's description and understanding of the painting was very deficient - someone had even suggested that the painting medium was water-based. In order to present a proper proposal it was essential to get permission to perform not only overpaint removal testing but some analyses of the original binding medium. Infra-red microspectroscopic analyses performed on paint cross-sections at the Getty Conservation Institute by Michelle Derrick not only confirmed the identity of the original linseed oil-based paint but showed that at least two of the initial overpaint layers were oil whereas later layers were synthetic paints. Paint cross-section also showed the coarse aggregate and the pink tinted mortar comprising the acoustic plaster. The pink tone forms an overall background for the painting.

Our treatment proposal included matrix testing of over forty solvent and solvent-gel cleaning combinations as well as tests for physical removal of overpaint layers. All of the chemical removal tests yielded far from acceptable results. Components of the overpaint tended to be driven into the porous plaster underlayers regardless of the use of gels and careful minimal application.

A large test carried out by another bidder was observed. This had caused smearing of original and overpaint and absorption of the paint into the soft, porous plaster.

> *Wait a minute! Do you really think that it is ethical to point out such a thing and criticize a colleague in such a casual way?*

It is essential that we be critical of actions and practices that lead to damages to works of art -- whether we do them ourselves or someone else does. Many of us are so afraid of being openly critical that we allow things like this to pass. Although there is no definitive sampling and testing protocol by which to judge it is pretty clear that a minimalist, systematic and careful approach to testing is the ideal to strive for. The kind of testing that we witnessed is unacceptable by any standards. IF I MAY CONTINUE ...

A comparison was made between the differences in purely mechanical removal (with scalpels and dental tools) of a section of overpaint versus the best chemical removal determined from the matrix testing.

The mechanical methods clearly left more of the subtlety of the original intact. Unfortunately, such meticulous mechanical removal would have taken years so a faster method was sought to speed the process.

In the treatment proposal some rough numerical estimates of recovery were made based upon use of a modified Italian fresco conservation technique called "strappo". The strappo tests were carried out using two different animal adhesives - hide glue and rabbit skin glue - and two different fabrics (cheesecloth and finely woven cotton rag). The adhesives were applied thickly by brush to a small area adjacent to uncovered original in order to assess removal efficiency and aesthetic effect. As the glue dries it begins to shrink causing large shear stresses at the overpaint interfaces. With some luck the most damaged interface is the oldest one since it is the most likely to have deteriorated with age and it was also probable that there was a somewhat isolating dirt layer over the original. The commercial hide glue was found to be generally superior to rabbit skin glue and 90% recovery of original was found in the test patches that totaled about 2 square feet in different areas of the room.

The proposal was somewhat of a shock to the city and was the only one that indicated that a semi-mechanical overpaint removal was likely to be more successful in recovering original paint than any strictly chemical method.

> *So you were the only ones capable of doing the job? Is that what you are trying to tell us?*

No, but we were the only bidders who took the time and care necessary to understand the chemical and physical problems that we were to face. The city had seriously considered a proposal to simply repaint those lost design areas. However, this would have led to a very unacceptable aesthetic problem in trying to coordinate the smoother overpainted area with the rougher original.

AS I WAS TRYING TO SAY . . . After seeing the total projected costs the city wanted to see a separate bid for the overpaint removal only so that they could be free to open bids for the inpainting and reintegration. We presented a second bid for just overpaint removal and this was accepted.

> *You should be ashamed! How unethical to agree to do just a portion of a treatment! How could you know what the outcome of the treatment would be? How could you trust someone else to complete what you had begun with the same "intentions"?*

Actually, the head of redevelopment had two more months left in office, and we suspected that he wanted to present a reasonable budget before he left. We objected strongly to this division for all the reasons you are well aware of, but there was nothing to be done. We simply had to hope that our bid for the second phase of reintegration would be favorably considered, knowing full well how difficult it would be for others to take up the project in the middle of work.

We began work on the west wall, which had the greatest portion of overpaint on it. Before starting, however, we had to consolidate approximately 20% of the entire wall using dilute PVA injections, as the strappo would have pulled off weak or detached plaster.

We soon discovered that the brittle oil overpaint separated from the original paint far more easily by using plastic strapping tape as the "strappo" material, as the warm hide glue tended to plasticize the layers and was inefficient both in terms of time and application. The strapping tape was carefully rubbed on with blunt tools to insure overall contact on the uneven surface and then jerked away, rather like leg waxing... This proved to be very successful until we got to layers of thicker overpaint containing synthetic layers. Here the strappo technique was only successful in areas of the original that had heavily painted outlines, highlights and heavily worked areas that filled in the pores of the plaster. The same was true on the south wall, whereas the overpaint on the east wall was almost entirely impossible to remove with this technique.

Although picking with scalpels and dental tools worked well, it was far too slow to be practical.

> *If you were worried about speed, why didn't you try sandblasting?*

We did, to remove the first five or six layers on the most heavily overpainted areas, but it was too difficult to control, considering the softness and roughness of the original surface. Shall I tell you what did work?

A crazy materials scientist I know suggested rapid heating followed by rapid cooling in order to increase the interfacial stresses in the overpaint layers. This was extremely successful in areas of heavy synthetic overpaint.

An industrial paint stripper gun was played across surface in a 3"x1/2" band until indications of blistering were evident. Immediately behind the head of the heat gun followed a spray of liquid nitrogen that cooled the heated paint layers to freezing. This prevented deterioration of the original and created extreme dimensional changes, aiding in removal of the overpaint.

In some areas the flaking of the overpaint layer was immediate upon going through the heating/freezing cycle. In other areas where heating did not raise any blisters immediately the freezing was carried out multiple times and overpaint removal was aided with a scalpel. The greatest success of the liquid nitrogen flash freezing was on the south wall where the synthetic paint layers were the thickest and softest.

> *So you decided to attack the wall by frying it, freezing it and otherwise brutalizing it? Surely you must have caused some damages.*

Yes, we did drastically treat the wall in this way because we felt that it was the minimum brutality required to recover the maximum amount of the painting. There were some small associated plaster detachments that had to be consolidated and there was a slightly charred area of about 6 square inches but it went very well in general.

> *Oh, come on, you can't be serious! This is such a load of ... baloney. How could you know that this was an optimum set of solutions?*

That's not baloney - maybe ham. But perhaps you are right. Maybe there is no optimum treatment. Or, more likely, there is no simple way to determine that what you are doing is correct.

> *If you didn't have the optimum solution and it was too difficult to determine whether you did, why did you go ahead with the treatment?*

Well, the city wanted their historic work of art, the police wanted their briefing room and the room had to be occupied "yesterday". The original suggestion by the city of painting on top of the overpaint was aesthetically unacceptable due to the difference in texture. Besides, just leaving it for future conservators was simply not an option! The painting, semi-covered, was neither mural nor just a wall and could not be kept in either state. A temporary cover-up was unacceptable as the conservation was the centerpiece to the full renovation of the building and had previously been the focus of fund-raising. Finally, the upper parts which had never been touched were so friable that they needed timely attention.

The east wall, which of course was the last wall, proved to be the most daunting. None of our tactics worked. Even our resident materials scientist was flummoxed. Finally, we arrived at a compromise. Mechanical techniques caused too much damage to the soft, porous plaster. In order to preserve the structural integrity of the wall and paint layers, methylene chloride in a thick gel was applied to bubble away the overpaint. The bubbled layers were carefully lifted away with a spatula in order to avoid any smearing of the paint layers and further damage to the layers below. What was left was a thin veil of white overpaint residue adhered to the original. Very small portions of this veil were then removable with the tape strappo method.

> *Well, so after all that you were left with 20% still covered with an obscuring veil of overpaint? Sounds*

like a pretty sad compromise to me. I'll bet you ended up overpainting all of that after all.

Yes, to a large degree, we had to. But at least we could see what the original looked like, and we had recuperated the original texture.

As I said, it was a compromise!

We subsequently won the second phase, for filling and reintegration. We filled all losses but not dents and hammer hits that still had original paint intact. The filling of the large losses was done in stages using a custom mixed mortar that was formulated to mimic the surrounding texture as closely as possible. We recreated large losses from old photographs.

All inpainting was done with Winsor & Newton watercolors or gouaches. Fortunately the veil of overpaint remaining on the east wall was white, so it was relatively easy to bring the area back to the color intensity of the original. However, it should be mentioned that we had the added difficulty of matching all of the recovered walls with the painting above which had never been touched but had faded and deteriorated over the 30 years that it had been exposed. Because each wall had overpaint up to a different height, this problem was easily overcome with subtle blending.

The entire painting was fixed with 3% Acryloid B72® in xylene applied with an airbrush, as the upper layers were particularly friable. Areas under the three windows on the south wall which had never been overpainted but which had very friable paint due to condensation and medium deterioration were cleaned with compresses dampened with water and then fixed.

Why didn't you just sign the mural next to Helen's signature?

I did - in invisible ink. If you use a UV light you can see it. I'm joking, of course, but the matter is a serious one. What degree and what kind of inpainting and reconstruction constitute a conservation, a restoration, a copy, a pastiche or a complete misrepresentation?

There is, whether we like it or not, an intractable, unresolvable aesthetic divergence in conservation. That is, between the deceptive inpainting or full integration versus the aesthetic neutralization of losses. The first affects the perception of authenticity and the second affects the readability and aesthetic appreciation of the work. The two trends are often at odds and we must resolve, in every situation, to attempt to judge the approach and the results objectively.

A necessary but not sufficient condition to determine the difference between conservation and restoration is the fact that conservation, at least the way we practice it, does not attempt to bring back the old painting as it was, but to stabilize it structurally and enhance its appreciation and interpretability.

So do you think that this was conservation or restoration?

Both. By necessity and circumstance.

What we have tried to do today is to vocalize those internal struggles that should occur in every conservation project throughout its duration and well after the fact.

It is important that we develop a critical and systematic method for looking at how we work and a type of ruthless honesty about the limitations of our knowledge, techniques and working circumstances. We must endeavor to examine as many options as possible and to re-examine those options on an ongoing basis.

We must not fall in love with our own recipes! We must recognize when the best that we can do has severe limitations.

EMBEDDING PAINT CROSS SECTION SAMPLES IN POLYESTER RESINS: PROBLEMS AND SOLUTIONS

Michele Derrick, Luiz Souza, Tanya Kieslich, Henry Florsheim and Dusan Stulik

Abstract

Polyester resins have been commonly used in art conservation for embedding paint cross sections prior to analytical studies. These resins set rapidly without heat, are clear, polish readily and microtome easily. However, while they work well in most cases, there are some specific samples for which these resins pose problems. The polyester embedding media have been found to dissolve wax and fresh natural resin layers in cross sections. Additionally, the embedding resin wicks into porous, low binder samples. This infiltration hinders the determination of the type of binder in the sample by producing blotchy, uneven staining results as well as obstructing infrared analysis. Alternate embedding materials and procedures are discussed in this paper. One method to prevent the infiltration of embedding media is also presented in which the samples are precoated with a thixotropic acrylic gel prior to embedding.

Introduction

Polyester resins were introduced in the 1940's. Because of their transparency and ease of preparation, they were soon used for the encapsulation of natural history objects (Purves and Martin 1950). Although it was later discovered that the long-term life of the polyester was not amenable to museum objects (Meurgues 1982), polyester resins are still commonly used by schools, scientists and hobbyists for embedding and casting many objects. Polyester resin is also routinely used as a medium for embedding multi-layer paint cross sections from art objects (Plesters 1956, Wolbers 1987, Tsang and Cunningham 1991).

The preparation of mounted paint cross sections has become standard practice for the examination of painted surfaces in art conservation as well as in forensic analysis. Large, sturdy cross sections can often be polished and microtomed without embedding, i.e. surrounding the sample with another material. However, tiny or fragile cross section samples need to be embedded in a supporting medium to hold them together and in the correct orientation for examination. The mounted cross section provides a valuable source of information on the layered structure, pigments and painting technique. Relating the structure to the materials can also provide indications of relining, overpainting or other restoration procedures.

In the analysis of mounted cross sections for their pigment components, no apparent problems have been noted with polyester embedding resins. However, recently more techniques, such as fluorescent staining and infrared microspectroscopy, are being used for the determination of the binder components in embedded cross sections. With these techniques, it has become apparent that the polyester resin and other polymeric embedding media can interact with some specific types of samples during the embedding process. This may result in interferences with the analysis of the organic portion (binder and coatings) of the sample and caution must be used when any results are interpreted.

The solvent in the prepolymer solutions can react on contact with some materials on the surface of embedded samples. Godla (1990) pointed out that polyester resin can dissolve wax in furniture finish samples often making it difficult to examine wax finishes after embedding. In addition, polyester resin was found to dissolve fresh (< 1 year old) natural resin samples of dammar, mastic and copal (Derrick et al. 1992). However, aged or oxidized resin layers on furniture finish cross sections did not seem to exhibit the same solubility problem.

The polyester medium has also been found to soak into or infiltrate porous, low binder samples. This has been observed by Baker et al. (1989) for embedded paper cross sections analyzed by infrared microspectroscopy. Embedding media infiltration also interferes with the use of fluorescent stains for binder identification in cross sections by coating the particles in the sample and thus inhibiting interaction of the stain with the binder. This paper will illustrate these problems as well as discuss alternate embedding materials and procedures.

Embedding Materials

An ideal embedding resin should meet the requirements listed below when used for the analysis of binding media in paint cross sections obtained from works of art.

1. The mounting medium and its solvent should not react with, soak into or otherwise interfere with the analysis of the binder in the sample.

2. The medium should cure at room temperature. The curing process should not be exothermic, since heat may adversely affect the organic materials or binders in the sample.

3. For samples that are to be analyzed by infrared microscopy, the resulting embedment and sample should be easy to microtome. An important factor, is that the hardness of the embedment is similar to the hardness of its sample. This minimizes stresses during microtoming that may cause the sample to ‘pop’ out.

4. The medium should be clear to ensure proper orientation of the sample in the medium for microscopic examinations as well as for positioning the mold in the microtome jaws.

5. The medium should not shrink upon curing because this will apply stress to the sample and may cause problems during microtoming.

Table 1 summarizes the advantages and disadvantages for several types of polymeric materials that were tested for embedding paint cross sections. Figure 1 shows example blocks of each of the polymeric media discussed in Table 1. Many other types and brands of embedding media are available, some of which are discussed in the text. Of the four types of embedding resins tested, the polyester was found to be the best for embedding and microtoming most types of art materials.

Table 1. Types and brand names of polymeric media tested for embedding and microtoming of paint cross sections.

Type	Brands Tested	Comments
Paraffin	Paraplast	Opaque, minimal shrinkage, soft, sliced well, elevated temps required for preparation
Epoxy	Epon 812 LX-112 Maraglas 655 SPURR	Generally needs elevated temperatures to cure, transparent though sometimes yellow, forms a very hard block that is difficult to slice
Acrylic	Quetol 523M Butylmethylmethacrylate LR White Krazy Glue (cyanoacrylate)	Exothermic cure reactions, transparent, shrinks more than polyesters, cuts well, may infiltrate some samples
Polyester	Caroplastic Bio-plastic Castolite	Cures at room temperature, transparent, cuts well, minimal shrinkage, may infiltrate some samples

One commonly used polyester embedding resin in art conservation is Bio-plastic (Ward's Biological Co.). Similar polyester resins are also sold under the brand names of Caroplastic (Carolina Biological Co.), Castolite (Castolite Co.), Castoglas (Buehler) and Vestopal W (Ladd). Polyester embedding resins contain a polyester prepolymer dissolved in styrene monomer to form a solution of appropriate viscosity (Horie 1987). When combined with a methyl ethyl ketone peroxide catalyst, a clear, uniform, solid block is produced that is readily polished and easily microtomed. The resin cures overnight at room temperature or in a few hours at slightly elevated temperatures. The resin shrinks minimally during curing at room temperature and slightly more when cured with increased temperatures. It is cheap, readily available, easily prepared and is only moderately toxic. These many positive features of polyester resin give it several advantages over the other embedding resins on the market (acrylics, epoxies, etc.) and account for its popularity as an embedding medium for paint cross sections.

While the polyester resins are typically used for paint cross sections in art conservation, forensic scientists (who generally only analyze modern paints) prefer epoxies, acrylics and cyanoacrylates. The reason often given is that they cure very quickly. We found that the epoxies tend to be too hard and brittle to microtome easily and are sometimes yellow in color. The acrylics were clear, but were very exothermic and shrank significantly upon curing. One acrylic embedding material became so hot during curing that it melted the one inch plastic mold. Samples from car finishes and house paints are typically harder than those found in works of art and this hardness makes the samples more compatible with the epoxy and acrylic media. However, for art conservation samples, the epoxies and acrylics were generally too hard and since they had similar problems of dissolution and infiltration as the polyesters, they are not recommended over the polyesters.

One method found in forensic science is the use of a drop of cyanoacrylate glue (Super Glue, Krazy glue, etc.) to mount a paint chip on the end of a small, wooden dowel (Cartwright 1977). While it was difficult to get the sample oriented correctly, this method did seem to work well for microtoming the sample. We did not have problems with infiltration, but dissolution of the sample is still a potential problem when the sample contains acrylic paints, waxes or fresh resin layers.

Gelatine is another material that has been used successfully in the forensic field for embedding paint cross sections (Wilkinson, et al. 1988). The procedure used by Wilkinson involved freezing the sample in a gelatine block for cryogenic microtoming. Afterwards, the thin section was warmed and the gelatine was washed away, leaving just the thin section of sample. This should be a good method for samples that are not susceptible to water, such as wax cross sections. However, this method was not tested in our lab because gelatine embedment could potentially interfere with the positive identification of glue binder, albumin varnish or other proteinaceous media. Also glue or gum binders in the samples may be susceptible to damage or alteration by the water solvent in the gelatine.

The biomedical field uses several types of embedding media (e.g., glycol methacrylate, methyl cellulose, acrylamide and epoxy) for cytology studies by electron microscopy. These studies often require ultra thin microtomy for producing thin sections below 1 micron in thickness. A low viscosity embedding solution, preferably water miscible, is used to allow easy penetration of the resin into the sample. For their purposes, this is desirable since it will stabilize the sample and maintain its shape. However, since we are trying to eliminate infiltration of the resin, we did not test any of these low viscosity media.

One embedding option is the use of low melting point waxes, such as Paraplast (Ladd). The wax melts at approximately 60 °C and solidifies rapidly. The wax does not pose any infiltration or dissolution problem to the samples, but it is unlikely that surface wax layers would be detectable. While wax embedments are too soft to be polished, they can be easily microtomed. The wax is opaque, so it is critical to know the positioning of the sample prior to microtoming. It is also important to work quickly when pouring a mold with the hot wax because delays can result in a block that contains many bubbles. One method that shows potential has been developed by Wolbers (1993) in which the wax is mixed with a clear inorganic salt, such as potassium bromide. This serves to increase the hardness of the wax and to make the mixture more transparent.

Several silicone rubbers have been tried for embedding samples. To this point, we have not found any which are hard enough to be microtomed or polished. However, we are still looking for other silicone materials which may work.

Since the use of non-polymeric mounting media would eliminate the dissolution and infiltration problems associated with the polymeric media, we tested several inert materials, such as salts (BaF_2, AgCl, KBr), cork, indium and gallium. The inorganic salts of barium fluoride, silver chloride and potassium bromide were powdered then placed in a pellet die with the sample. The salt was pressed into a transparent pellet with no apparent distortion to the sample. At this point, it was difficult to proceed further. We were not able to microtome any of the pressed pellets without the salt crumbling into a powder. And while the salts themselves could be easily polished, they did not polish at the same rate as the sample and tended to disintegrate.

Problems also occurred with cork embedments. A small slit was made in a piece of cork with a razor blade, the sample was inserted, then the sample area was sealed with cyanoacrylate adhesive (Krazy glue, etc.). The cork itself was difficult to microtome because it was so soft. It tended to move and compress as the microtome blade tried to slice through the sample. However, the area of cork and sample coated with cyanoacrylate exhibited some additional stiffness that permitted it to be microtomed into sections approximately 10 micron thick. We were not able to polish the sample and it was necessary to use a fairly large sample (1 mm x 2mm) in order to be able to position it correctly. The same dissolution problems mentioned above for cyanoacrylate would still apply.

Malleable metals, gallium and indium, were tried for embedding. In this test, a small pieces of metals were placed above and below the sample, then some pressure was applied to compress the metal around the sample. The metals held the samples well for microtoming, but it was difficult to orient the samples properly because of the opacity of the metals. Also, because the metals are expensive and toxic, this method was discarded as non-ideal.

Because an alternate embedding material was not found that had as many advantages as the polyesters, we focussed our efforts to understanding the interaction of the polyester resins with the sample in hopes of finding conditions, samples and methods for which the polyester works well.

Embedding Paint Cross Sections with Polyester Resin

Procedure

To embed a typical paint sample in polyester media (brands noted in Table 1), 6 drops of catalyst (methyl ethyl ketone ether) are mixed thoroughly with 10 ml of polyester/styrene resin. The resin is initially light blue in color, then it turns yellow when the catalyst is well mixed and quickly becomes clear as the reaction proceeds. Excess catalyst will speed up the curing process, but will also make the final mount more brittle and difficult to microtome. A mold is initially half-filled with the well-mixed embedding medium and cured at room temperature for 3-6 hours. A representative portion of the sample containing all the layers is transferred the center of the hardened base layer in the mold with forceps or a probe and positioned in the desired orientation. It is then covered slowly with a small amount of freshly prepared polyester embedding medium and set aside to cure. The polyester is cured within 12-24 hours. When microtoming the sample for infrared microanalysis, the best results are obtained by waiting 36-48 hours before slicing. The medium continues to cure slowly over time (Demmler 1980). After one month, the microtoming becomes noticeably more difficult and the samples tend to crumble. The bottom half and the top half of the block should be prepared within a few days of each other to prevent a hardness differential between halves that would interfere with microtoming.

Initially, plastic peel-away molds (1" cube, shown in figure 1) were used for embedding. However, because the presence of excess medium stresses the sample during microtoming, most of the plastic around the sample needed to be trimmed away to minimize the area of contact with the microtome blade. To trim, a razor blade or diamond saw is used to remove all but a supporting cone of plastic with at most 1 mm of embedding media surrounding the sample at the cutting surface. Since trimming can be very time consuming, a switch was made to Pelco (Ted Pella, Inc., Tustin CA) silicone rubber molds for embedding (7 x 15 x 3mm, also shown in figure 1). These molds produce small embedments with trapezoidal tips that do not require much trimming.

Infiltration

The penetration of the liquid embedding resin into the interior of a paint sample can occur when there are voids or open spaces in the sample. Typical porous samples are stone, pigment, paper or textile. Paints are porous when the amount of binder is low enough that it does not fill the void spaces around the pigment particles (Hansen et al 1992). The embedding resin can then seep into the sample and fill these void spaces. In the process, the embedding resin may coat the particles. Matte or porous paints are often found in wall paintings, polychrome sculptures, ethnographic objects and glue gessos. If several samples of this type are to be embedded for analytical studies of the binding media, it is prudent to test one sample initially to see if the infiltration occurs.

Visual examination of a paint cross section can often detect infiltration of the embedding resin due to the discoloration or darkening of the sample. This is particularly noticeable for white paints and grounds. Samples that appear very white and opaque prior to embedding can take on a darker, transparent appearance after resin penetration. Due to the presence of embedding resin inside and outside the sample, there is less contrast at the sample edges and the edges may seem poorly defined. Figure 2 shows a photomicrograph of an paint cross section from a polychrome sculpture that was infiltrated with resin during embedding. For comparison, figure 3 shows an embedded paint cross section from an oil painting that did not experience infiltration. This sample has very well defined edges and the opaque white ground remained white after embedding.

Resin infiltrated samples do not uniformly retain fluorescent stains even though the binder is uniformly distributed throughout a layer. This is due to the embedding resin coating the paint particles and inhibiting the stain from reaching the sample, which results in a blotchy appearance of the fluorescent color. Figures 4 and 5 illustrate that the infiltration problem occurs with samples containing a low binder content. In a test sample prepared with a 40 w/w% glue/gypsum concentration, no indications for penetration of the embedding resin were found. The paint cross section stained uniformly and brightly with fluorescein isothiocyanate (FITC)(figure 4). A corresponding sample prepared with 5 w/w% glue/gypsum was clearly infiltrated with the polyester resin. Figure 5 shows its uneven staining pattern with FITC. Other samples with concentration of 20 w/w% of glue and less were also found to experience infiltration to varying degrees.

Infiltration of the embedding resin into the sample is readily recognizable when infrared microspectroscopy is used to analyze the sample. An infrared spectrum of a cross-section will contain absorption bands for each component in the analysis area. Thus, if a paint sample is infiltrated, the spectrum will show bands for the polyester, the binder and the pigment. Since the polyester resin absorbs so strongly in the infrared and since the binder is likely to be in a low concentration, it may be difficult to identify the binder. Figure 6 shows an infrared spectrum of an area of an infiltrated paint cross section along with a reference spectrum of a polyester resin (Caroplastic). Infrared spectroscopy can confirm infiltration of the resin by the presence of the polyester absorption bands in the spectrum for the sample. The characteristic absorption bands for polyester are marked.

Cure time

The polyester prepolymer after mixing with the catalyst has a fluidity similar to corn syrup. This allows the resin to flow readily around the sample and any bubbles to migrate to the surface. However, since this fluidity may also enhance the penetration of the resin into the sample, a test was done to allow the resin to partially cure prior to pouring the second half of the mold. After 41 minutes, the polyester was so thick that it did not form a uniform layer over the sample. However, infrared analysis of a paint sample coated with the polyester after 39 minutes of curing showed that the paint sample was infiltrated (figure 7). Thus, it is not practical to use cure time to prevent the infiltration of the resin.

Barrier Methods

Since polyester resins are the embedding media of choice, several barrier methods were investigated to encapsulate the samples and prevent the polyester from infiltrating. These methods use a non-interfering material to surround the sample with a thin, impenetrable layer prior to embedding the sample in the polyester, thus keeping the good qualities of the polyester without allowing it to touch the sample.

The barrier methods tried included the following treatments of the samples prior to embedding in the polyester resin:

sealing the sample in wax, parafilm, shrink-wrap or aluminum foil;
sputter coating a thin, uniform gold layer on the sample;
spray coating the sample with an acrylic coating;
coating the sample with a gel formulation.

Only the last of these methods proved to be successful.

Figure 8 shows photomicrographs for an unstained and FITC stained paint cross section that had been coated in wax prior to embedding. The sample microtomed easily but the wax did not prevent the infiltration of the resin. In fact, the resin dissolved the wax and created a halo image around the sample.

Figure 9 shows the photomicrographs for an unstained and FITC stained paint cross section that had been wrapped in Parafilm prior to embedding. The sample did not microtome easily because the Parafilm stretched with the glass knife rather than cutting readily. It also allowed movement of the sample within the embedment during microtoming. In addition to these problems, the Parafilm did not keep the polyester resin out of the sample.

Shrink wrap was tested for encapsulating samples. However, the high temperatures required to shrink the material are not recommended for sample preparation and in the few attempts tried by this lab, the samples could not be prepared without bubbles being trapped with the sample inside the plastic. The presence of bubbles keeps the sample from being held uniformly and thus makes microtoming difficult.

The next test used a sputter coater to coat samples with several nanometers thick layer of gold. Several samples were prepared by this method, some of which were infiltrated by the polyester and some of which were not. It appeared that the smoothness and lack of crevices in the sample was important for success, since complete coating of all surfaces is necessary to keep out the polyester. Additionally, careful handling of the sample after coating was required, because, in some cases, a small portion of the coating would attach to the forceps and come off the sample. Figure 10 shows photomicrographs for an unstained and FITC stained paint cross section of a sputter coated sample that experienced resin infiltration.

Completely sealing samples in an aluminum foil sandwich with crimped edges was also tried. This was an extremely time consuming task that resulted in an opaque, difficult to position sample. Resin infiltration with this method was inconsistent and thus it is not recommended. Figure 11 shows photomicrographs for an unstained and FITC stained paint cross section coated with aluminum foil that experienced slight resin infiltration around the edges.

Several conservation treatments for papers and painting relinings use non-penetrating gel-like solutions such as methyl cellulose (Baker 1984), acrylic dispersions thickened with toluene (Keyser 1981, Mehra 1984) and acrylic dispersions thickened with fumed silica (Byrne 1984). Some of these methods were tested for encapsulating the samples and the acrylic/silica mixture was found to be successful. Many other thixotropic, quick drying solutions may also work in the same manner. Of the other gels tested by this lab, the cellulose ether (Klucel G) film was found to dissolve in the polyester resin. The toluene thickened acrylic (Rhoplex AC-33) was found to retain toluene resulting in a pliable film that tended to stretch during microtoming. Neither of these gels uniformly kept the polyester resin from infiltrated.

The initial test for the acrylic dispersion (Rhoplex AC-33) thickened with fumed silica (Cab-O-Sil) used 50% by volume of each material. This resulted in an extremely viscous gel that dried to a film within minutes. The films prepared from this mixture were opaque, so further testing will be done to investigate different proportions and materials for the gel in hopes of obtaining a mixture that will produce transparent dried film.

A five step procedure was used to encapsulate the samples (figure 12). The first step was to prepared the bottom half of the mold with polyester resin as usual. At this point a small drop of the gel solution was placed at the tip of the mold and the sample was positioned on the gel drop. Since the silica thickened acrylic gel dries in minutes, this step had to be done quickly. Once the sample was in place another drop or two of the gel was placed over the top of the sample. This was allowed to flow down the sides of the sample for complete encapsulation. Any open areas or cracks would defeat the purpose for encapsulation. Once the gel has dried to a film, the top layer of the polyester resin can be prepared as usual and poured over the sample. Upon curing, the embedded cross section can be polished or microtomed for analysis.

Figure 13 shows a photomicrograph of a paint cross section from a polychrome sculpture that was encapsulated in the silica/acrylic then embedded in polyester resin. The sample exhibits no visual signs of infiltration and the glue containing ground layer of the sample stained uniformly with FITC. The lower portion of figure 13 shows the infrared spectrum obtained from a thin section of the embedded sample. Infrared analysis confirmed that the ground layer of the sample did not experience infiltration of the polyester. Thus, the encapsulation of the sample was successful.

Conclusions

Polyester resins work well for embedding most paint cross sections. In a comparison of several types of polymers, polyester resins met the requirements for an ideal embedding media for paint cross sections much better than epoxies or acrylics. However, embedding resins, such as the polyester, can dissolve some wax and resin layers. Additionally, during the embedding process, porous, low binder paints experience penetration of most types of polymer solutions including polyester. This is visually detected by examining the cross section for poorly defined edges, darkening or discoloration and blotchy stain results. Infiltration may be confirmed by the analysis of the sample by infrared spectroscopy, where the presence of the embedding resin in the sample will produce a spectrum containing absorption bands characteristic of the resin. For any type of visual or analytical testing of the sample, infiltration is undesirable and steps should be taken to prevent the infiltration from occurring.

In this paper, several barrier methods were tested for coating the sample with materials prior to their embedding in the polyester resin. Rhoplex AC-33, thickened with fumed silica, worked the best of the methods tested. It formed a uniform coating around the sample that dried almost immediately. The sample was then embedded in polyester and no evidence of infiltration was found. Many other types of high viscosity or thixotropic materials, such as used in the lining of paintings, would probably work as well for the pre-coating of the sample.

Experimental Conditions

Samples

Three types of samples were embedded in this study. The first type of sample used consisted of known mixtures of glue and gypsum in order to test the effects of binder concentration. The second set of samples were obtained from a facsimile painting that had a glue/calcium carbonate ground layer. The third set of samples were small portions obtained from a larger sample (CAO42) that had fallen off of a polychrome sculpture. Quantitative analysis of the protein content of the sculpture sample by gas chromatography found that it contained 12 % by weight of glue in gypsum.

Microtoming

A RMC Model 7000 microtome configured with a glass knife was used to produce 5 micron thin sections of the embedded samples. The optimum thickness for infrared transmission analysis is 1-10 µm. Glass knives are made by scoring and breaking a 1" square of glass to give two triangular pieces, each with a sharp edge. The thin-sections are taken directly from the microtome, placed on a BaF_2 window and transferred to the sample stage of the infrared microscope for analysis.

Infrared Spectroscopy

A Spectra-Tech IRµS organic microprobe was used for the infrared analysis of the thin sections of each sample. It is equipped with a narrow-band, cryogenically cooled mercury cadmium telluride (MCT) detector. The spectra are the sum of 200 scans collected from 4000-800 cm-1 at a resolution of 4 cm-1. The IRµS is continually purged with dry, CO_2-free air.

Fluorescent Staining

Fluorescein isothiocyanate (FITC) was used as the reagent for staining the proteinaceous media in each of the samples. It gives a characteristic, bright yellow fluorescence that is most visible in light color pigment areas. A mercury light source and a D filter cube were used for the detection of the fluorescence.

Suppliers

Materials tested in this study were obtained from the suppliers listed below. These products are also available from other suppliers that specialize in general lab products and microscopy products.

Butylmethyl methacrylate (acrylic), Ladd Research Industries Inc., Burlington, Vt 05402, (802) 658-4961

Bio-Plastic (polyester), Ward's Natural Science, PO Box 92912, Rochester, NY, (800) 962-2660

Caroplastic (polyester), Carolina Biological Supply Company, 2700 York Road, Burlington, NC 27215, (800) 334-5551

Castolite (polyester), The Castolite Company, Woodstock, Illinois 60098, (815)338-4670

Epon 812 (epoxy), Ted Pella, Inc. P.O. Box 2318, Redding, CA 96099, (916) 243-2200

Krazy Glue (cyanoacrylate), B. Jadow & Sons, Inc. New York, NY 10010

LR White (acrylic), Ladd Research Industries Inc., Burlington, Vt 05402, (802) 658-4961

LX-112 (epoxy), Ladd Research Industries Inc., Burlington, Vt 05402, (802) 658-4961

Maraglas 655 (acrylic) Ladd Research Industries Inc., Burlington, Vt 05402, (802) 658-4961

Paraplast (wax), Ladd Research Industries Inc., Burlington, Vt 05402, (802) 658-4961

Quetol 523M (acrylic), Ted Pella, Inc. P.O. Box 2318, Redding, CA 96099, (916) 243-2200

SPURR (epoxy), Ted Pella, Inc. P.O. Box 2318, Redding, CA 96099, (916) 243-2200

Vestopal W (polyester), Ladd Research Industries Inc., Burlington, Vt 05402, (802) 658-4961

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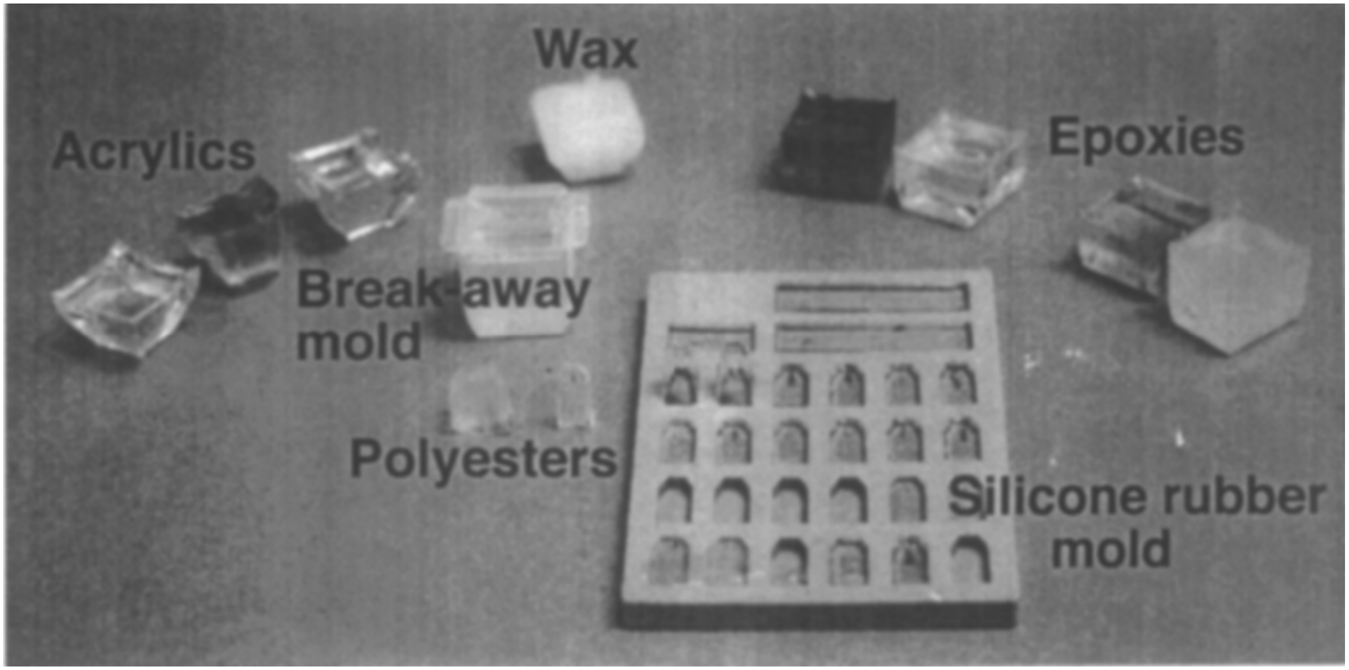


Figure 1. Example blocks of embedding media for paint cross sections corresponding to Table 1. Break-away molds and small, flexible silicone rubber molds are shown.

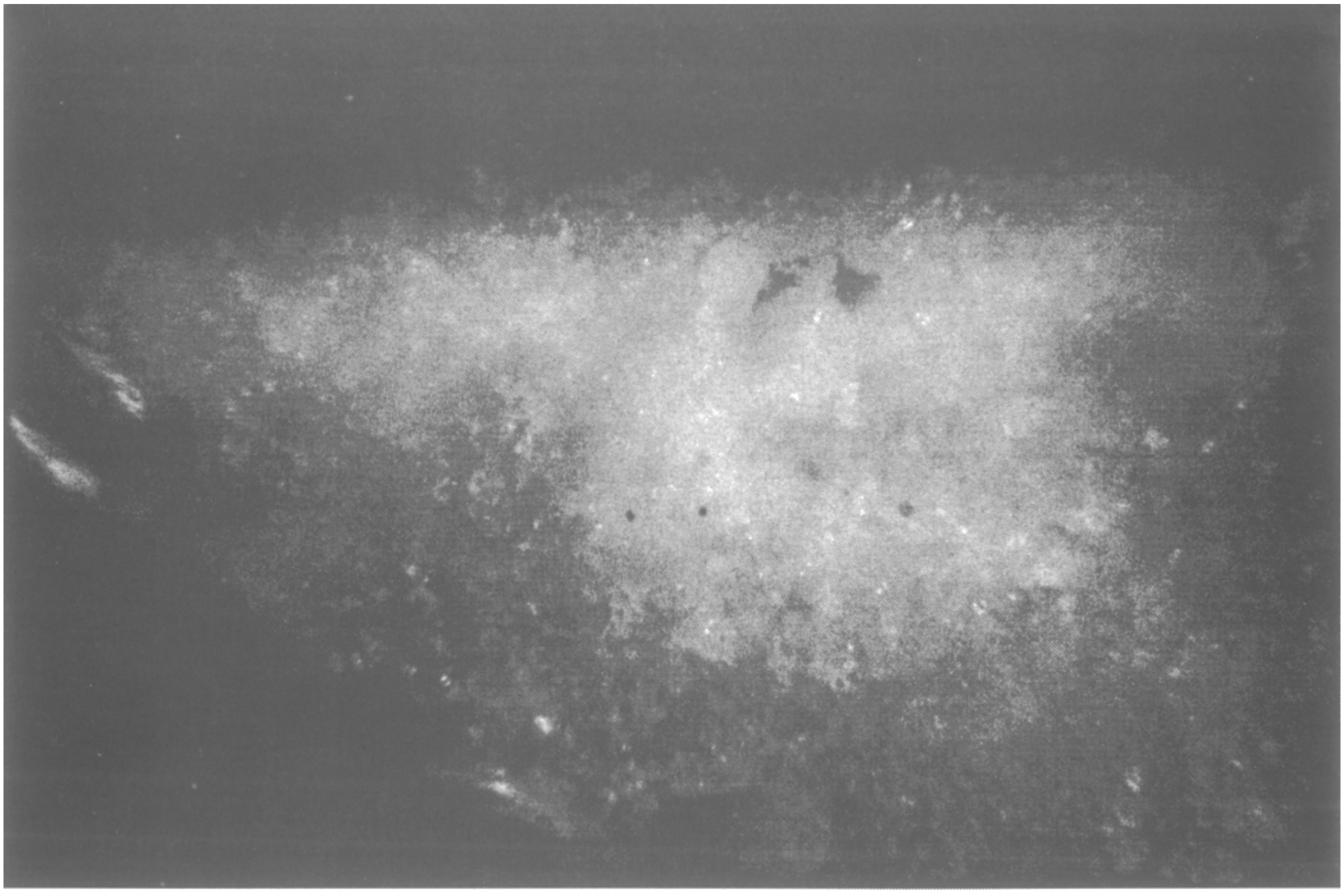


Figure 2. Photomicrograph of embedded cross section showing the visual effects of resin infiltration into the sample. Prior to embedding, the ground layer was an opaque white. The resin infiltrated edges are now darker and more transparent.

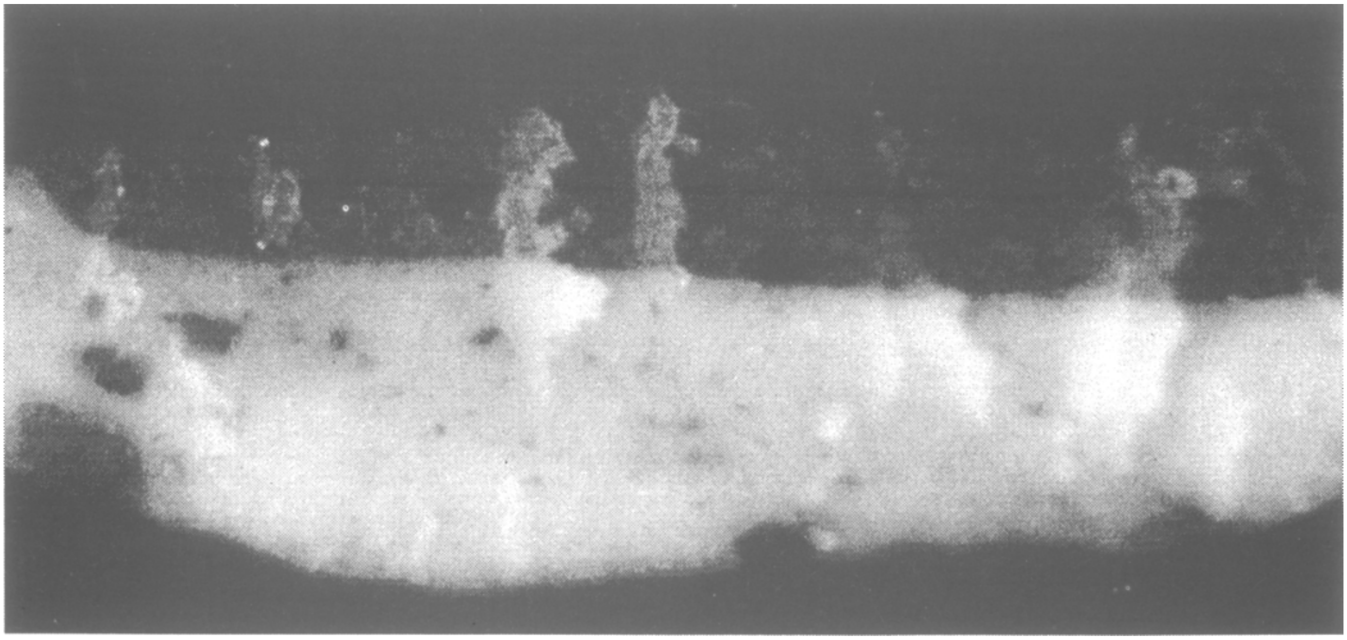


Figure 3. Photomicrograph of embedded paint cross section that is not infiltrated with embedding media. The edges are well-defined, the sample appears opaque and except for pigment variations, the colors are uniform. Most embedded cross sections are similar to this sample.

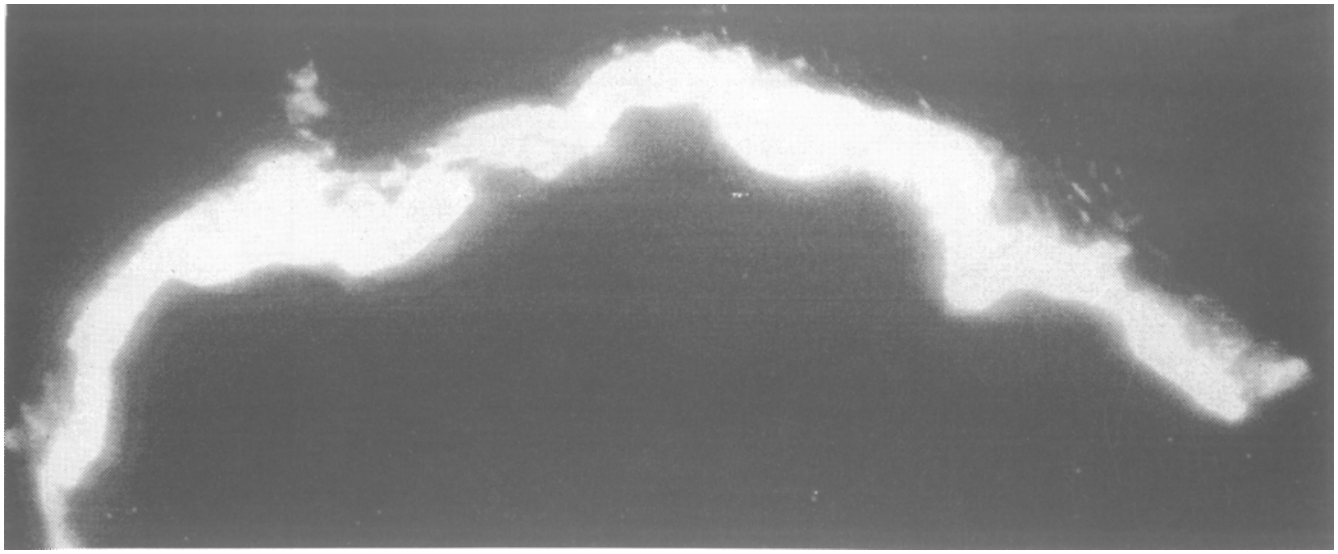


Figure 4. Photomicrograph of embedded cross section containing 40 w/w% glue in gypsum after staining with FITC. The high binder content results in a non-porous sample that is not infiltrated by the embedding resin. The FITC stains the protein in the sample uniformly and fluoresces a bright yellow color (white in black/white photo).

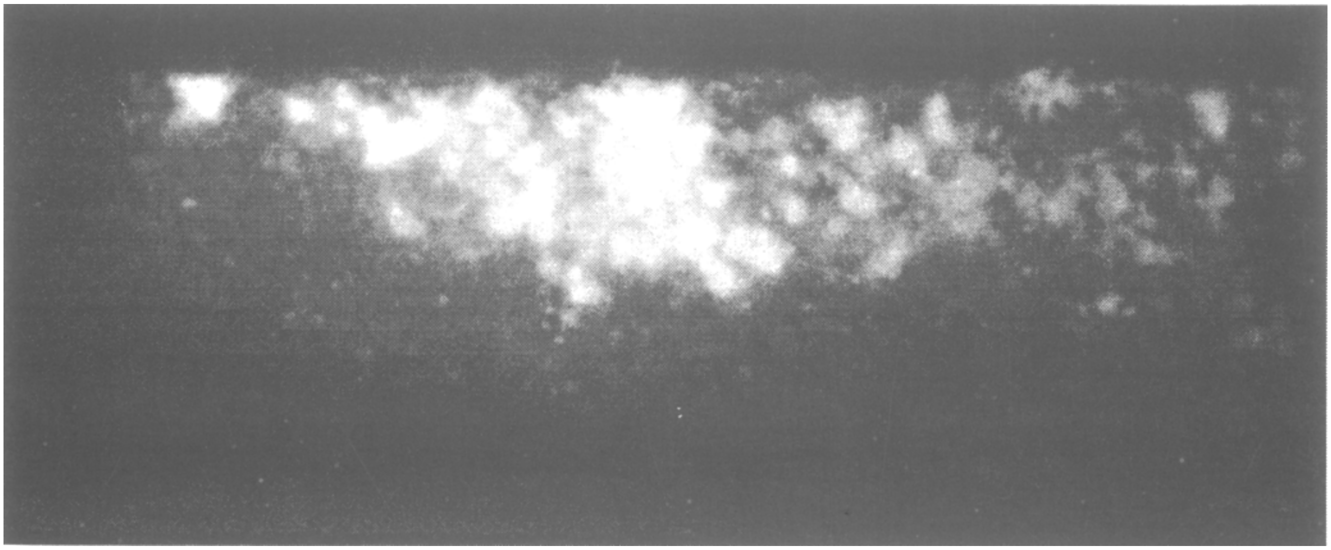


Figure 5. Photomicrograph of embedded cross section containing 5 w/w% glue in gypsum after staining with FITC. This low binder content results in a porous sample that rapidly wicks in embedding resin. The resin coats the sample particles and causes uneven fluorescent staining with FITC. The stained areas appear bright white in this black/white photo.

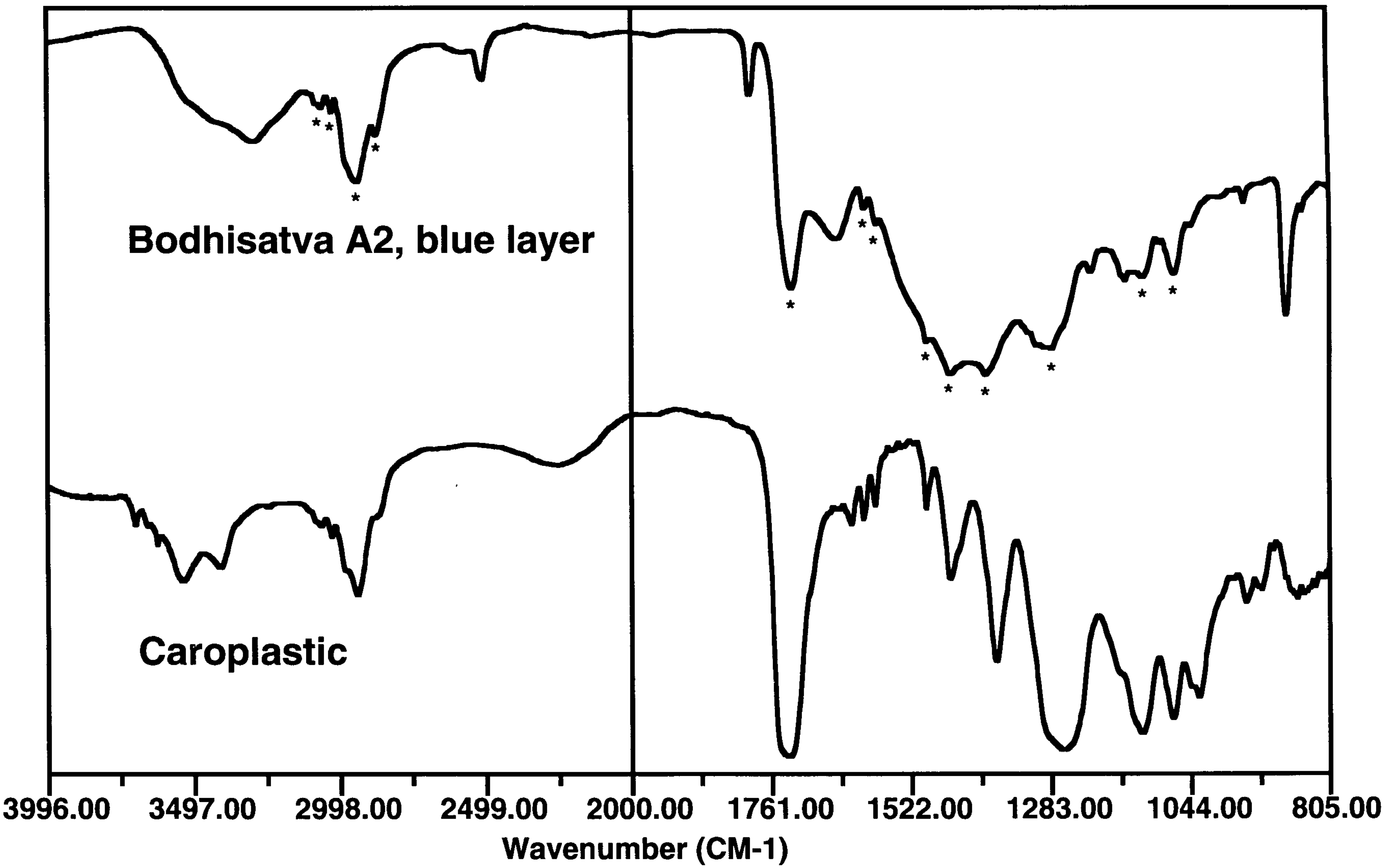


Figure 6. Infrared spectrum of paint cross section sample (top) and Caroplastic resin (bottom). The spectrum for the paint sample contains absorption bands corresponding to the embedding resin (marked *). This shows that the embedding resin has soaked into the paint sample.

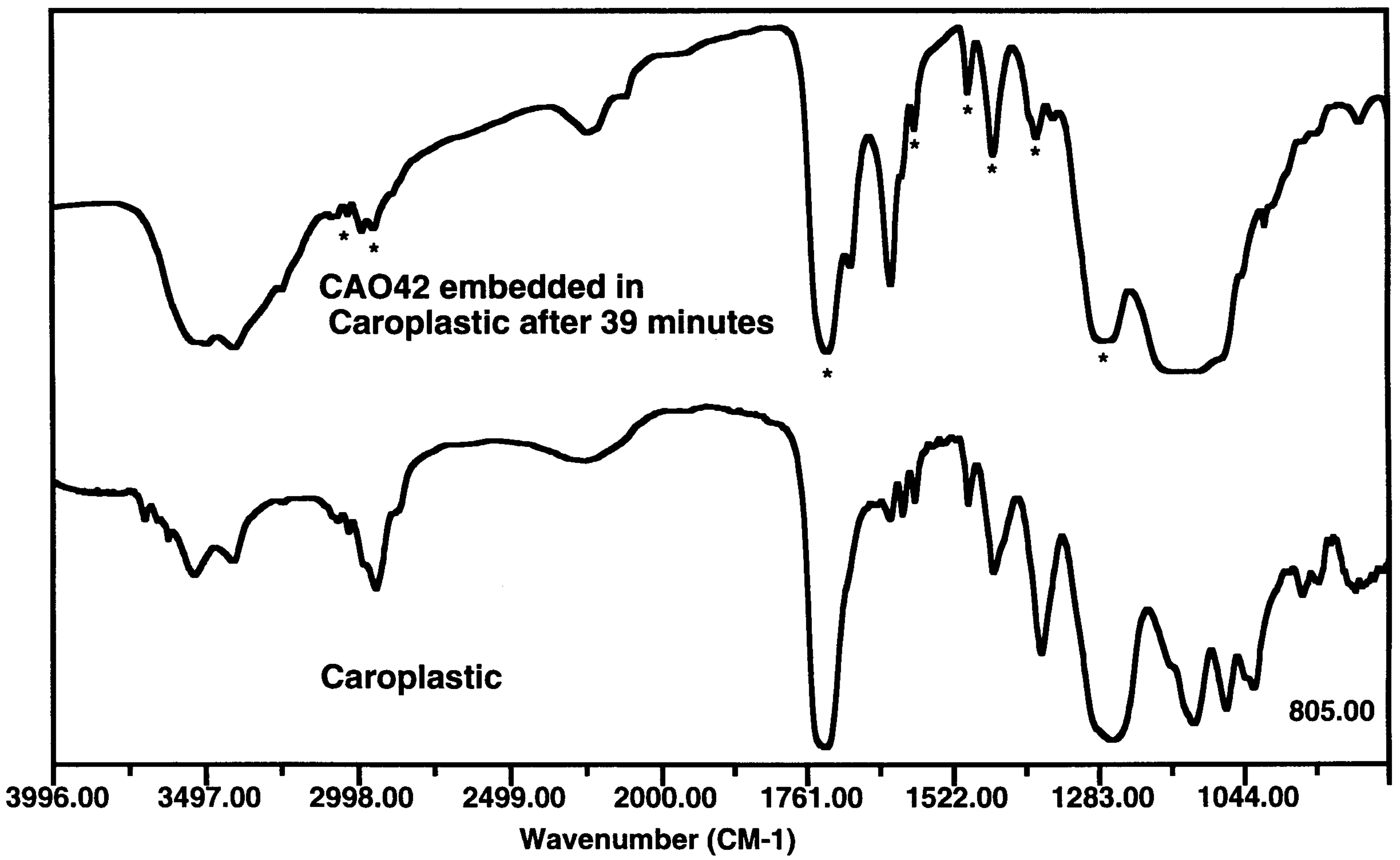


Figure 7. Infrared spectra of Caroplastic (bottom) and paint cross section (top) that was embedded in Caroplastic 39 minutes after the catalyst was added to the resin solution. Even though the embedding resin was extremely thick when it was placed on the top of the sample, the paint sample was still infiltrated by the resin. This is shown by its spectrum, which contains absorption bands corresponding to the embedding resin (marked *).

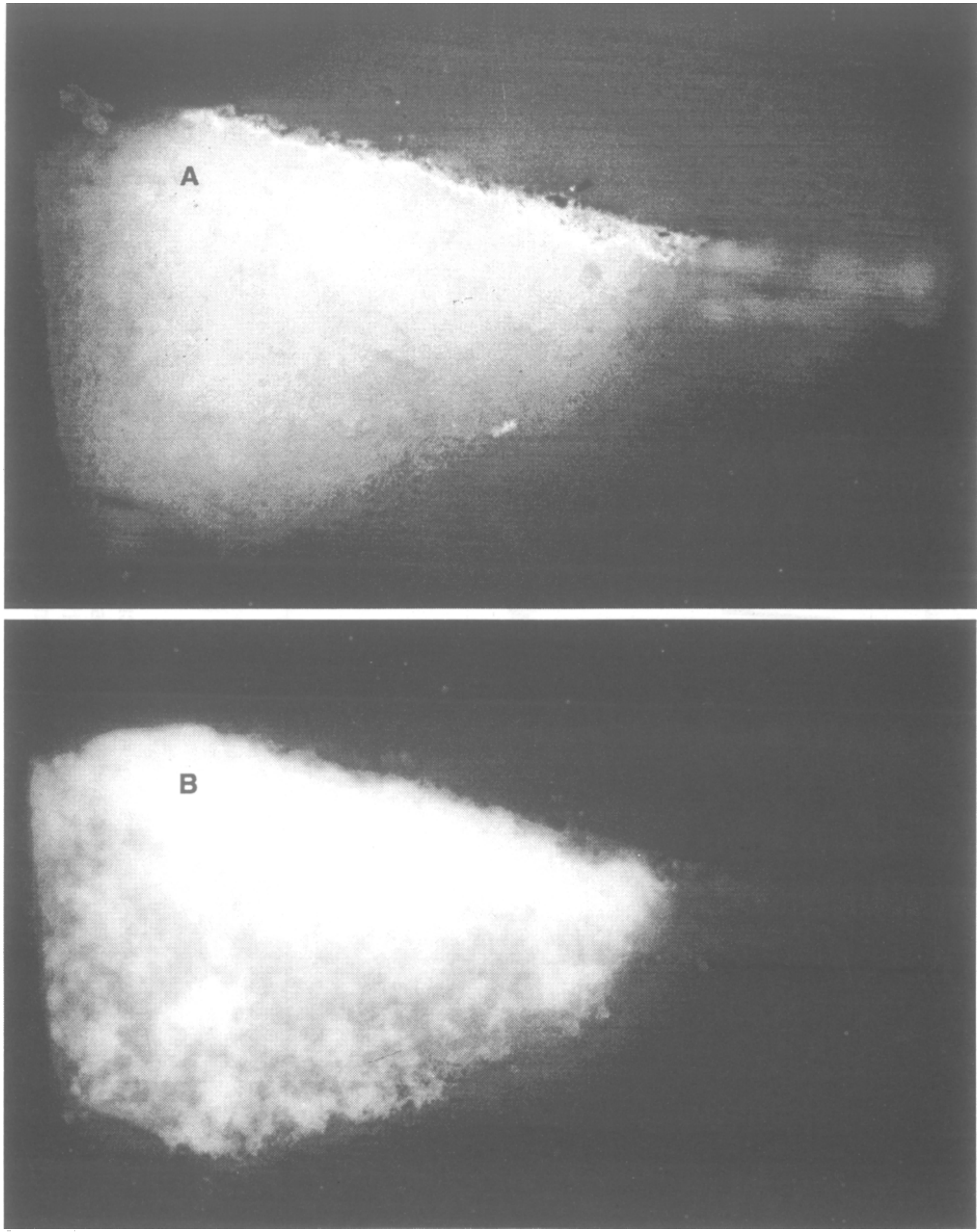


Figure 8. Photomicrographs (A=unstained and B=stained with FITC) of embedded facsimile cross section coated with wax prior to embedding in polyester resin. The wax did not prevent the infiltration of the resin. In fact, the resin dissolved the wax, creating the 'halo' effect seen around the sample. Even though, in photo B, the bright fluorescent yellow stain appears as white due to the black/white image, it can be seen that the acceptance of the stain by the sample is not uniform due to the infiltration of the embedding media.

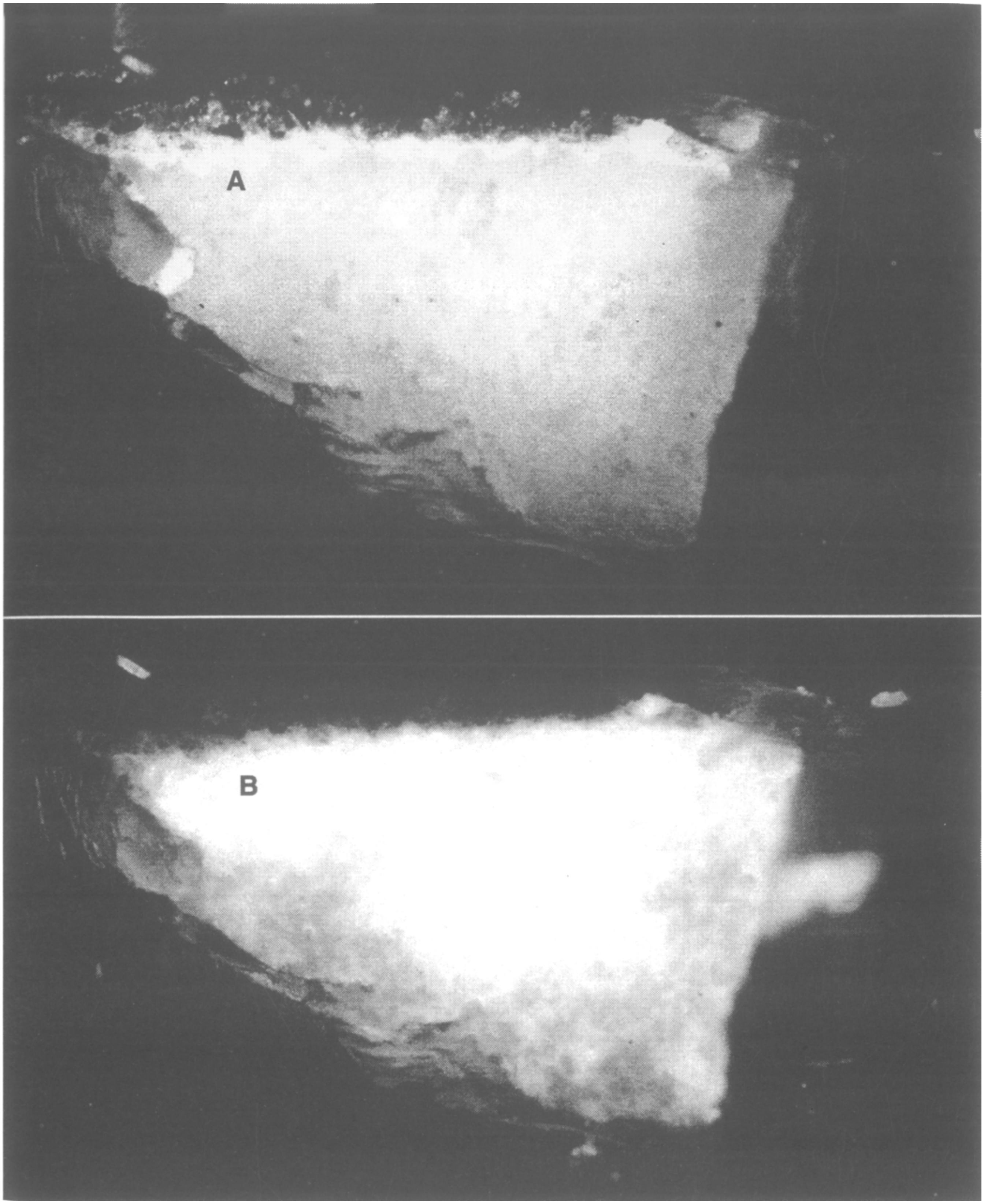


Figure 9. Photomicrographs (A=unstained and B=stained with FITC) of facsimile cross section wrapped in Parafilm prior to embedding in polyester resin. The Parafilm did not prevent infiltration of the resin. Even though, in photo B, the bright fluorescent yellow stain appears as white in the black/white image, it can be seen that the stained area is not uniform due to the infiltration of the embedding media.

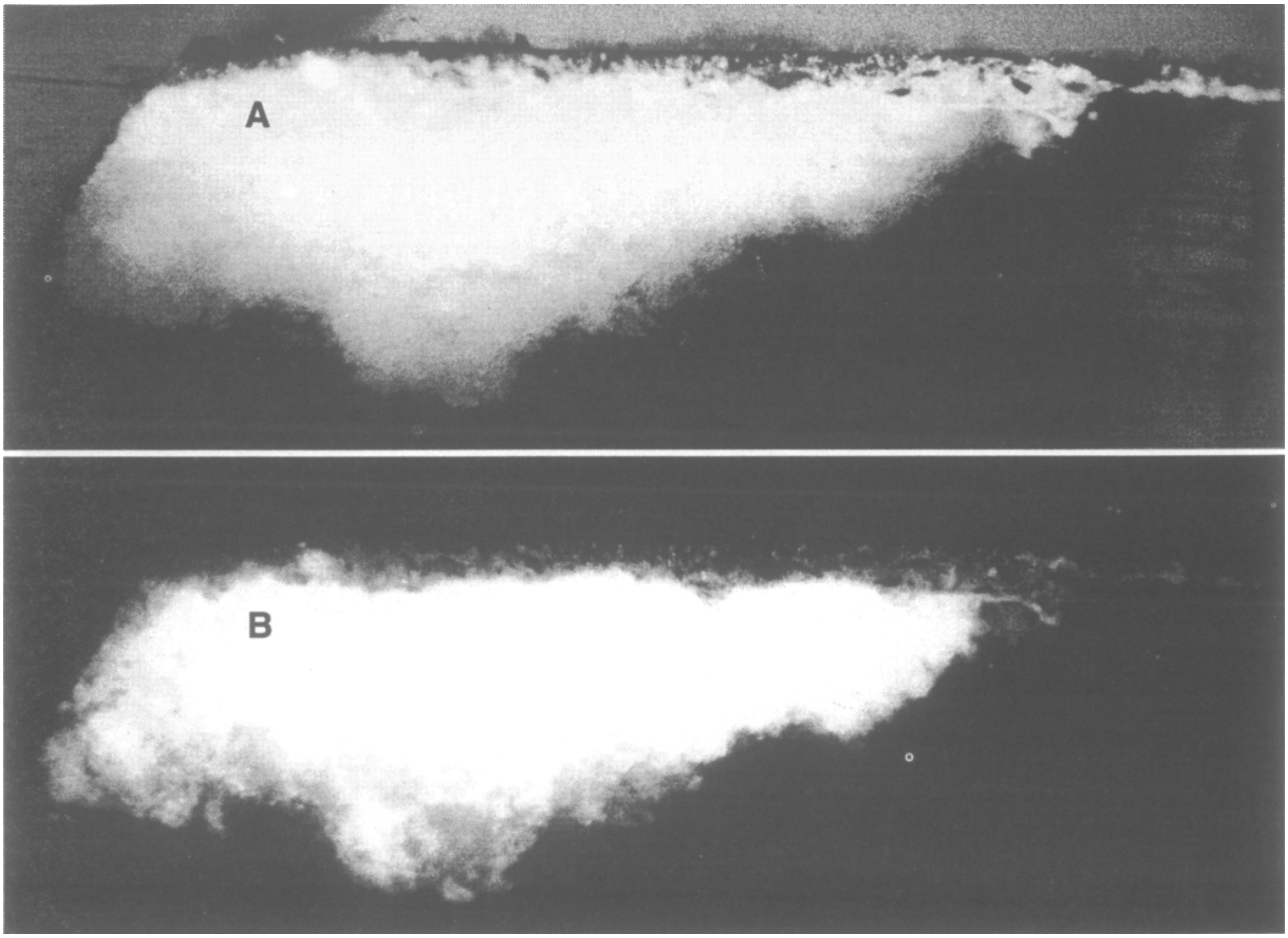


Figure 10. Photomicrographs (A=unstained and B=stained with FITC) of facsimile cross section sputter coated with gold prior to embedding in polyester resin. The gold layer did not prevent infiltration of the resin. Even though, in photo B, the bright fluorescent yellow stain appears as white in the black/white image, it can be seen that the stained area is not uniform due to the infiltration of the embedding media.

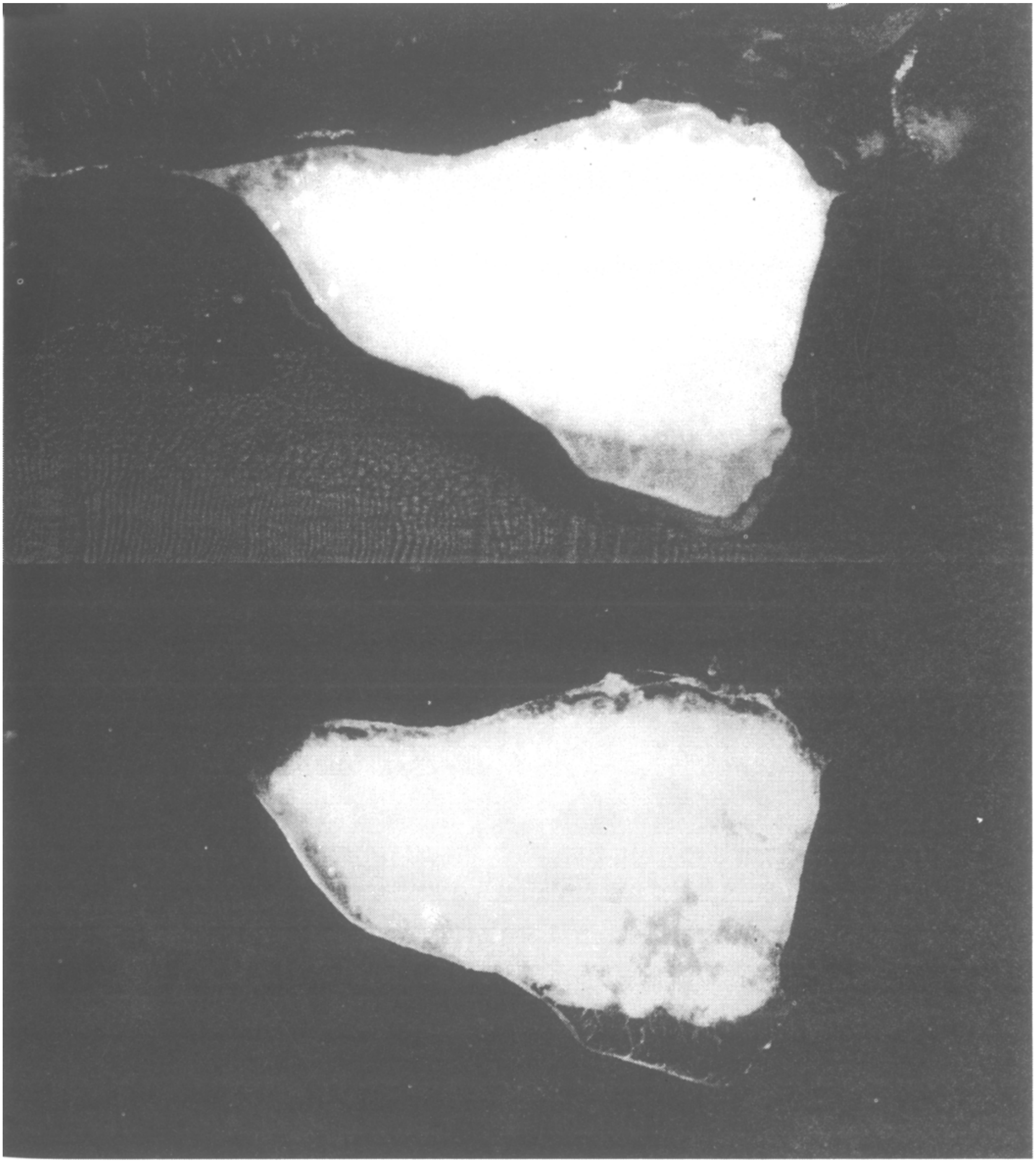


Figure 11. Photomicrographs (A=unstained and B=stained with FITC) of facsimile cross section wrapped in aluminum foil prior to embedding in polyester resin. The aluminum foil did not prevent infiltration of the resin. Even though, in photo B, the bright fluorescent yellow stain appears as white in the black/white image, it can be seen that the stained area is not uniform due to the infiltration of the embedding media.

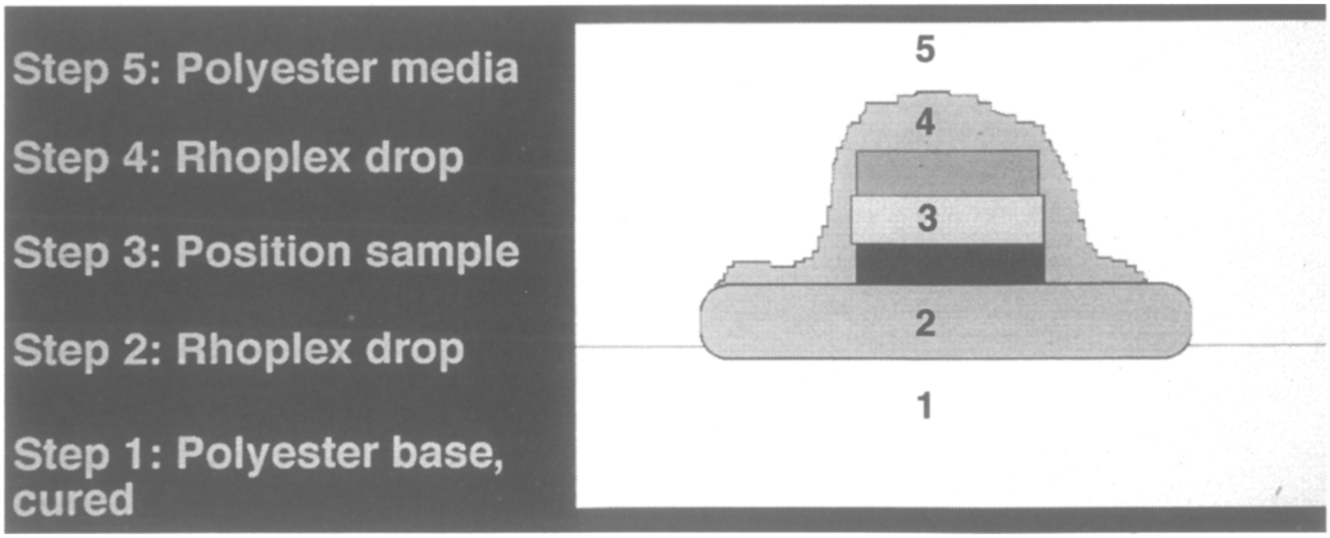


Figure 12. Diagram showing the steps used for encapsulating a cross section sample with a barrier material inside a polyester embedding resin.

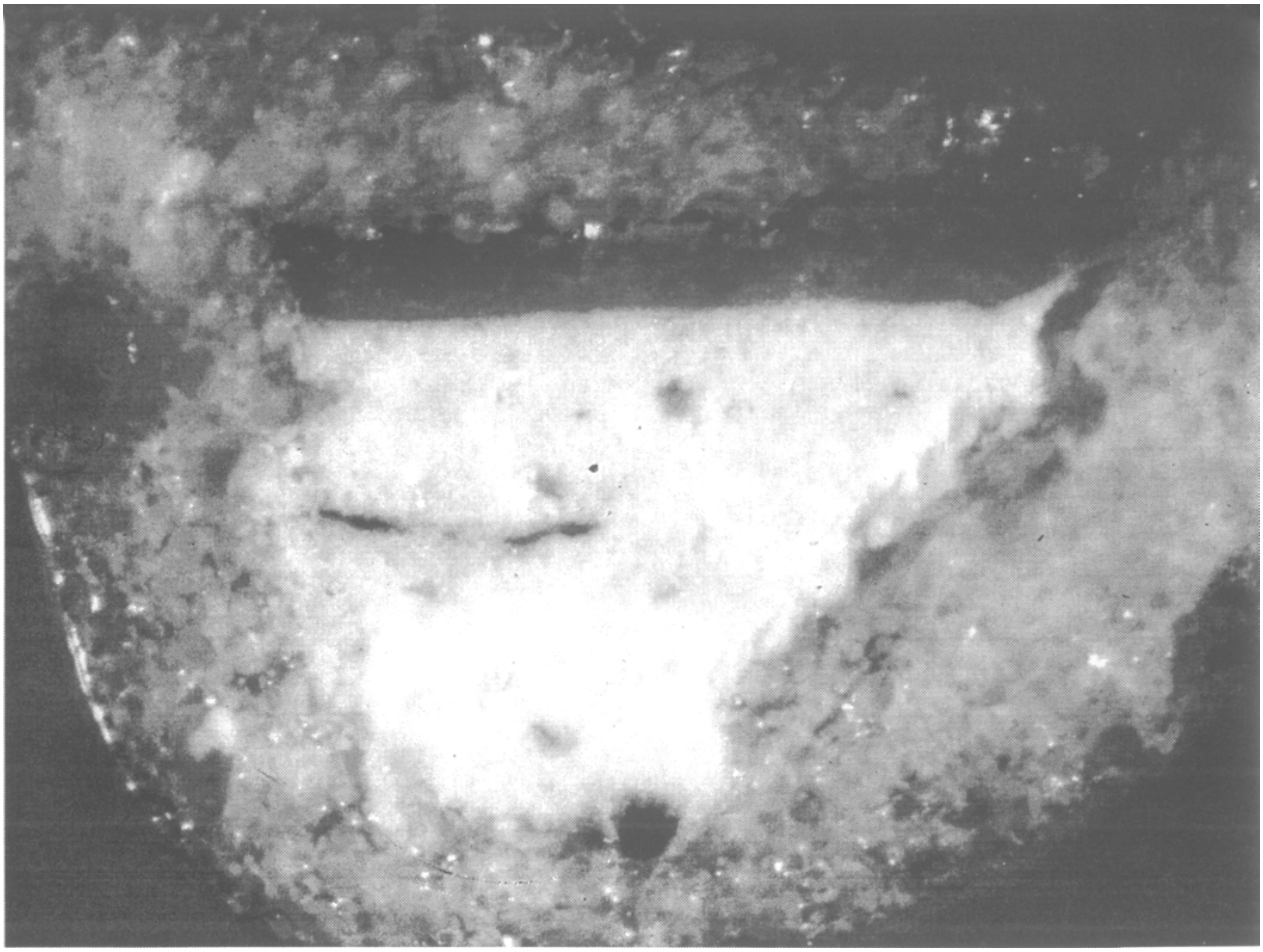
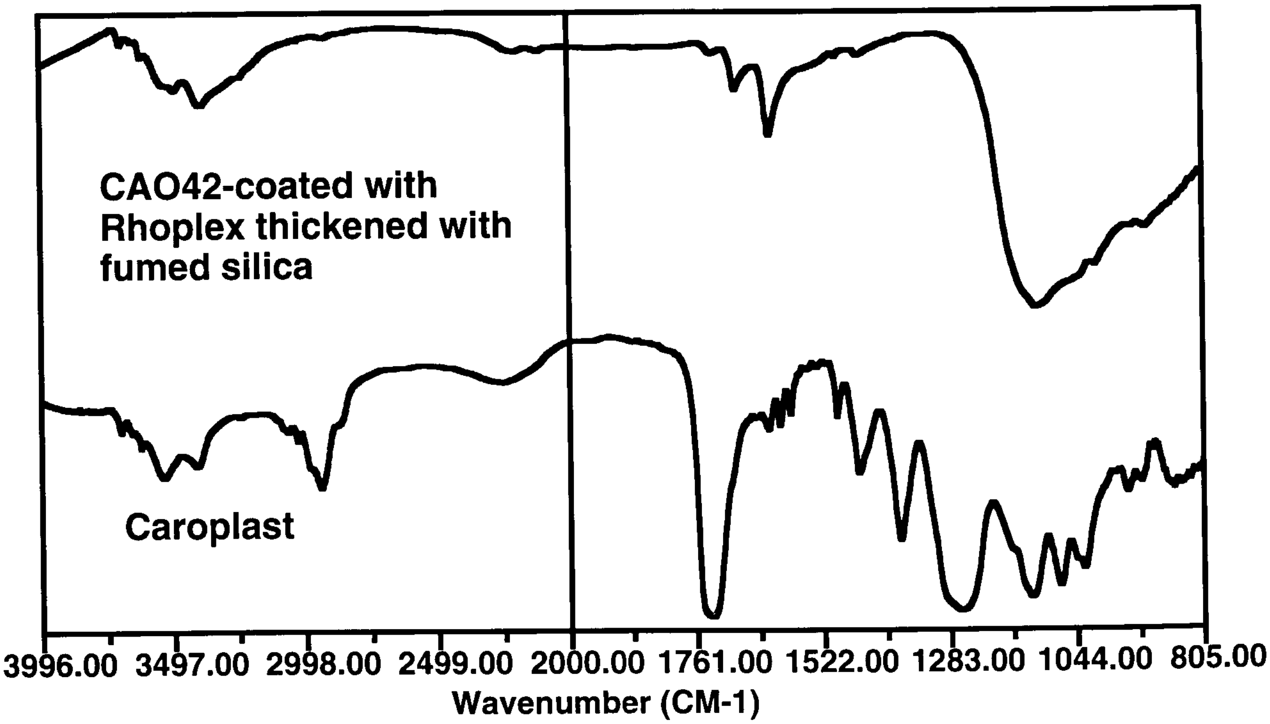


Figure 13. Photomicrograph (above) of paint cross section encapsulated in Rhoplex-AC33/fumed silica prior to embedding in polyester resin. Analysis by infrared spectroscopy (below) showed that the embedding resin did not penetrate the sample.



THE CONSOLIDATION OF MATTE, POROUS PAINT: EXAMPLES FROM ETHNOGRAPHIC OBJECTS AND CONTEMPORARY WORKS OF ART

Eric F. Hansen*, Paula Volent**, Mitchell H. Bishop* and Rosa Lowinger***

ABSTRACT

Matte, porous paint, highly friable and difficult to consolidate without darkening and discoloring, is found in a wide range of objects. Some physical and optical properties of this type of paint, as a result of high pigment volume concentration and diffuse surface reflectance, are presented with a stress on ramifications for treatment parameters. The problems encountered in transferring the results of controlled laboratory studies into effective conservation treatment procedures are also discussed in reference to painted ethnographic wood objects and contemporary works of art on paper (with a cautionary note on undesirable solvent sensitivity).

PHYSICAL AND OPTICAL PROPERTIES OF HIGH PIGMENT VOLUME CONCENTRATION PAINT

The difficulty encountered in the consolidation of matte, porous paint is a change in appearance following the application of a consolidant. Application of a consolidant to the surface of a powdering matte paint may cause darkening, an increase in gloss or a noticeable "tide-line" (a dark outline defining the extent to which the consolidant solution has spread). An adhesive solution, applied at the interface of the substrate and a porous flake, may wick into the flake resulting in similar changes in appearance.

These changes in lightness and chroma are often due to changes in the ratio of the volume of pigment to the volume of resin in the paint. This property, the Pigment Volume Concentration (PVC), is directly or indirectly responsible for much of the behavior of some coatings systems (Asbeck 1949) including matte, porous paint. Another primary factor affecting the appearance is the surface roughness which affects the specular reflectance and is related to changes in types of gloss.

The coatings industry has long been aware of the importance of an understanding of PVC, especially the property of Critical Pigment Volume Concentration (CPVC), because CPVC affects the manufacture, application, performance and appearance of all coatings (Asbeck 1992). It is just as imperative for conservators working with painted surfaces as for coatings manufacturers to be aware of what PVC and CPVC are and how they influence various treatment parameters. In the case of consolidation of porous, matte paint, treatment parameters of greatest interest are those which control the penetration, distribution, and leveling of added resin solutions; two of the most important are solution viscosity and solvent volatility.

Starting in the late 1920's (Steig 1973), it has been recognized by the coatings industry that the formulation of paint needs to be approached on the basis of volume relationships rather than weight relationships. The reason for this is illustrated in the pigment volume "ladder" (Figure 1). The ladder is a schematic of the paint system with a 10% increase in each "step" from 0% pigment, totally comprised of vehicle, to 100% pigment (high PVC). As the percentage of vehicle is increased, the void space between pigment particles decreases as it is filled.

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In the system illustrated, at 50% pigment volume concentration all the void space is filled with vehicle. This point is known as the Critical Pigment Volume Concentration (CPVC). Below the CPVC, with excess vehicle, the surface becomes smoother and glossier. Many coating properties change radically at CPVC, because this is the point where the coating changes from being a porous system to a solid system. This can be demonstrated by plotting properties, such as gloss and permeability against the PVC ladder, where representative curves are illustrated figure 2. Both the physical and optical properties of a paint depend upon the PVC. A matte, porous paint is at a PVC above the CPVC. Because little binder is present, extensibility and strength decrease at higher PVC. This lack of physical integrity is a reason why porous paint often needs consolidation.

In general, because surface roughness causes diffuse reflectance and thus perceived lightening due to the additive mixing of the scattered illuminant radiation, a similar PVC paint with a rougher surface that reflects less light specularly appears lighter, with lower gloss and reduced chroma, depending upon the angle of the viewing. When the volume of the pigment is increased sufficiently, scattering also increases due to the greater volume of air/pigment interfaces. Thus, factors that influence both the leveling of solutions on the surface and distribution of solutions within a porous paint affect the appearance.

Darkening results from reducing the void spaces; localized surface concentrations of resin are particularly troublesome. Solution viscosity and solvent volatility, which control the penetration and distribution of the resin, are important factors to be considered in designing treatment strategies. Individual resin properties, such as refractive index (Feller and Kunz 1981), are of little importance. The concept of "reverse migration" of a resin to the surface with solvent evaporation has also been shown to have little relevance to these systems (Hansen et al 1993b).

Previous studies at the Getty Conservation Institute (Hansen, et al 1990; Hansen et al 1993b) have revolved around understanding what occurs when different application procedures are used. When increased penetration and distribution are desired, low volatility solvents, pre-wetting, multiple applications of dilute solutions, surfactants, the use of small particle size dispersions, and working in an atmosphere saturated with solvent vapors have been considered (Hansen and Lowinger 1990).

When a solution composed of a resin and a volatile solvent is applied to the paint surface, solvent evaporation causes an increase in concentration of resin flowing into the paint as the solution flows inward and outward (figure 3). This may result in greater concentrations of resin both at the surface and at the final front of outward flow, resulting in a tide-line (figure 4). Thus, instead of "reverse migration" outward with solvent evaporation, with a highly volatile solvent a resin may not have initially penetrated to much extent. This particular method was developed because in many instances an alternative method, using a low volatility solvent like diethylbenzene, simply didn't work or could not be used because of negative effects due to long term solvent retention (Hansen et al 1993b).

ETHNOGRAPHIC AND CONTEMPORARY ART OBJECTS

Matte paint, although the matte effect is not necessarily the result of an intentional effort, is found on a wide variety of objects including ethnographic objects, archaeological and historic wall paintings, Medieval tuechlein panel painting, Colonial American distemper architectural wall paints and contemporary works of art. In some cases little or no binding media was used, or a locally available binder that deteriorates rapidly may have been used. However, the matte effects on more contemporary works of art, achieved by using little binding media or even leaching binding media out of an oil or acrylic paint with turpentine, have often been the result of a desire for a matte aesthetic effect (Hansen et al 1993a, 1994).

Figure 1. Pigment Volume Concentration ladder with CPVC arbitrarily at 50%. From Asbeck 1992.

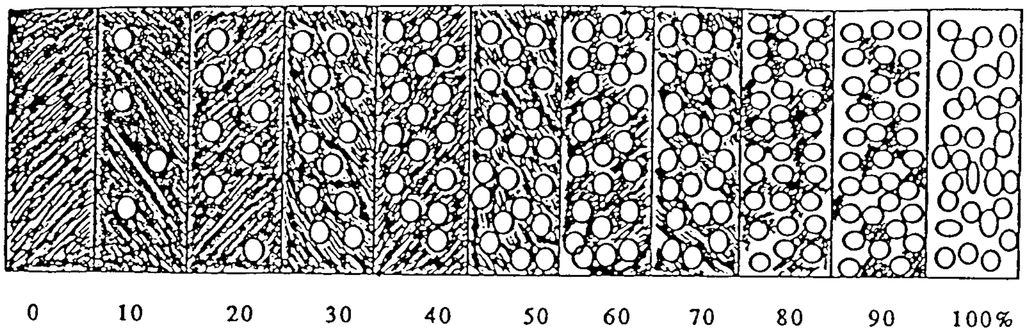
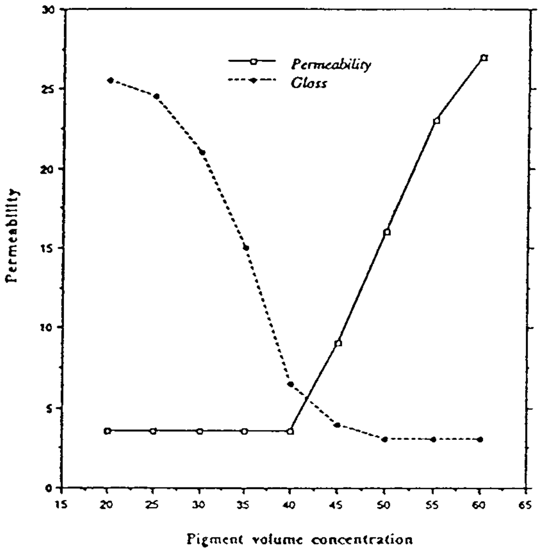


Figure 2.
From Asbeck 1992.



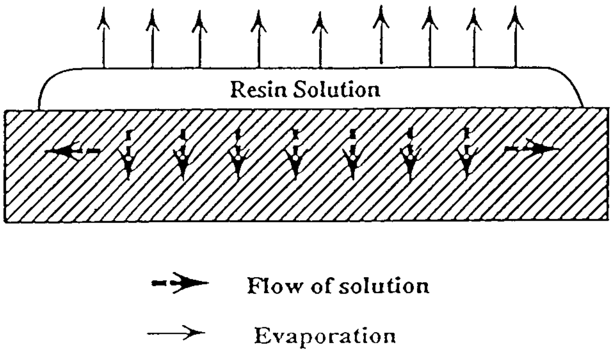
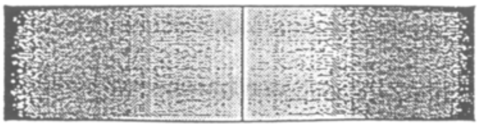


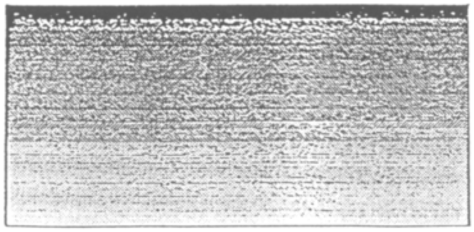
Figure 3. Schematic drawing of resin solution applied in air. From Hansen et.al. 1993.

4a.



"Tide" mark

4b.



Darkening, gloss

Figures 4a and 4b. Possible concentration profiles of resin solution, shown in cross section (darker areas indicate higher resin concentration). From Hansen et.al. 1993.

Paintings of a relatively simple composition, such as many Australian bark paintings (consisting of red and yellow ochres, white clay, and other inorganic pigments) have been successfully consolidated in an air bag in a vapor saturated atmosphere (Walston 1993). Because this system depends upon control of solvent volatility, treatment modifications based upon this phenomena have also been successful. Powdering paint on extremely large, Egyptian wood sculptures that could not be placed in an arm-bag in a fume hood were successfully consolidated by creating a saturated vapor micro-environment. In this case, an impermeable sheet of plastic was laid down immediately following the brush application of a consolidant solution, delaying solvent evaporation and achieving the desired effect (D' Alessandro 1993).

However, when this technique was used in the conservation of a contemporary work of art on paper (consolidation of porous paint in a vapor-saturated atmosphere) certain practical limitations were discovered that should be addressed prior to the use of this type of treatment in the conservation laboratory. The limitations involved the possibility of increased solvent sensitivity of materials due to the prolonged solvent exposure necessary in the use of a solvent vapor chamber.

The vapor saturated atmosphere was considered in the preliminary treatment design of the consolidation of a severely flaking gouache on paper, *Untitled Figure* 1953, by the artist Karel Appell. Traditional techniques for consolidation of the gouache, including the use of dilute gelatin or cellulose ether solution, proved extremely time intensive as well as resulting in discrete changes in appearance. Lowinger had successfully used a vapor saturated chamber to consolidate extensively flaking porous paint on wooden objects in a labor saving manner: introducing the resin by brush in a vapor saturated atmosphere, which penetrated the porous paint in large areas without discoloration, and subsequently laying down the flaking paint which had been saturated by resin solution by applying a hot spatula to Teflon sheeting laid on the surface. This approach was considered for the gouache not only to reduce changes in appearance but also to reduce the time involved in the meticulous adhering of small, friable paint flakes over large areas.

After careful solubility tests on the Appell gouache, a solution of poly (vinyl acetate) (PVAC) AYAF in ethanol was chosen as a possible consolidant. PVAC is an extremely stable resin (Class A in Feller's [1980] classification) with excellent characteristics as an adhesive or a consolidant. Tests with the resin in other solvents, both toluene and acetone, caused various colored staining to develop in the area of application. Outside the vapor atmosphere use of an ethanol solution caused no stain formation but, apparently because the consolidant had not sufficiently penetrated into the porous paint layer, both inadequate consolidation and a slight change in the appearance of the treated area was apparent. In order to achieve maximum penetration and distribution of the consolidant, thus preserving the matte quality, the consolidant solution was tested in the vapor atmosphere.

The drawing was placed in the glove bag along with open pools of ethanol which saturated the atmosphere with solvent vapor. A small amount of the consolidant was applied to several test areas of the paint. On removal from the bag, discoloration and staining of the areas tested was observed, similar to the staining observed when aqueous and organic solvent solutions were applied in an open atmosphere. This method was then rejected, and the flakes laid down individually with a very viscous methyl cellulose solution (which, because of the lack of flow and relatively rapid drying time, did not result in the staining evident when dilute aqueous solutions were employed) .

In a subsequent interview with the artist by Volent, Appell disclosed that he often included colored magazine page collage pieces beneath the drawing surface. It is possible that solvent interaction between the dyes present in magazines illustration and the ethanol was promoted by the longer exposure which results from the use of the vapor saturated atmosphere technique (solubility being time dependent). Thus, solvent interaction tests must be done under the conditions in which they will be used. Careful testing should be done with increased exposure to solvent prior to the use of any solvent atmosphere, including pretreatment of tape stains and adhesive staining with solvent cups or poultices, and new applications of solvent vapor through permeable materials such as Gore-tex.

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THE RECOVERY AND TREATMENT OF A STOLEN 16TH CENTURY PANEL PAINTING BY AMBROSIUS BENSON FROM A WHEAT FIELD

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This article focuses on the recovery and subsequent treatment of a stolen 16th century panel painting by Ambrosius Benson entitled "Lamentation" which was found in a wheat field.

The painting belongs to the Columbus Chapel and Boal Mansion, located in Boalsburg, Pennsylvania, which is about 2 miles from State College and Penn State University. The Boal family has lived on this same estate for nine generations and are related to three signers of the Declaration of Independence, a Maryland Governor, an employer of Howard Carter who discovered King Tutankamun's tomb, Robert E. Lee, St. Bernard who trained the dogs to rescue people in the Alps and most notably, are direct descendants of Christopher Columbus. A stone building, on the grounds, was built in around 1912 specifically to hold the contents of a chapel from the Columbus family castle, "Lamas Del Mouro", near Asturias, Spain. Many of the reliques date from the time of Columbus, including a desk which is said by the family to have belonged to Christopher Columbus or his don Diego (Fig. #1). The family tree, hanging on the wall, beginning Christobal Colon (Christopher Columbus) shows his descendants through the 1793.

In honor of the five hundredth anniversary of the Admiral's discovery of America, an exhibition was held at The State Museum of Pennsylvania in Harrisburg opening in December of 1991. Since this institution is one of our museum commission's sites, the Commonwealth Conservation Center prepared many of the Boal Mansion/Columbus Chapel artifacts for exhibition. I personally conserved a dozen paintings, included in which was Benson's painting of the "Lamentation". This was to be the first time I conserved this painting. Little did I realize it's impending fate.

In preparation for exhibition I thinned it's heavily discolored natural resin varnish and removed the gross areas of previous over-paint with acetone. I consolidated isolated areas of flaking paint with Beva 371 which was thinned with naphtha. An isolating coating of acryloid B-72 was spray applied and it was inpainted with Magna Colors and Maimeri Artist Restoration Colors. A final spray surface coating of B-72 was applied.

On Sunday June 14th, 1992 approximately two months after the artifacts were returned to Boalsburg from The State Museum's exhibition, the Columbus Chapel was broken into and Benson's Lamentation along with two other paintings, nine swords and a conquistadors helmet were stolen. The State Police and the FBI were immediately brought in to investigate the crime.

To begin this story, I would like to discuss the illustrative and sorted carrier of the artist, Ambrosius Benson, whose catalog Resonee by George Marlier, written in 1957, is entitled "Ambrosius Benson and the painters of Bruges in the time of Charles the 5th (1). Benson was born in Italy around 1500, and is first mentioned when he arrived in Bruges in 1519. He lived his entire life in this area with the possible exception of a three to four year period from 1532-36 when he might have been in Spain, which is when the painting is thought to have been commissioned. He died in Bruges in 1550. Surprisingly enough, none of his paintings remain in Bruges, but exist in large quantities in Spain where he had many patrons. It is not through his art that information about Benson's life survives, but through the court system which he seemed to have frequented many times. For a long period of time he worked with Gerard David, not studying under him, but working in the same studio in something similar to an artists colony. In fact, he had lived with David, which is when his troubles began. When Benson finally moved out, David refused to return belongings of his which were stored in two trunks in his house. Contained in these trunks, as translated from Marlier's Book in French, "A great many projects and various models concerning the art of painting and illumination, then a little book containing portraits and nude figures, a panel representing Our Lady which Benson had painted for his father, and a little Pieta panel, also finished, another Pieta panel and a magdelene, begun in terre-verte, plus a book of various colors, several models that David had removed from Isenbrant's house (another artist of the period) and several models Benson had borrowed from Aelbrecht, for which he had paid 2 florias." The court found that these documents did indeed belong to Benson and demanded that David return them, judgement rendered January 28th 1520. David didn't and Benson had him thrown in jail. These articles were very important to Benson, many of which were sketches by the old Italian masters. He continued through his entire career to refer to or use his predecessors compositions in many of his portraits and devotional paintings.

In 1530 Benson's friend Isenbrant was accused of committing adultery with the wife of a local inn keeper in an inn that they both frequented. After she denied any wrong doings, she admitted to having relations with both Isenbrant and Benson. She and Isenbrant both asked that court for pardon. Benson seemed for the mean time to have gotten out of this situation. In an August 18th, 1530 document, it states "Ambrosius Benson, presumed to have committed adultery with the owner of the "Five Stars Inn". He denied the fact. No sanction was recorded," and then "March 16th, 1531 Benson was condemned to pay 4 pounds, 4 escalis to his illegitimate daughter Jozine." No more contesting, I guess?

The artist was both very prolific and successful in his carrier which lasted at least thirty years. He was elected to many position of authority in the artist guild in Bruges. He was a member of the "Sermont" or "The Oath" as a sworn advisor in 1521, 1539 and 1545. His title was "Vinder of the Guild". In 1540 he was elected Governor, in charge of financial management and was twice elected "Elder" in 1537 and 1543. Also pictured, in an 1951 article in Connoisseur Magazine and in Marlier's book is this version of the Lamentation by Benson, which appears to be the central panel of a trypitch (Fig. #2). Although the where-a-bouts of the flanking panels was unknown when Marlier wrote his book, the center panel was then part of the collection of C. F. Turner of Pinchbeck, Lincolnshire, England. I had hoped to find this painting, to aid me in the treatment of the Boalsburg Lamentation but for the present, it's location eludes me. I found after several calls to England that Turner was a wealthy mill owner and had a large art collection. He unfortunately died in 1972. Friends of his in England directed me to his daughter who now lives in Scottsdale, Arizona. She also unfortunately was not in England during the time her father owned this painting. I was given several other leads to follow but regrettably, this AIC Conference was coming up to quickly for me to continue my pursuit. I will however, compare this other Benson version to the Boalsburg painting later in my discussion.

Back to Columbus! As I said previously, Benson did a large number of commissions for Spanish patrons. One of these, Lucas de Castro known as the "Merchant of Spain", brought Benson once again into the Bruges courts. Benson bought a house from Lucas and paid him half in cash and half in paintings, eight to be exact. When the paintings were delivered Castro said they were not of enough quality to be worth half a house. So back to court they went, Benson won!

In reviewing the Columbus family tree I noted that Columbus' grandson, Don Luis Colon married as his fourth wife a Dona Ana de Castro. This would have been about the same time as the Lamentation painting would have been painted, circa 1530-35, corresponding to Bensons possible visit to Spain. The Columbus family records mention Ana de Castro's mother and brother, Rodrigo de Castro, Bishop of Zamora who was a member of the Spanish Inquisition, but no mention of her father who could quite possibly be the link to both the Columbus family and Benson if he is Lucas de Castro who Benson brought a house from.

On June, 27th 1992, exactly thirteen days after the paintings had been stolen from the Columbus Chapel I received a frantic telephone call from the institution's director saying that the Benson painting had been found in a wheat field, over a quarter mile from the museum earlier that morning by a girl riding a horse. Finding no fingerprints, the police would be returning the painting to the museum shortly. The director made the two hour trip down to Harrisburg and met me at nine o'clock at night at our conservation facility.

When he arrived, I discovered much to my horror that the painting had endured a thunderstorm, four days of over ninety degree temperature, a small rodent living, eating and deficating on it, all face up in a wheat field. There were animal droppings and paw prints over the entire surface of the painting (Fig. #3). I explained to the director that the painting was liable to get much worse before it's all over. Surfaces were blanching, glazes were cracking and crazing, and paint was lifting and cupping everywhere. Old panel joins and cracks were beginning to open up even though the panel was still flat and the cradle battens still seemed to function, although not nearly as smoothly as before. The following morning I made many telephone calls to solicit advice on how to stabilize this painting. I thank everyone I spoke with, but particularly Barbara Heller of the Detroit Institute of Arts, David Miller of the Indianapolis Museum of Art and Sarah Fisher of the National Gallery of Art in Washington, D.C. I finally decided to place the painting, face up, under a five-sided Plexiglas vitrine that I originally used to control this painting's environment when on exhibit in The State Museum, which was fortunately still in the laboratory. I concluded that although the surface of the painting seemed dry, the interior of the panel probably still contained a high moisture content. I filled four 250ml beakers with 50% deionized water and 50% ethanol and placed them with the painting. The water was used to raise the relative humidity and the ethanol to help evaporate the water and to prevent mold growth. The temperature in the laboratory remained a constant 66 degrees Fahrenheit and the relative humidity rose from 55% to 78% relative humidity in a eight day period. I allowed the vitrine to equilibrate, and it remained at the same level for seven days. I removed the beakers of water and ethanol and replaced them with two Gortex silica gel tiles conditioned for a 5% decrease in relative humidity (73% relative humidity). I then continued to reduce the relative humidity using reconditioned tiles over the next month until it reached 55% relative humidity consistent with that of the paintings conservation laboratory. Unfortunately, the panel painting sat in this vitrine under our watchful eyes for over eight months because of difficulties with the insurance company. After this length of time elapsed the family decided to advance the money for conservation because of the quality of the painting and because of their commitment to the public to bring it back to view. However, this was actually fortuitous for the painting, because much of the cupped paint, panel splits and surface mold disappeared. I, on the other hand was becoming a nervous wreck, because having already been accepted for making this presentation at the AIC Conference over six months ago I still didn't have permission to treat the painting.

When I finally was told by the institution that the funding was in place, I took the panel out of the vitrine and began my examination. The painting is executed using standard Netherlandish techniques of the period. The panel is 35 3/8" H x 24" W x 3/16" TH. It is comprised of three tangentially cut vertical oak panels which are approximately the same width. When compared to the London panel, which is the same height but almost 2" wider, I quickly realized that this painting also use to be winder. The proper right edge of the panel shows a broken join with glue remnants, confirming that this panel was larger originally, probably including the entire figure of the man standing to the left of Christ this would make it compositionally the same as the London painting. The panel has a number of vertical panel splits which were repaired when the panel was cradled. All of the joins and splits have been previously filled and retouched. They have however, all opened up as hairline cracks as a result of the recent damage. Several of the panel splits have reinforcement glue blocks attached on the reverse between the vertical cradle members. It is suspected that the panel was originally thicker and was planned down and cradled during a previous restoration process.

The painting has undergone at least three distinct treatments in the past in addition to my first treatment, two of which consolidated, filled and overpainted panel cracks and joins. In addition the painting has been cleaned selectively and unevenly in the past. Ultraviolet light showed heavy varnish and dirt residues in the intersticies of the paint and evidence of several natural resin varnish layers. Visual examination showed that the foreground and city scape, of Jerusalem was chemically abraided or skinned during at least one of the previous cleanings. In preparation for placing the painting in the humidity chamber, I had to mechanically separate the painting from the frame where the varnish was firmly bonded to the frame's rabbet. This resulted in some detachment or delamination of original paint, which was attached to the inside of the rabbet. This was removed and reattached to the painting's surface later where possible. Secondly, I removed animal tracks and excrement with water on cotton swabs with the aid of a scalpel. If left intact, the ammonia and urea in the excrement may have eaten into the paint. The painting's frame is not of the period and is a recent creation.

During examination I noticed several costume differences between the London and the Boalsburg painting. These costumes were all raised, or more thickly painted than the rest of the painting's surface. The most notable changes are that of the two kneeling Marys and the central male standing figure. The Madonna, iconographically denoted by a blue robe on the right, has a change in her neck line. The Boalsburg painting clearly shows evidence of three different changes in this area (Fig. #4). It is with these potential cleaning problems that I first decided that the painting should be X-radiographed to see if I could find evidence of costume changes, which either could be by the hand of the artist searching for a better composition or by the hand of a restorer because of a fashion or stylistic change. I felt that the execution of these garments was not consistent with the appearance of the London painting. I took the painting to a local hospital which was kind enough to help us with this project. The resulting X-ray, was not terribly revealing except that it faintly confirmed that the edge of the chemise and skin layer are continuous behind the final dress configuration.

It was at this point that I felt that additional analysis was necessary. I took a combined total of 12 cross sectional and pigments samples and sent them to James Martin of the Williamstown Regional Conservation Laboratory for identification. Some of the resulting analysis was not what I had expected, nor clear cut. For example, it was found that none of the garments appear to be overpainted. There is only one layer of coarsely ground pigments in addition to the ground layer. In the case of the cross section which I had visually categorized as an emerald green dress on the right hand kneeling figure of the Madonna, it was primarily azurite, with trace mounts of red lead, yellow ochre, and gypsum. The cross section looks like it has two upper layers, but in reality has only one, with it's top half saturated or stained by a surface applied coating or from the remnants of orange overpaint which can be seen in the crack. The overpaint was probably removed during a previous cleaning. There is no evidence however, of any green pigment.

The robe of the women on the left also tells a similar and unexpected story. It might be interesting to note that Ambrosius Benson seemed to use alot of fur in his costuming, Marlier's book notes that he suspects this was because Bensons brother-in-law was a furrier and Benson would have presumably had easy access to these types of garments for his models to use.

Quoting from Mr. Martin's report "cross-sectional examination of the bulk sample reveals one or two paint layers composed primarily of angular, glassy particles and occasional globular red particles. In oblique visible illumination, the layer separates into two zones: the upper of these zones exhibits dimmer autofluorescence (these zones are believed to be part of the same layer)." He continues, "several rose-colored particles were observed in the thin-section by transmitted illumination; these particles...may be madder. A dispersed sample from the surface reveals a multitude of glass particles and a lesser amount of fine, rounded, highly birefringent clear particles which may be naturally occurring minerals (calcium and magnesium alumino silicates)." He continues by concluding that the glass particles are smalt with trace amounts of cobalt and red lead. Again, I have a orange/brown robe that is composed of a glass that usually produces the appearance of a blue pigment.

Analysis of the central figures' robe indicates that it is also composed of smalt. It too is a solid orange/brown color. I do not suspect that either of these past two garments exhibit what could characteristically be called smalt disease. Is it possible that colored glass could have been used intentionally to provide the orange/brown color?

From this analysis it can be concluded that the following pigments are present in Bensons palette: rose madder, red lead, vermilion, azurite and malachite, yellow ochre, lead tin yellow, calcium carbonate, (which is Benson's white ground later), cinnabar and smalt.

Finally, I would like to give you an over-view of the treatment of this painting. Cleavage was set down using a 5% gelatine solution in water heated on a hot plate (Fig. #5). Gelatine was applied by brush and then pieces of Japanese tissue paper were tamped lightly in place. Gelatine was melted slowly into the cupped paint's surface with slight pressure, which allowed the paint to set down with minimal cracking and no loss. When consolidated, the discolored overpaint and varnish layers were removed with acetone. Some overpaint required the use of di-methyl formamide to dissolve cross linked oil paint films. The blue robe of the Madonna on the right was further cleaned using a Richard Wolbers acetone/benzyl alcohol gel. This removed a significant amount of yellow/orange medium or coating on this figure. The figure now looks a lot bluer in tone than it originally did but still does not look like azurite (Fig. # 6). The painting was given an isolating brush coating of dammar resin to fully saturate the colors. No additional filling was required. Some old fills were carved down and some I scratched crack lines in to texture the surface with the back of a scalpel. Some areas of the composition were glazed-in to enhance fading passages such as the figures in the distance and part of the city of Jerusalem. These were reconstructed to establish continuity in consultation with the owners wishes. This inpainting was accomplished in a little less than a week and a half. I again used Magna Colors and Maimer Restoration Colors and applied a final acryloid B-72 spray varnish coating (Fig. #7).

I would like to in addition to those mentioned previously especially like to thank Laurence Ullmann, a Paintings Conservator in Washington, D.C. for her time in translating, reading and outlining Marlier's catalog resonee for me for this project.

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(1) Marlier, George, Ambrosius Benson et la Peinture A Bruges au Temps de Charles-Quint, Editions du Musee van Maerlant, Damme, 1957.

Fig. #1.
Interior of Columbus Chapel.

Fig. #2.
Second version of Lamentation by Benson once belonging to C. F. Turner

Fig. #3.
Detail of painting after recovery from wheat field.

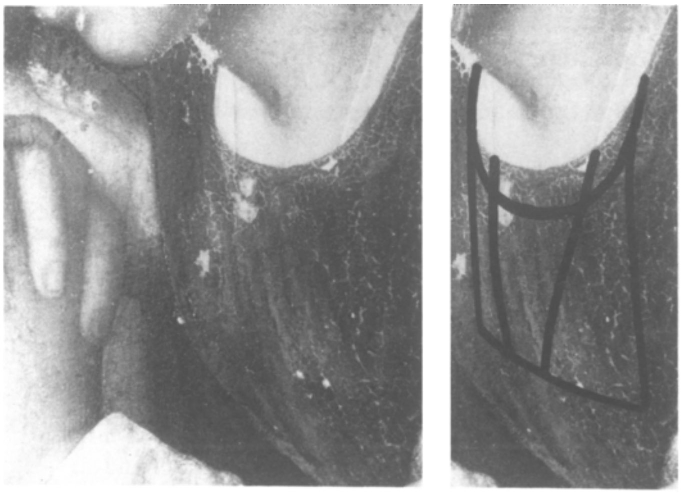

Fig. #4. Detail of changes to the Madonna's dress neckline.

Fig. #5. Setting down cleavage with gelatine and Japanese tissue paper.

Fig. #6. Discolored varnish and overpaint removed prior to inpainting.

Fig. #7. After treatment.

ARTHUR DOVE'S BINDING MEDIA: AN ANALYTICAL STUDY

Richard Newman and Irene Konefal

Introduction

Arthur Dove, who was to be one of the first American abstract painters, was born in 1880 and died in 1946. A trip to Europe between 1907-1909 exposed him to avant garde art and theory, and upon his return to the United States, he began to develop his characteristic non-representational style. Perhaps one of the clearest, most succinct descriptions of Dove's paintings is by Duncan Phillips, who described the artist's work as a search for "abstract equivalents to the character of his immediate environment and of the objects of his everyday experience" [1].

Dove was a self-sufficient, sociable, very humorous man who was highly disciplined in his work as an artist. While his work often received critical praise, relatively few collectors purchased any of it, and, except for the 1940s, Dove was often in serious financial difficulty. Three people who were of enormous importance to him during his career were his second wife, Helen Torr Dove; Alfred Steiglitz, who was Dove's only dealer and an unceasing advocate of his work; and Duncan Phillips, Dove's sole patron whose stipends virtually sustained the artist from the 1930s on.

Given Dove's chronic financial problems, and, after 1936, chronic health problems, his output is astonishing: over 1,000 finished works by him are known.

From the start, Dove's work was characterized by an intense preoccupation with materials and craftsmanship; constant exploration of subtle yet rich color relationships and surface texture; and a deliberate refined awareness of the work as a result of the interplay of all the layers from the support up. Dove spent a lifetime exploring the use of his materials for very specific aesthetic ends.

Dove left an extensive written record that provides information about his materials and how he prepared them: diaries maintained from the early 1920s well into the 1940s (from 1925 until the early 1940s, the diaries were primarily written by Helen Torr Dove); a card file of paintings (mostly dating from 1927-1932); letters (especially to Steiglitz); and heavily annotated copies of artists' manuals. The first summary of this documentary information, coupled with observations of paintings by Dove in the Phillips Collection (Washington, D.C.), was presented by Justine Wimsatt in 1982 [2]. One of the aims of our study is to corroborate and augment current knowledge of Dove's painting materials through the application of modern paint media instrumental analysis. We are working with a group of approximately twenty finished paintings and six small sketch paintings in the collection of the Museum of Fine Arts, Boston. The paintings date from the mid-1920s to 1944, representing most periods of the artist's work.

In this paper we present some results of the study to date, which has involved visual analysis of selected paintings, infrared reflectography, and media analysis of paint and some ground layers. Ultimately, we hope to combine specific media identifications from all layers with observations about Dove's underdrawing, absorbent grounds, underpainting, and application of final paint and possible varnish layers.

A summary of Dove's work

While oil paintings on canvas or panel are known from the earliest years of Dove's career (1907-1911), the majority of works from 1912-1920 are highly worked charcoal drawings and pastels, the latter done on paper, panel, and linen. (During these years and continuing through the late 1920s, much of Dove's income came from work as a magazine illustrator.)

In the 1920s Dove explored a remarkable array of supports. Using primarily oil paint (at least so far as is known at the moment), he painted on wood, metal, fabric, and even Bakelite plastic. Sometimes collage elements were incorporated into these paintings and, in fact, during this period he created nearly two dozen collages that integrated all manner of materials: plants, metal, wood, fabric, sand, printed paper.

In the 1930s Dove returned to easel painting on canvas. During these years until his death in 1946 Dove's primary focus was on binding media. He developed a sophisticated system of using grounds and underpainting, modified by top layers of paint to achieve very specific effects of color and texture.

Throughout his career Dove studied artists's manuals, but in 1935, prompted by Georgia O'Keeffe, he read Max Doerner's book, *The Materials of the Artist and their Use in Painting*, which had been released in its first English translation in 1934. Dove seemed to have been particularly intrigued by Doerner's discussion of wax emulsion media. According to Doerner, paintings carried out in the wax emulsion medium "possess a wonderful softness and enamel-like quality" [3]. Judging from Dove's earlier drawings and oil paintings, these characteristics would have had great appeal.

Visual examination and documentary references suggest that most of Dove's paintings from the late 1930s until his death included paints that contained wax. Diary entries for these years often mention batches of wax emulsion, sometimes made on a weekly basis. Dove also consulted other books for wax emulsion recipes, including Hilaire Hiler's *The Painter's Pocket Book*, which he first read in 1939, and Daniel Mayer's *The Artist's Handbook*, which first appeared in 1940. While the wax emulsion can be used by itself, Doerner advised that it could easily be mixed with drying oils, natural resin spirit varnishes, egg tempera, and other types of tempera such as casein or even plant gums [4]. Dove mentions some mixtures of wax and other media in diary entries, but it is not clear how extensively he experimented with them.

Dove's diaries and card files also provide some information about the media in his grounds and underpainting,

Some form of drawing was fundamental to Dove's working method through much of his life. His early work included the highly finished charcoals and pastels already mentioned. Beginning in the 1930s, frequent mentions of "drawings" appear in the diaries and correspondence. Also called "ideas," these were small sketches, sometimes simply pen and ink, but more often painted over a light underlying (pencil?) drawing. From the mid 1930s into the early 1940s Dove made up to 100 sketches per year, and from the group selected about 20 to expand into paintings. In the 1940s Dove's sketches were said to have been mechanically enlarged to serve as the compositional basis for paintings.

To briefly summarize the documentary evidence, Dove used oil paints (which he often made himself) in paintings carried out prior to 1935. After 1935, wax emulsion was one of his principal paint media, but underpainting may have been carried out in other media. The card files mention casein grounds and "half chalk" grounds.

The nature of wax emulsion

Beeswax consists of long-chain hydrocarbons, some free fatty acids, esters of fatty acids and long-chain alcohols, and other compounds. Doerner's recipe for a wax emulsion called for melting some beeswax in water, then adding ammonium carbonate, which immediately caused the wax to effervesce as it began to saponify. The mixture was to be heated until the fizzing stopped, then stirred until cool. Complete saponification of beeswax results in a mixture of the original nonsaponifiable components (such as the hydrocarbons) and large amounts of fatty acids and alcohols derived from the original esters. Our preparation of some small batches of wax emulsion following Doerner's and Hiler's recipes and subsequent analysis of the products indicates that only a little saponification may take place, but enough free fatty acids and alcohols are liberated to allow the product to form a stable emulsion in water. The emulsion can be diluted with turpentine, spike oil, and mixed with other water-soluble or water-insoluble materials, after which pigments would be added.

After drying, wax emulsion is at least somewhat soluble in water as well as weak organic solvents; its solubility could obviously be affected by other admixed media. In addition to solubility in a wide range of solvents, another problematic property of the medium from a conservator's point of view is that when rubbed or slightly abraded, the originally matte surface is easily burnished to a shiny appearance, for which there is no ready remedy.

Analytical procedures

Although many of Dove's paintings contain multiple layers, in general it is possible to mechanically separate ground and single paint layers from samples taken at the edges of his paintings. Most of the binding media analyses in this project are being carried out on such isolated samples. The intitial analytical procedure is Fourier transform infrared microspectrometry (FTIR). If sufficient sample is available, instrumental chromatographic procedures are then applied for more detailed identification of different organic components. Table 1 briefly summarizes the procedures and types of binders that each is utilized to identify. To cover the full range of binders that Dove may have utilized, three separate portions of a given sample would need to be analyzed: two by different gas chromatography/mass spectrometry (GC/MS) procedures [5,7], and one by high performance liquid chromatography (HPLC) [6]. In general, at least three samples from each painting are being analyzed. All are analyzed by the first GC/MS procedure, only some by the other two procedures.

The condition of the paintings included in this project is generally quite good, so sampling for chromatographic analyses was restricted to edges. In order to study underpainting and surface coatings, sampling often had to be carried in interior areas. Only very small scrapings could be sampled from these areas, and the sizes of these samples permitted only FTIR analysis to be carried out on them. Some cross sections are also being prepared to study layer structures.

As the project is in progress, the remainder of this paper will summarize some of the results from a selected group of the paintings.

Table 1. Summary of analytical procedures.

	Gas chromatography/ mass spectrometry (procedure 1)	**High performance liquid chromatography**	**Gas chromatography/ mass spectrometry (procedure 2)**
Sample preparation	Saponification, extraction with ether, methylation with dimethylformamide dimethyl acetal	Hydrolysis, derivatization with phenylisothiocynate	Hydrolysis, two-step derivatization with hydroxylamine hydrochloride and trimethylsilylimidazole
Primary binders identified by procedure	Drying oil Beeswax Natural resins	Animal or fish glue Casein Egg yolk Egg white	Plant gums

Paintings from the 1920s through the early 1930s

*Clouds (*1927) is painted in oil directly on a sheet of gray metal with a shaped strip of sandpaper in the composition. The painting is in keeping with Dove's interests during the 1920s in non-fabric supports and collage. Except for the sandpaper, the surface has a uniform soft gloss. Fluorescence under ultraviolet light indicates that natural resin varnish is present. Whether the varnish is original or not has yet to be resolved. This is an important question, since Dove's card file from the late 1920s and early 1930s contains occasional notes that a painting required varnishing in the next year. We do not know if such delayed varnishing was actually done. The simple mention of varnishing implies that for some paintings Dove desired an even surface gloss.

In contrast with *Clouds, Wednesday Snow* (1931) has never been varnished. The highly textured surface is very matte with pronounced drying crackle, the cause of which is not yet certain. The paints, confirmed by analysis as drying oil, are thinly applied, with some scraping back to blend colors and locally reduce the texture.

Wednesday Snow was painted on an artist-primed canvas with a thick beige-colored sizing and dense bright white ground, which certainly contribute to the surface texture and may also have been used to provide a particularly absorbent base. References to casein-bound white grounds exist in the artist's card file for other paintings of this period, but analysis of the ground of this painting has not yet been carried out.

Summer (1934-35) displays intricate surface textures, the result of delicate wet-in-wet brush work over a highly textured support and a thick bumpy white ground. Also striking are the gloss and matte variations. In some cases a very glossy paint has very matte paint pulled over. Selective varnishing may provide extra gloss in some areas, but analysis has not confirmed this as yet.

This painting dates around the time Dove first read Doerner. The GC/MS analyses do not indicate any wax or resin in the medium, nor is a significant protein component indicated by HPLC. Yet the azelaic acid levels in paint samples analyzed to date are quite low for drying oil, so some non-drying oil may be present in this paint. Additional analyses of solvent extracts by GC/MS will hopefully give us a better idea about the exact nature of the binder or binders in this work.

Paintings from the late 1930s through the 1946

In *Motor Boat* (1938), the matte upper paint layers definitely contain wax, and a small azelaic acid peak indicates that some drying oil is also present. In addition, one sample contained some dammar resin. According to Doerner, drying oils (which he cautioned to use sparingly) and natural resin varnishes are excellent in combination with wax emulsion.

While Dove always manipulated the color interaction between lower and upper paint layers (be they ground and paint, paint over paint, or wet-in-wet paint), he seemed to adopt a more distinct system of underpainting during the late 1930s and early 1940s. *Motor Boat* is the first painting in our study group with underpainting of this kind. The underpainted colors are generally intense and pure. Top layers are darker or lighter and/or chromatic opposites of the paint below. Modified through variations in thickness, color and tone of the overlying paint, the underpaints play a carefully calculated role in the final appearance of the surface.

Some of Dove's notes mention "tempera" underpainting for wax-emulsion paintings. To date, however, FTIR analyses of small scrapings of underpainting from a number of Dove's later paintings have not indicated the presence of a proteinaceous (tempera) binder. Much more analysis, applied to all of the paintings in the study group, will be necessary to pursue this important question.

Motor Boat also has a distinct, porous white ground, clearly artist-prepared, as is the case with most of Dove's grounds. Dove's card files indicate that he employed "half-chalk"grounds during the 1930s. This type of ground, bound with glue and linseed oil, was highly recommended by Doerner [8]. Analysis by HPLC and GC/MS indicate that both glue and drying oil are present in this ground. The pigments are gypsum and zinc white, both ingredients in Doerner's recipe. To date, this is the only ground in the study group of paintings that has been completely analyzed for media.

Somewhat surprising is the simplified preparation and technique of *Neighborly Attempt at Murder* (1941). It is painted on a commercially prepared thin white ground, and underpainting is limited. While there are instances where a dark muted color modifies a brighter underpainted color, in most areas the ground is visible directly below the loose brushwork. The paint binder is wax with a little drying oil.

Square on the Pond (1942) has the simplified, highly abstract composition, thinner paint layers, and somewhat less textured surface that characterize Dove's last style. The painting is grounded on both sides. On the front, the ground is porous, bright white and somewhat crumbly; the ground on the reverse is thin, cream-colored and commercially prepared. Of the paintings examined to date, *Square on the Pond* has the most complete underdrawing. (For example, *Summer* and *Pieces of Red, Green and Blue* show no underdrawing under IR, while *Motor Boat* and *Neighborly Attempt at Murder* have some underdrawing.) Many of the lines in *Square on the Pond* are clearly visible in normal light. No sketch has been associated with the composition, but one may yet be found since most of the hundreds of Dove's small sketches remain uncatalogued.

A complete underpainting is present and many of the underlying paints are remarkably vivid, for example a brilliant blue lies beneath a blue-brown upper layer, and a teal blue beneath a beige layer. Unfortunately, this painting has an unoriginal synthetic varnish.

Pieces of Red, Green and Blue dates to 1944, two years before the artist's death. The upper paint layers are again wax emulsion with a low drying oil content. Underpainting is found under all the color areas; for example, maroon paint lies under the large lower area of green. The binder appears to be wax or wax/oil in the underpainting.

Further work

To date we have focussed mainly on two areas: visual examination and media analysis of the upper paint layers. The intent has been to confirm and give certainty to information in Dove's extensive documentary material. Outstanding aspects to be studied are the nature of Dove's grounds and underpaintings and possible use of selective varnishing. The ultimate goal, of course, is to understand as fully as possible Dove's remarkably accomplished use of materials and how his various subtle and sophisticated decisions were intended for very specific aesthetic ends.

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6. The HPLC procedure is similar to that described by Susana M. Halpine, "Amino acid analysis of proteinaceous media from Cosimo Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse," *Studies in Conservation* 37 (1992), pp. 22-38.
7. GC/MS procedure 2 is similar to that described by Erhardt et al., *op. cit.*, pp. 82-83.
8. Doerner, *op. cit.*, p. 233.

THE EXAMINATION AND TREATMENT OF A DOUBLED-SIDED PAINTING BY ROBERT HENRI

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ABSTRACT

This paper examines Robert Henri's painting, "The Beach", produced during his stay at Concarneau, in the French Bretagne. At the time, Henri was experiencing a conflict between the influence of French impressionists and his previous academic training.

The painting is double-sided. The image in the front, " The Beach" was very yellow and discolored. This work was of particular artistic interest, since it is one of the first outdoor paintings done by Robert Henri. On the back there is a portrait which was barely visible . In some places its outlines were almost invisible.

This paper will discuss the technical aspects of these two works of art and propose hypotheses to account for their darkened state.
It will also describe the cleaning process and the method used to stretch the double-sided canvas.

INTRODUCTION:

"The Beach" was originally brought to the Center for Conservation and Technical Studies for conservation and treatment in September 1992. During our initial examination, we discovered a portrait on the back. The images on both sides were very dark. Our question was how much of the darkening was due to the paint medium and how much to some sort of coating.

Robert Henri was born in 1865 in Cincinnati, Ohio. He studied at the Pennsylvania Academy with Thomas Pollock Anshutz, and at the Academie Julien and École de Beaux-Arts, in Paris, from 1888 to 1891.

After his stay in Paris, he returned to Philadelphia in 1891 to teach at the School of Design for Women. He became the intellectual force behind the creation of the Eight, a group who opposed the current academic dreariness. From 1916 to 1928 he taught at the Chase School, the Henri School, and the Art Students League.

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Henri believed in painting with feeling, memory, imagination and gesture. A talented teacher, Henri helped to promote freedom of artistic expression in America and left a lasting imprint on the work and mind of many of his students.

Robert Henri died in New York in 1929.

Robert Henri painted "The Beach" -- the front side of the painting being discussed here -- during his stay in Concarneau, France, in the summer of 1889. In Concarneau, a sea resort then popular among artists, Henri spent many hours in his studio painting portraits and Breton figures. He also spent considerable time studying light and color outdoors.

As a result of his outdoor studies, Henri became interested in the techniques of the French Impressionists, which he compared to the academic techniques in which he had been trained.

Comparison soon evolved into a conflict between the two influences, with Henri hesitating between his new discoveries and his former academic training.

TECHNICAL DESCRIPTION:

The seascape is signed in the lower right corner. The portrait on the back side, however, is not signed. Curiously, it contains an inscription in red paint: "The Beach, Robert Henri, A44". This inscription probably refers to the seascape on the front side. The inscription has no relation to the portrait on the back side, which shows only a man with a kerchief who resembles a Spaniard.

The canvas is a fairly fine, plain-weave linen in good condition. It was stretched over the original keyable five-membered stretcher. There is no evidence of priming on the tacking margins.

The paint layer of the portrait has several scratches and some losses. Small losses have occurred along the crease line, caused likely by folding the painting in half. The paint layer of the seascape is in stable condition.

The tacking margins are the same on both sides. We can safely presume Henri used the same stretcher, and apparently the same nail holes, since no additional nail holes were visible when the stretcher was taken off.

Given the complexity involved in the cleaning of the two paintings, althorough analysis of its materials and techniques became necessary.

TECHNICAL ANALYSIS

The painting was submitted to the following analyses:

1) Colorimeter

The colorimeter provided us with a quantitative measure of the darkness of the painting. It also allowed us to compare the reflection spectra before and after cleaning.

Before treatment, reflectance spectra were taken on the following colors on the front side: white, yellow, blue, green, and red. Spectra were taken from five sites on the back side. Not much difference was seen before and after cleaning on the back side. The paint layer was so dark that spectra were taken only of the red-black and black tonalities.

Nonetheless, the reflection curves of the spectra taken before and after treatment showed an interesting result. Those parts which were blanched before treatment became darker after treatment, as a result of the removal of the blanching.

The equipment used was Perkins Elmer UV/VIS Spectrophotometer, with a Labsphere for reflectance spectroscopy.

2) X-Ray Fluorescence Spectrometry Analysis

We then submitted the painting to X-Ray Fluorescence Analysis in order to establish the quantitative composition of the elements of the painting.

Lead and iron were found in almost all areas of the painting. Chromium and calcium were detected in 80% of the areas examined. Barium and manganese were also detected. (Table 1)

The x-ray fluorescence spectrometry unit used for the examination was Noran Instruments Voyager, Z Max 30 Series Light X-Ray Energy Dispersive X-Ray Spectrometer.

3) X-Ray

The X- radiographs allowed us to identify yet another painting executed on the same side as the portrait. It seems to be a women seen in profile.

Examination with raking light revealed that this portrait was painted beneath the figure of the Spaniard, on the back side. (Slide 12).

The x-ray unit used was Baltospot 100/5 with variable Kv 5-100 and fixed milliamperage of 5 milliamps. It is used with an aluminum filter when x-raying painting. The film used was DuPont Cronex, NDT 55 Day Pack. The painting was X-Rayed at 45 KV and 5 Ma (milliamps) for 60 sec.

4) FT- IR

According to the literature, Henri was extremely concerned with materials and techniques. This is also evident from his very detailed personal notes and letters on these matters.

Leslie Carlyle, a Canadian conservator, in her paper on the nineteenth-century British instruction books for oil painting, describes the vehicles and mediums used at that time. Some of those recipes were made by grinding lead acetate, raw linseed oil, and mastic resin. A popular recipe of the late nineteenth-century prescribed the dissolution of lead acetate in water as a saturated solution, and then the addition of linseed oil and mastic varnish to it. Another popular encaustic recipe mixed gum Arabic, water, mastic resin, white wax and powdered pigment. We hypothesized that possibly one of these recipes was used by Henri during his stay in Concarneau.

At this point in the investigation, the samples taken from the seascape indicated the presence of resin, oil and probably protein. The material extracted from the portrait contained resin, protein, oil, wax and pigment.

Also according to the literature, Henri was deeply influenced by Whistler, who is known for his use of Megilp. (Megilp is a mixture of mastic resin, turpentine and linseed oil). And as we know, many of Whistler's works have also darkened considerably much in the same way as Henri's painting.

In order to establish Whistler's influence on Henri's painting, a sample from the Whistler's "Self- Portrait" at the Fogg Art Museum was examined with FT-IR and compared to a group of standard materials collected by Rutherford Gettens in 1931. A reasonably good match was made to oil and hide glue with doublet peaks around 1740, suggesting the presence of a resin with the oil.

Another sample was taken from the surface of both sides of Henri's paintings and again of Whistler's "Self-Portrait." A good match was found between them. It was also found that Whistler's varnish had an approximate match with the Gettens' mastic resin.

On the back side of Henri's painting we detected the presence of a kind of blanched wax, which we tentatively identified as Japan Wax -- a fat that physically resembles bleached beeswax. The examination of the media suggested the presence of oil, protein, and possibly another type of resin.

On the basis of the evidence collected, we formulated the following provisional hypothesis:

The lead, which was used as a dryer, was responsible for some of the discoloration and darkening. Church wrote in his book ***The Chemistry of Paints and Painting***, that different kinds of lead such as metallic lead, litharge, red lead, lead peroxide, lead acetate, and white lead were used as siccatives during the nineteenth century, to make oils dry faster. Leslie Carlyle also wrote that painters were advised to add various dryers --lead among them-- to the medium during damp and cold weather or in areas near the sea. Henri may well have been aware of these instructions.

The chemical reaction that probably took place in this painting was the formation of lead soap as a result of the combination of the linseed oil and some sort of lead. This type of the reaction is well explained by Brill, in his book ***Light : Its Interaction with Art and Antiquities*** ""The pigment most commonly found to form the soap in a paint is lead white"(p.90). Basic lead carbonate reacts with fatty acids to form lead linoleate and lead stearate.

To establish this hypothesis, the mixture of the lead and the linseed oil was reproduced at the laboratory at the Fogg. After 2 hours under light, the mixture became yellow and then dark brown, tonalities which were similar to the one found in the back side of Henri's painting. (Appendix 3). A sample of the mixture was then examined with FT- IR and a good match to a lead drier was found. Notwithstanding those matches, the possibility of the resin component in the media contributing to the darkening cannot be dismissed.

The equipment used was a Spectra-Tech IR-Plan microscope attached to a Nicolet 510M spectrometer with an auxiliary MCT detector. Data was collected for 200 scans at a spectral resolution of 8 cm-1m, and displayed between 625 and 4000 wave numbers. Samples were mounted on a Spectra-Tech Micro sample Plan fitted with diamond window. For consistency, the CO2 peak was removed and spectra were baseline corrected.

8) UV FLUORESCENCE MICROSCOPY

This examination helped establish that oil and protein were used by the artist.

Prior to staining, the cross-sections from the back of the painting was examined with visible light. The examination did not reveal the different layers of the sample. The same sample was then examined with auto-fluorescence D filter and auto-fluorescence I-3 filter. With the help of those filters, it was possible to distinguished the different layers of the painting.

Cross-section samples from the front of the painting were stained with Rhodamine 123 and Rhodamine B. The results indicated the presence of oil and protein components. The same sample was stained with TRITC and

LISSA, indicating an inconclusive result because the presence of protein was found in very small areas. A cross-section from the back of the painting was stained with TRITC (Tetramethyl Rhodamine Isothiocyanate) for protein and DCF (Dichlorofluorescein) for oil, and both substances were found on the painting. The first layer of the sample proved to be pure oil. All of the stained samples were examined with a D cube filter. A more visible image of the staining was obtained with this examination. (Table 2).

The equipment used was a Sony 3CCD Color Video Camera No. DXC 930. The camera is coupled through a Diagnostic Instruments 0.45x HRPO45-ENG12 High Resolution Video Coupler and Leitz bottom clamp No. KSC-NLW. The microscope is aLeitz Laborlux S with 3 Lambda Ploemopak 2.5, 100 watt ultra high pressure mercury lamp for UV, 6v 20 watt tungsten lamp for transmitted light, and a DJI Fiberlite series 180 20v - 150 Watt 2 bundle fiberoptic lamp for visible light illumination. Leitz D, and I-3 filter cubes provide UV Filtrationfor the following spectra:

D (UV-Violet ER) Excitation filter 340-380, Suppression 430
I 2/3 (Blue ER) Excitation filter 450-490, Suppression 515

The camera is powered by a Sony CMA-D2 Camera Adaptor and connected to the computer by a 9 pin RGB Sync cable.

The computer is a Macintosh II FX 20/200 and 425 meg external HD, with a Raster Ops 24 XLTV board and Apple 13 "RGB monitor". Captured images are manipulated with Adobe Photoshop 2.5 and stored in Image Access software.

9) PIGMENT ANALYSIS

Next, we undertook an analysis of the pigments contained in the painting.

With the help of the microscope the following pigments were then identified with on both sides of the canvas: viridian, yellow ocher, lead white, vermilion, lead chromate, bone black, ultramarine, cobalt blue. (Table 3). Those pigments were chemically analyzed with Scanning Electron Microscopy (SEM)and the Scanning Transmission Electron Microscopy (STEM).

The sample for the STEM was first dissolved in Dimethyl Formamide, making possible the observation of the particles without their medium. We also found an abundant amount of well developed white crystals in the sample used in the (STEM). We presume they are lead white. The (STEM) examination revealed the presence of phosphorus and calcium, indicating that Henri used bone black. Iron, chromium, and lead were identified in the same sample.(Table 4)

The SEM examination revealed the presence of lead, iron, chromium, barium, and cobalt. (Table 5). The pigments are composed mainly by metals and minerals.

The microscope used was Leitz Laborlux 12 POL binocular polarizing light for reflected and transmitted microscopy. The light source was E. Leitz Model 050260 with 6V 20W tungsten halogen lamp. The camera was Vario Orthomat, Leitz and the film Kodak Ektachrome, 160 Tungsten. The mounting media for the samples was Bio-Plast. The slides and cover slips were VWR micro slides, 3" x 1" thickness 1.2 mm.

The SEM instrument used was a JOEL 6400 Scanning Electron Microscope with a Noran Instruments Z Max 30 Series Light X-ray Energy Dispersive using ZAF matrix corrections.

10) GCMS (Gas Chromatography/ Mass Spectrometry)

The GCMS examination revealed the presence of drying linseed oil, and some pine resin on the back side. Drying linseed oil, some copal resin, some mastic resin and possibly some pine resin was found on the front sides. The instrument used see appendix 3.

CONSERVATION AND RESTORATION

The treatment consisted of three stages:

1. Restretching.

The painting was removed from the stretcher. The canvas was strip lined with monofilament polyester, Beva film and mounted on a Lebron double-sided stretcher in order to allow both sides to be viewed. The canvas was placed on the stretcher with pins, adjusted at the flat and back side of the stretcher and stapled. The staples were put very close together to allow an even and sufficient stretching.

2. Cleaning.

The solvent sensitivity of both sides of the painting were checked, since cleaning swabs had presented a very dark color. The swabs were analyzed with X-Ray fluorescence. The results indicated the widespread presence of lead on both sides of the painting.

A variety of solvents were tested on both sides of the paintings and they all removed some of the pigment. However, two emulsions produced good results without affecting the paint layer [1]. An emulsion composed of water (solvent), aerosol (surfactant), carbopol (thickener), and triethanolamine (base and buffer) was used to clean the portrait. As a result, the portrait outline and the hues became more visible.

Another emulsion made of citric acid (chelator), water (solvent), ethanol (solvent), polyoxiethylene (thickener) and triethanolamine (base) was used to clean the seascape ("The Beach"). With this process it was possible to thin the varnish and to reduce the yellowed effect of the seascape. However, it was not possible to produce an even surface, because Henri had not used a homogeneous emulsion. The portrait surface on the back was polished with a brush and the results were uneven: some areas shone while others remained matt.

3. Inpainting.

After cleaning, the losses on the back of the painting were filled with Polyfilla (PVA and whiting) and inpainted with Lefranc & Bourgeois pigments for restoration (pigments ground in B67 and F10). The strip lining monofilament polyester, which was still visible after the stretching, was also inpainted with Lefranc & Bourgeois. A mixture of Windsor & Newton Matt and Winton Retouching varnish (ketone resin) in a 50% proportion was applied to saturate and even out the paintings surface. Matte areas on the seascape painting were reformed using cellosolve, and the painting was left unvarnished.

CONCLUSION

The medium used in the two paintings was not the same. However, the darkening was due to discolored media and not to surface or embedded dirt.

The FT- IR analysis revealed that the media in the "The Beach" was found to be protein, oil and probably resin. The media of the back painting (the portrait) was composed of resin, probably fat or wax, oil and protein. Comparing with the gas chromatography/mass spectrography we concluded that there are some differences between the analyses. With the gas chromatography it was found in "The Beach" painting drying linseed oil, beeswax, pine resin, mastic resin, and copal resin. On the portrait painting it was found just drying linseed oil and pine resin. It was not found neither wax or fat.

The media of Henri's painting are complex and very difficult to analyze. The artist used many different ingredients and applied them in a non uniform way.

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[1] Richard Wolbers's emulsions. See WOLBERS, Richard, Workshop on New Methods in the Cleaning of Paintings, The Getty Conservation Institute, 1990.

We presume that Henri used some kind of lead as a drier. We could not determine what type of lead was used. Whistler did not use lead in his Megilp emulsion, but Henri was not solely influenced by Whistler and used more than one recipe containing lead.

We are tempted to believe that the discoloration of both paintings was caused by a leadsoap formed by the combination of lead and linseed oil. Lead soap are know for the darkening they produce. During cleaning, the swabs absorbed a great quantity of lead.

Still another possible cause has to be taken into consideration for further study, since the darkening of the resin component of the medium may also have been a contributing factor to the discoloration of the painting.

The cleaning could be carried out only to a certain point because the lead, which darkened the painting, was not only on the surface, but throughout the paint layer.

More work would be necessary to confirm our hypothesis. Yet, our analysis already enables us to suggest a tentative explanation for why many paintings produced during that period often darkened so markedly.

Our initial impression that cleaning would be difficult was confirmed by the analysis.

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ROBERT HENRI'S MANUSCRIPTS, Center for Conservation and Technical Studies, Fogg Art Museums

ARTICLES:

1) CARLYLE, Leslie: "British Nineteenth-Century Oil Painting Instruction Book: A Survey of Their Recommendations for Vehicles, Varnish and Methods of Paint Application". Cleaning, Retouching and Coating, IIC Preprints Brussels, 1990,

2)FARREL, Eugene and NEWMAN, Richard: "Summary of Some Important Instrumental Techniques", revised , Fogg Art Museum, Cambridge, 1991.

APPENDIX 1

X-RAY Fluorescence Analysis (Table 1)

No	Color	Sample Area	Measurement	Chemistry
1	Blue, Gray	Beach	27 x 8	Pb, Fe, Ba, Ca, Cr, (Mn), (Sr)
2	Brown	Dunes	25 x 21	Pb, Fe, Hg, Cr, Mn, (Ba), (Ca), (Sr)
3	Green	Vegetation	25,5 x 26	Pb, Fe, Hg, Cr, (Ba), (Ca), Sr
4	Dark - green	Vegetation	25,5 x 31	Pb, Hg, Fe, Cr, (Ba), (Ca), (Sr)
5	White	Sky	25,5 x 55	Pb, (Fe), (Ba)
6	Ocher	Dunes	25,5 x 18	Pb, (Fe), (Mn), (Cr), (Ba), (Ca), (Sr)
7	Red	Girl	30 x 4	Pb, Hg, (Ca), (Ba), (Sr), (Fe+)
8	Blue	Sky	30 x 59,5	Pb, Co, Fe, Cr, (Ba), (Ca), (Sr)
9	Red	Hat (back)	35 x 73	Pb, Hg, Fe, Cr, (Ca), (Ba), (Sr)
10	Green ?	Background (back)	41 x 62	Pb, Fe, Cr, (Hg), (Ca), (Sr).
11	Dark blue ?	Suit (back)	39 x 29	Pb, Hg, (Fe), (Cr), (Ca), (Sr)

UV Fluorescence Microscopy (Table 2)

No	Color	Sample Area	Measurement	Dye	Results
B1	Red	Back - vest	25,5 x 39	TRITC	Protein
B1	Red	Back - vest	25,5 x 39	DCF	Oil
F4	Green	Vegetation	76 x 31	Rhodamine 123	Oil
F4	Green	Vegetation	76 x 31	Rhodamine B	oil
F4	Green	Vegetation	76 x 31	TRITC	?
F4	Green	Vegetation	76 x 31	Lissa	?

Microscope Pigment Analysis (Table 3)

No	Color	Sample Area	Measurement	Pigment Identification
1 front	Dark Green	Right center edge	72 x 29	Ocher, vermilion, bone black, viridian
2 front	Light Green	Sky, upper center edge	70 x 47	Bone black, lead, vermilion, viridian, ocher
3 front	Blue	Sky, upper center	39 x 60	Viridian, cobalt aluminate or ultramarine
4 front	White-ocher	Sky, upper center	33 x 58	Viridian, ocher, vermilion
5 front	Brown	Beach, left center edge	5 x 19	Ocher, bone black, quartz, lead white?
6 front	Beige	Beach, right bottom	23 x 10	Viridian, ocher, lead chromate, quartz, lead
7 front	Light green	Beach, right bottom	24 x 8	Viridian, bone black, lead white, ocher.
8 front	Red	Girl	30 x 5	Viridian, vermilion, lead, bone black or charcoal
9 front	Brown	Where girl is sited	29 x 2	Emerald green, bone black, lead white, lead chromate, ocher.
10 back	Green	Left bottom corner	13 x 6	Lead white, red lake, vermilion, viridian, lead chromate, ultramarine
11 back	red	Sash	29 x 13,5	Vermilion, viridian, ocher, red lake
12 back	Dark Blue	Suit	29,5 x 18	Ultramarine or cobalt aluminate, viridian, vermilion, lead white, ocher, red lake.
13 back	Beige-green	Cuff	50 x 13	Viridian, lead sulfate, lead chromate, vermilion, bone black, ultramarine.
14 back	Brown	Hand	44 x 8	Viridian, red lake, ultramarine, vermilion, lead chromate, calcium?

STEM Elemental Analysis (Table 4)

No	Color	Sample Area	Measurement	Chemistry
1	Brown	Beach	75,2 x 10,2	PB, Ca, Cr, Fe, K, P, Al, S, Ba, Si,

SEM Elemental Analysis (Table 5)

No	Sample Name	Position	Color	Chemistry
1f	right center edge	74x25	green	Pb, Fe, Si, Ca, Si, (Mn), (Cr), (Ba), (P), Al.
2f	right center edge	72x29	dark green	Pb, Ca, Si, (Fe), (Cr), (P), (Al), (Mg) (Mn).
3f	upper center edge	70x47	light green	Pb, Ba, S, Cl, (Fe), (Cr), (Ca), (Si), (Al), (Mg), (K).
4f	sky-upper center	39x60	blue	Pb, Ba, S, Al, Si, Ca, P, (Fe), (K), (Co), (Cr).
5f	sky-upper center	33x58	light ocher	Pb, Cr, Ba, Si, S , Al, Zn, Mg, (Fe).
6f	beach-left center edge	5x 19	brown	Pb, Mg, Al, Si, Fe, Al, K, Ti, (Ca), (Mn), (Cl).
7f	beach-right bottom	23x10	beige	Pb, Si, S, Ca, Cr, P, Fe, Al, (Zn), (K), (Ba).
8f	beach-right bottom	24x8	light green	Pb, (Ba), (S), (Fe).
9f	girl	30x5	red	Pb, Si, Al, Hg, S, Fe, (Ba), (Ca), (K).
10f	where girl is sat	29x2	brown	Pb, Fe, Si, Al, Cl, Ca, K, (Cr), (Ba), (Mg), (Mn),, (Ti).
11b	left bottom corner	13x6	green	Hg, S, Ca, Si, Cr.
12b	sash	29x13,5	red	Pb, Si, Hg,_Al, Cr, (Fe), (Ca), (Na+).
13b	suit	29,5x18	dark green	Pb, Ca, P, Si, Al, S, (Mg), (K), (Fe), (Co), (Cr).
14b	cuff	50x13	light beige-green	Pb, Cr, Al, Si, (Na+), (Ca), (Co+), (Fe+).

APPENDIX 2

Beam describes the preparation of the lead linolate, which is prepared by saponifying linseed oil with a weak caustic soda solution and a lead acetate solution and a lead acetate solution. The brownish mass of lead linolate formed was well washed and dried at a low temperature.(See slides #19/20).The proportion that was used was:

20 ml linseed oil.
10 ml caustic soda.
10 ml lead acetate

After 24 hours, the mixture turned in to a soap. The soap was filtered and than washed about 3 times.

ACKNOWLEDGMENTS

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HIGH PERFORMANCE THIN-LAYER CHROMATOGRAPHY FOR THE IDENTIFICATION OF BINDING MEDIA -- TECHNIQUES AND APPLICATIONS

Mary F. Striegel* and Dusan Stulik*

ABSTRACT:

While sophisticated analytical methods for the identification of binding media can be used in a research setting, conservators are often limited in the techniques available to them. Thin-layer chromatography is an analytical method useful for the analysis of binding media found in paint. It provides a relatively simple, inexpensive method of identification with high sensitivity and low detection limits for samples ~ 500 µg in size.

This paper presents the application of thin-layer chromatography to the identification of binding media. An update of recent advances in the field of thin-layer chromatography that can benefit binding media analysis is provided. The paper details the step by step application of thin-layer chromatography in the identification of protein, carbohydrate, wax, and natural resin binders. It also details the use of computer technology in the evaluation of chromatograms.

1. INTRODUCTION

Identification of binding media in paintings or painted surfaces of artifacts is an important step before any cleaning or conservation treatment. The detailed knowledge of binders and their use within the artifact allows the art restorer or conservator to design a working strategy that would be safe and effective. Art historians would also like to know the exact nature of binding media when studying an artist's style and technique, since itr is the paint medium that determines the technique of painting (encaustic, tempera, oil, acrylic, mixed media). Binding media are typically organic substances that are inherently complex natural products. An example of a very complex binding medium is egg used in tempera paintings. Egg is composed of various proteins, oils, carbohydrates, vitamins, sterols, dyes, inorganic salts and water. Before their use as binding media, many of these natural products are treated to separate impurities (e.g., animal glue) or to improve their properties (e.g., pre polymerization of a raw linseed oil to produce a more viscous stand oil). All of these factors make the identification of binding media very challenging and difficult.

Identification of binding media and binding media mixtures was the focus of the GCI's Binding Media Research Project that started in 1989. The project had three major goals. The first goal was to update existing methodology of binding media analysis and adjust it to modern analytical standards to achieve higher sensitivity, reliability, and cut the time needed for analysis. The second goal was to develop new analytical strategies for binding media identification, taking advantage of recent developments in analytical instrumentation, and to test new analytical instrumentation that had good theoretical potential for use in binding media analysis. The third goal of the project was to apply advanced analytical methodology developed for binding media analysis to the verification of "low-tech" analytical methods that would not require expensive instrumentation, highly

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trained personnel and that can be adapted by a majority of museum laboratories and private conservators. One of the outcomes related to the third goal of the projects was the development of the "Binding Media Identification Kit" (Stulik and Floresheim1992). The second is a body of work focused on the application of Thin Layer Chromatography (TLC) to the analysis of binding media.

The major aims of this paper are to provide an update on recent advances in TLC methodology that can benefit binding media analysis and to provide museum laboratory personnel and practicing conservators with step-by-step procedures for TLC analysis of binding media.

2. THIN-LAYER CHROMATOGRAPHY

The application of TLC is not new to art conservation. Several studies exist on the application of TLC, including identification of dyes, proteins, gums, and resins (Flieder 1968), (Roelofs 1972), (Matousova and Bucifalova 1989).

Descriptions of the general theory of thin-layer chromatography are given in (Kowalska 1991), (Poole and Poole 1991), (Fried and Sherma 1986), and (Brenner et. al. 1965).

Thin-layer chromatography is an analytical method used to characterize chemical compounds or mixtures based on the separation pattern of its individual components. A solution made from a sample is placed on a coated plate. The plate is placed in a sealed vessel containing a small volume of an appropriate solvent mixture. As the solvent mixture travels up the plate by capillary action, the components from the sample travel up at different rates due to their interaction with the coating on the plate (the stationary phase), and the moving solvent system (the mobile phase). This process is called the development of the plate. Once the plate is developed, the components are visualized. This usually involves reacting the component with a reagent that produces a visible or fluorescent spot when observed under either visible or ultraviolet light. The pattern of spots seen for the sample of binder is called the chromatogram.

Identification of compounds by TLC is based on the comparison of chromatograms for known and unknown materials. To make this comparison easier, the locations of the spots are quantified by a Rf value. The Rf value is a basic parameter used to describe the migration of the component. It is calculated as the ratio of the distance moved by the solute (component), to the distance moved by the mobile phase front (Sherma 1991). This can be expressed as:

$$\mathrm{Rf} = \frac{\text{distance moved by the solute}}{\text{distance moved by the mobile phase front}} \qquad (1).$$

Rf values are used as guides to the relative migration and sequencing of components within a compound. There are many factors that can cause variance in the Rf values of a chromatogram. Known materials must be run next to unknown samples on the same chromatographic plate for comparison.

Advantages of thin-layer chromatography are its low cost and relative speed of analysis. The materials needed to perform thin-layer chromatography is minimal. They include a development chamber, chromatographic plates, solvents, detection reagents and reference materials. The equipment needed is shown in Figure 1. Another advantage that thin-layer chromatography can be used to analyze multiple samples on one plate, while

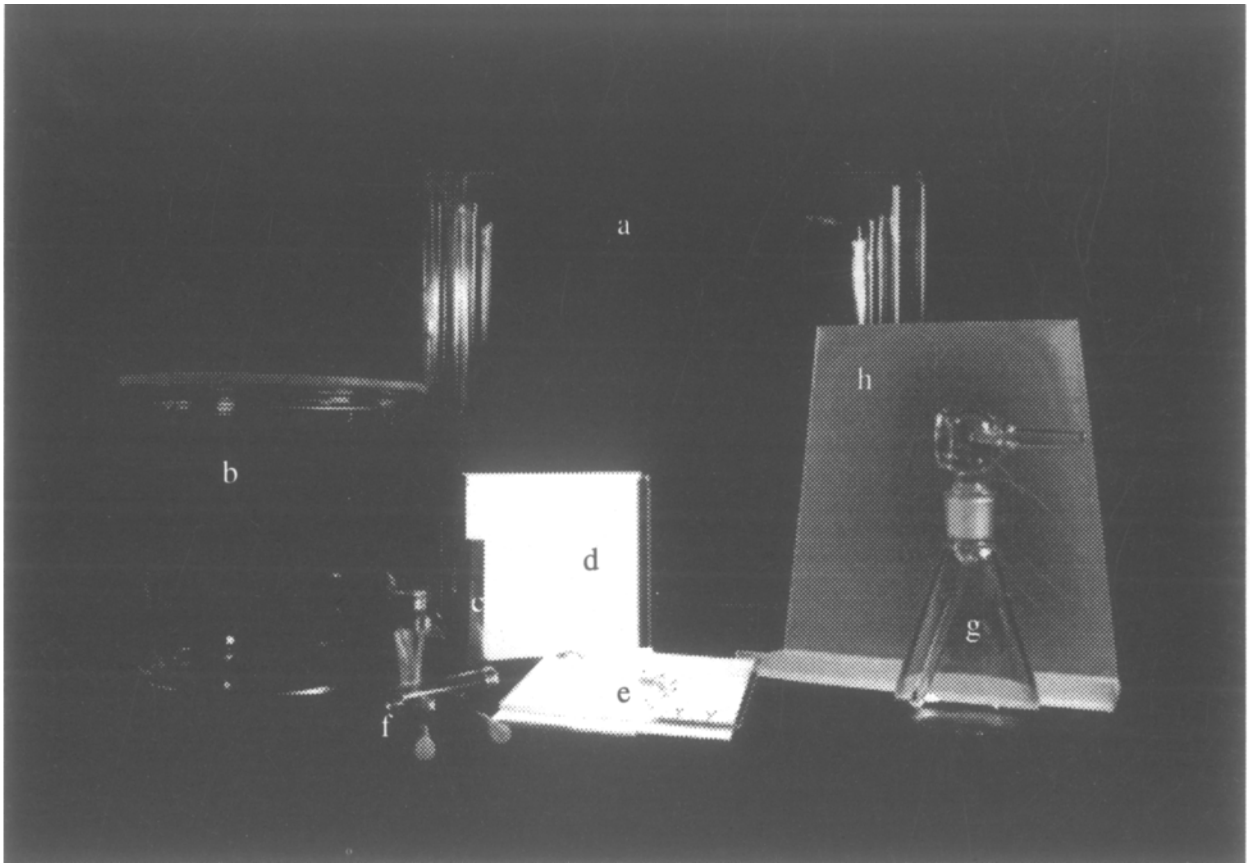

Figure 1. Equipment used for TLC analysis of binding media: a and b. conventional chambers, c. sandwich chamber, d. HPTLC plate, e. template, f. micro pipettes, g. reagent sprayer, and h. spray stand

more sophisticated techniques such as high performance liquid chromatography (HPLC) and gas chromatography (GC) are limited to the analysis of a single sample at one time (Touchstone and Dobbins 1983). TLC uses a much smaller volume of solvents than HPLC, making it more environmentally friendly. Also, TLC can be applied to a wide range of materials, like those found in binding media.

Disadvantages of TLC analysis are its need for a larger sample size and its lower sensitivity in comparison with other methods such as HPLC or GC. For binding media analysis by TLC, sample size is usually 500 μg.

2.1. Practice of Thin-layer Chromatography:

The process of thin-layer chromatography involves a series of steps, shown in Figure 2. The first step is the preparation of the sample, which depends on the type of material being analyzed. For binding media analysis, two methods of sample preparation are used principally, dissolution of the sample in an appropriate solvent (for waxes or resins) or acid hydrolysis of the sample into its components (for proteins and carbohydrates). The choice of the solvent is dependent on the solubility of the sample. The properties of the solvent are also important since it is the vehicle used to apply the sample to the plate.

For proteins or carbohydrates, the sample must be broken into its components using acid. Apparatus for acid hydrolysis is shown in Figure 3. This equipment includes a sample incubation unit, gas manifold, vacuum pump, and special vacuum tubes (hydrolysis tubes). The sample is weighed directly into the hydrolysis tube. Acid is added to the sample, then a vacuum is pulled through the side arm of the tube to remove air that might cause sample oxidization when heated. The tubes are placed in an aluminum block that evenly distributes the heat. Then the aluminum block is placed inside a heating or incubation unit. The samples are usually heated 12 to 24 hours depending on the concentration of the acid being used in this step. After acid hydrolysis, each sample is dried under a stream of nitrogen that flows from a gas manifold, through a needle, into the tube, and over the sample. Once dry, the samples are reconstituted in a carrier solvent.

The second step is the selection of the chromatographic plate. Resolution of the components of a sample depends on both the stationary phase and the mobile phase chosen for the application. Silica gel is the most widely applicable stationary phase used in thin-layer chromatography. Prepared plates of silica gel are commercially available from several manufacturers. It is important to note that variances in the manufacture of a TLC plate can greatly affect the separation of the components. To avoid problems of this sort, the plates are purchased from the same manufacturer and prepared consistently for better reproducibility. The plate is usually pre-washed in methanol and activated by heating.

There are two basic types of thin-layer chromatographic plates, conventional (TLC) and high performance (HPTLC). The major difference between TLC and HPTLC plates are the particle size, the size distribution of the particles, and the thickness of the stationary phase. HPTLC plates have optimized particle size and thinner layers that result in a higher efficiency in the separation of components. Analyses using HPTLC plates require less development distance, and therefore less time. One draw back is the low volume of sample that can be loaded onto the HPTLC plate for optimum performance. Large amounts of sample on the plate results in a poorer separation.

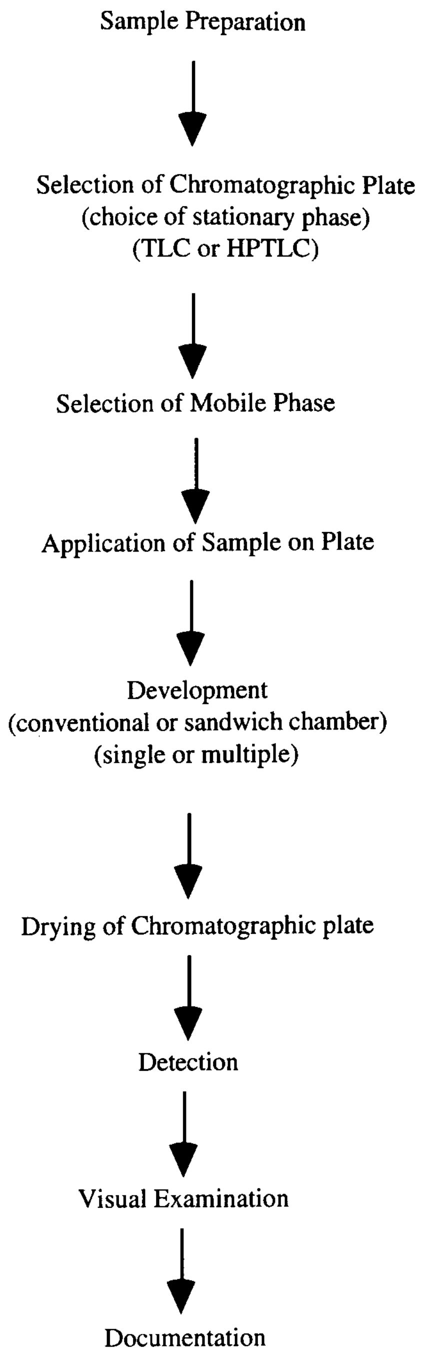

Figure 2. The process of thin-layer chromatography.

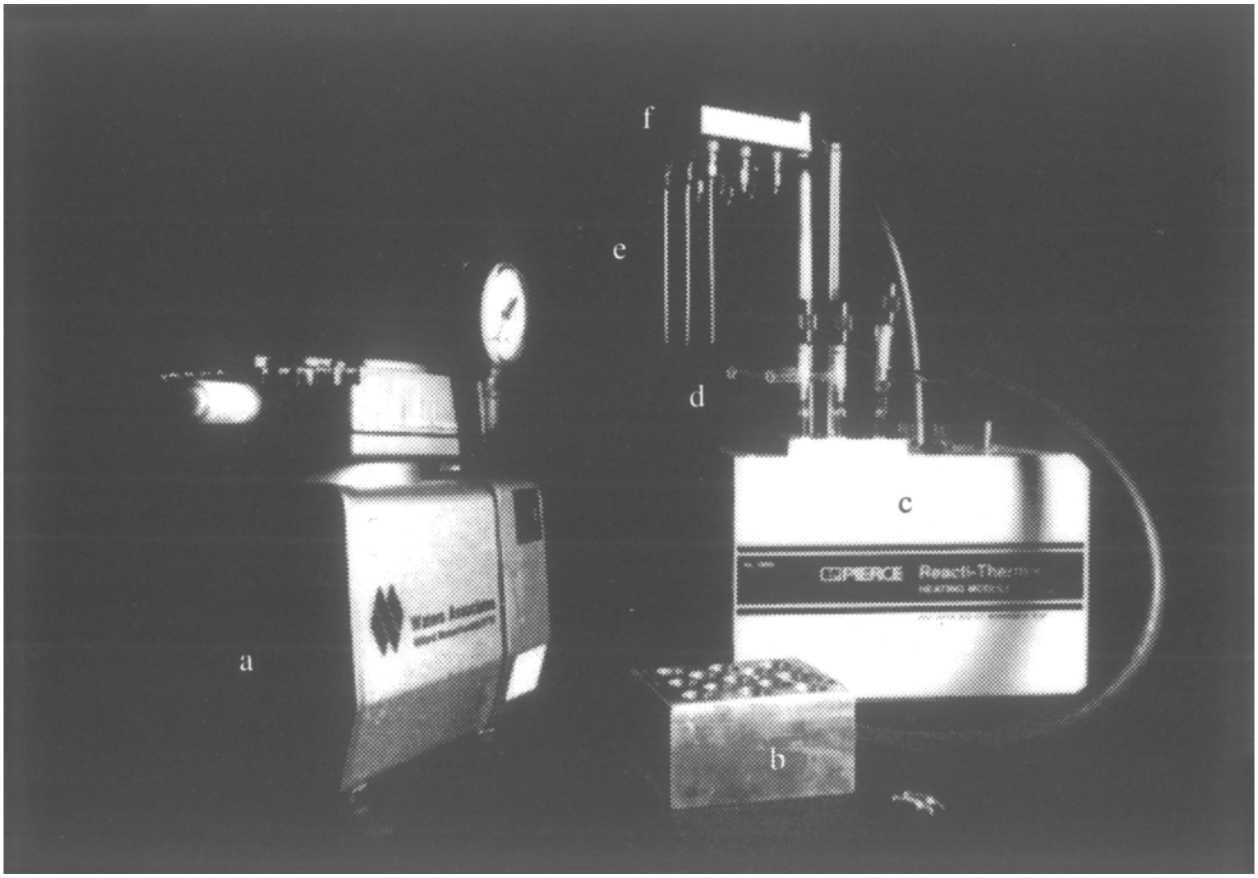

Figure 3. Pierce Reacti-therm sample incubation for acid hydrolysis of proteins and carbohydrates. Components of this system include: a. vacuum pump, b. aluminum heating block, c. heating unit, d. vacuum hydrolysis tubes, e. needles, and f. gas manifold.

A key step in the development of a TLC application is the choice of the solvent system to be used. While there are several theories on the optimization of solvent systems (see (Spiegeleer 1991)), the selection of solvents for this work was based on testing systems from literature sources including (Bruno and Svoronos 1989).

The forth step in the process is the application of the sample solution on to the prepared TLC plate. The sample solution is drawn into a glass capillary tube that is known as a micro pipette. A volume of 0.5 to 1.0 microliters of the sample solution is usually spotted on the baseline of the plate. A template is often used so that the spots are equally spaced along the baseline. The application of the spot is an important step, often requiring practice to get optimally small, round spots.

After the spots dry, the plate is placed in a development chamber that contains a solvent or mixture of solvents. There are two types of chambers used in the analysis of binding media, the conventional chamber and the sandwich chamber. The conventional chamber is easiest to use, although it must be prepared before use by placing the solvent system in the chamber, then sealing and allowing the chamber to become saturated with solvent vapors. The process usually takes several hours. This type of chamber requires approximately 30 ml of solvent system.

The sandwich chamber is often used with HPTLC plates. The sandwich chamber uses a much smaller volume of the solvent system. The chromatographic plate is attached to backing plate with a minimal vapor space between the plates. It is then placed into a trough of the sandwich chamber, containing about 5 ml of the solvent system. Since the vapor space is minimized, there is less solvent evaporation from the surface of the chromatographic plate, thus less solvent can be used. One disadvantage of the sandwich system is that highly volatile solvent systems may evaporate from the chamber before the development is complete. Also, the solvent front may become uneven as a result of preferential evaporation at the edges of the plate caused by air currents. Both of these problems can be minimized by placing the entire sandwich chamber inside a tightly sealed vessel. This decreases the evaporation of the volatile solvents and helps keep the vapor space saturated.

The plate is developed for a specified distance, usually 8 cm for 10 cm HPTLC plates in a sandwich chamber and 17 cm for 20 cm TLC plates in a conventional chamber. Then the plates are removed from the chamber and allowed to dry at room temperature in the fume hood. This process is dependent on the solvent system used, but usually takes about 30 minutes.

The detection of the individual components is aided by reacting the components with a chemical reagent to form recognizable spots under visible or ultraviolet light. The detection reagent can be applied by dipping or spraying. Spraying is the most commonly used method, since it requires minimal amounts of the reagent. Reusable spray bottles dispense an ultra fine mist that is optimal for the detection of components on a TLC plate. After detection, the plate is examined to determine the location of the components.

The chromatogram is carefully documented. The documentation includes: a record of the materials analyzed; the type of plate used; the solvent system used; the type of chamber; and other conditions. In addition, a Xeroxed copy and photographs of the TLC plate are made. The photographs represent permanent documentation of the experiment.

The plate is photographed on both black and white print and color slide film. Figure 4 shows a simple custom chamber used to photograph TLC plates under ultraviolet light. It is constructed of a cardboard box, with panels inserted to support UV lamps at 45 degree angles to the plate.

Finally, the location of each spot is measured, recorded, and respective Rf values for each component are calculated.

3. PROTEIN ANALYSIS

Proteins are a class of materials used as binders in paintings throughout history. This class includes glues, egg (egg white, egg yolk or whole egg), and casein. Glues made from animal or fish skin, bone, and other parts, have been used as binders or adhesives, in the sizing of paper, and in the ground of paintings. Egg white has been used in the illumination of manuscripts, as the bole of gold leaf, and as a temporary varnish on paintings. Egg yolk has been used as a binder in tempera paints. Casein, a milk by-product, has been used in wall paintings, panel paintings, painted furniture, painted textiles, and theatrical stage sets (Kuhn 1986).

Proteins are long organic molecules that are composed of amino acids arranged in combinations specific to each protein. There are twenty-two naturally occurring amino acids that may be found in the chemical framework of a protein. The amino acids are bound to each other by peptide linkages (-CO-NH-). The molecular weight of proteins ranges from 10^4 to 10^7 (Mills 1986).

3.1. Analytical Methodology

Identification of proteins by thin-layer chromatography is based on the presence or absence of certain amino acids within the protein. First, the protein in the sample is hydrolyzed or broken down into its component amino acids. Next, the sample, individual amino acids, and reference materials are analyzed by conventional thin-layer chromatography on a cellulose stationary phase. A butanol, acetic acid, and water solvent system is used. The amino acids are visualized on the TLC plate using a ninhydrin detection reagent.

3.2. Sample preparation

Samples for protein analysis included reference materials, samples taken from facsimile paintings, and a sample from a museum object. Commercially available reference samples included casein, rabbit skin glue, egg white, egg yolk, whole egg, and fish glue. Once the method was tested and verified, samples from facsimile paintings and a sample from a fourth century AD. Romano-Egyptian sarcophagus, in the collection of the J. Paul Getty Museum, were analyzed. All samples were prepared similarly. Reference materials from the GCI binding media collection were hydrolyzed and prepared in a concentration of 1.0-2.0 µg/µl. The Romano-Egyptian Sarcophagus was hydrolyzed and prepared in a concentration (paint sample wt./solvent v.) of ~160 µg/µl.

The procedure for acid hydrolysis uses a sample incubation unit (Pierce Reacti-therm, model No. 18800), 1.0 ml vacuum hydrolysis tubes (Pierce, model No. 29550), an aluminum heating block (Pierce, Reacti-block H), and gas manifold fitted with Teflon® coated needles for evaporation of samples (Reacti-vap, model No. 18780).

The sample, 0.5 to 0.7 mg in size, was weighed directly into a one ml vacuum hydrolysis tube. A 150 µl volume of constant boiling 6N hydrochloric acid (Pierce,

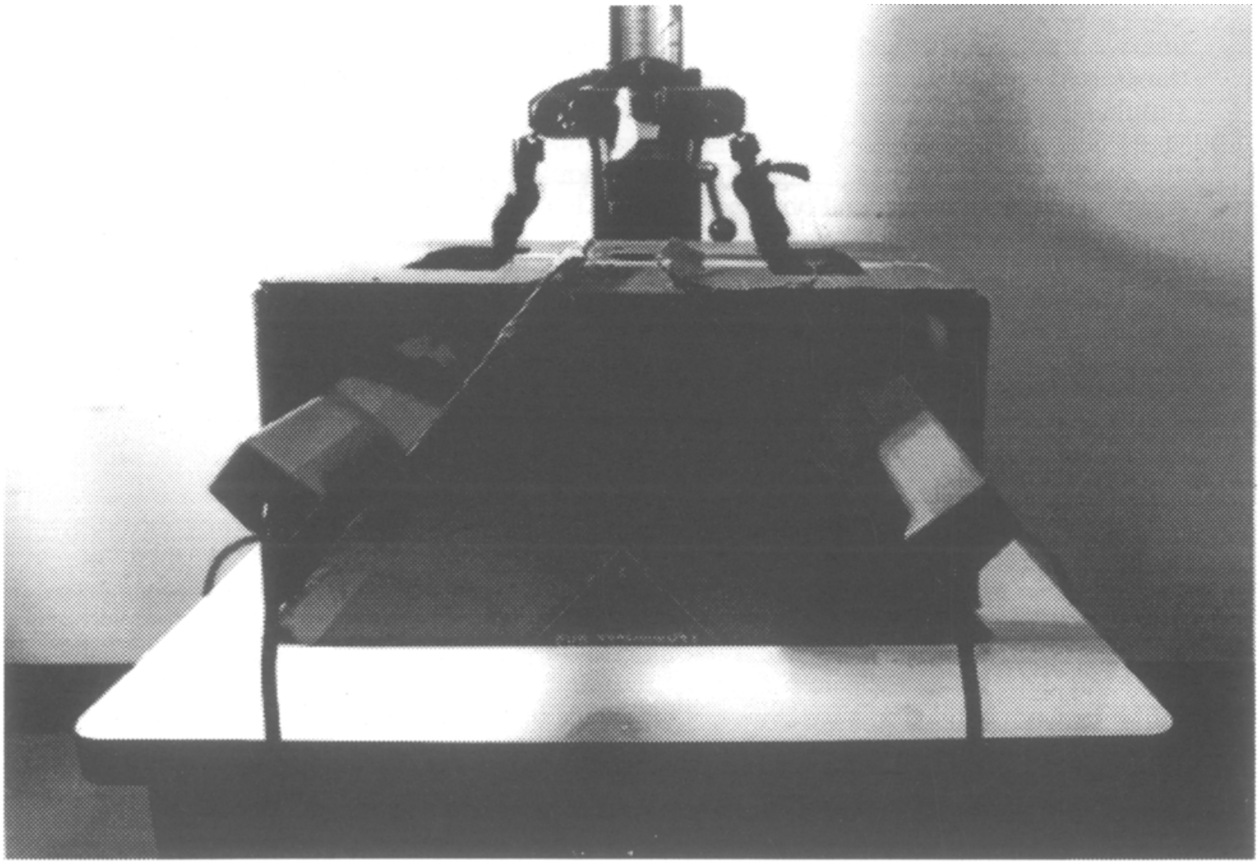

Figure 4. Photographic equipment: A simple photographic housing for ultraviolet documentation of thin layer chromatograms, made from cardboard, and fitted with two handheld ultraviolet lamps.

sequanal grade) was added to the sample. The tube was placed in an aluminum heating block set in a sample incubation unit. The tube was loosely capped with a Teflon® stopper. Tubing was used to connect the sidearm of the hydrolysis tube to a portable vacuum pump. Air was evacuated using the pump, and the tube was tightly sealed. The sample was heated at 130°C for 12 hours, then cooled to room temperature for two hours before opening. The gas manifold fitted over the hydrolysis tube so that the Teflon® coated needle was placed just above the sample. The sample was evaporated to dryness under a stream of nitrogen, then reconstituted in 400 µl of 0.1 N HCl. The solution was transferred by way of a Pasteur pipette to 1 ml vial. Up to nine samples may be prepared simultaneously.

Standard solutions (1 mg/ml concentration) of glutamic acid, hydroxyproline, lysine, serine, threonine, and tyrosine (Sigma Chemical Company) were prepared using freshly prepared 0.1 N HCl.

3.3. Procedures

During developmental stages of the TLC application, HPTLC silica gel plates were used for all binders analyzed. It was found the this stationary phase did not give acceptable results for the separation of the amino acid components of proteins. Review of literature indicated cellulose, a highly polymerized polysaccharide, provided advantages over other stationary phases for separation of amino acids (Bhushan 1991).

A Macherey and Nagel (MN300) 20 cm x 20 cm cellulose plate was washed in reagent grade methanol 24 hours before analysis. Approximately 30 ml of methanol was placed in a conventional TLC chamber. The plate was placed in the chamber and developed completely to remove any organic impurities on the plate. The plate was dried in the fume hood and stored in a dessicator until its use. One microliter of each of the standard solutions were applied to a baseline 1 cm from the bottom of the plate. Two microliters of each paint sample solution were also applied to the plate.

Thirty milliliters of freshly prepared solvent system (butanol, acetic acid, and water in a ratio of 80:20:20) were placed in a clean, dry, conventional chromatography chamber. A piece of TLC Whatman paper was placed in the solvent inside a sealed chamber to act as a saturation pad. The chamber was pre-equilibrated for three hours. The chromatographic plate was placed in the chamber and developed to a distance of 17 cm in approximately four hours.

The developed plate was dried at room temperature in a fume hood for about 30 minutes, then was evenly sprayed with ninhydrin reagent. The ninhydrin reagent was prepared as a 2% (w/w ratio) solution in ethanol. After spraying, the plate was dried, then heated at 100°C for 10 min. in an oven. The plate was evaluated and photographed 24 hours after spraying with the detection reagent to ensure complete development and visualization of the colored spots. Photographs were taken with a 35 mm camera on a copy stand using Kodak 160 ASA tungsten balanced slide film and Kodak 400 ASA black and white film.

3.4. Results

Proteinaceous binders were analyzed and identified by the presence or absence of amino acids in the chromatogram. Samples included six amino acid reference solutions, six hydrolyzed reference proteins, and a hydrolyzed sample taken from the sarcophagus. In addition, two pigment-binder mixtures made using proteinaceous binders were analyzed to examine possible interferences by pigments. Figure 5 shows the thin-layer chromatogram for this analysis.

This chromatogram has seventeen lanes containing a series of spots or patterns for each sample. Most spots are colored violet to purple. Two amino acids, proline and hydroxyproline, are colored yellow making them more difficult to see. The six most important amino acids for identification of proteinaceous binders are spotted in the first six lanes of the plate. They include glutamic acid, hydroxyproline, lysine, serine, threonine, and tyrosine.

Lanes 14-16 contain hydrolyzed pigment/binder mixtures. The sample in lane 14 is a mixture of rabbit skin glue and vine black pigment. The sample in lane 15 is a mixture of whole egg and lead white pigment. Lane 16 contains the hydrolyzed sample of an egg yolk and lead white mixture. The presence of the pigment in these samples does affect the retention of the components, seen as slight tailing of the spots, but does not limit the ability to identify the material.

As seen in Figure 5, animal glues, such as rabbit skin glue and fish glue, contain relatively large quantities of hydroxyproline, while other materials, such as egg and milk products, do not. Thus, animal glues can be identified by the presence of hydroxyproline. However, different types of animal glues cannot be distinguished by the chromatographic pattern. Casein can be identified by the presence of larger concentrations of proline and the absence of hydroxyproline. Other distinctions in the chromatographic patterns are not readily obvious by eye. A computer method for identification, based on a scanned digital image and statistics, is in development. See Appendix A for further details.

A red pigmented sample from the sarcophagus was analyzed for the presence of a protein binder. Located in lane 17, the sarcophagus sample is highly concentrated and near the loading limit of the plate. Its chromatographic pattern is very similar to that of a hide glue (rabbit skin glue reference). In addition, it contains large quantities of both proline and hydroxyproline. Thus, the sample is identified as an animal glue. This result was confirmed by gas chromatography.

4. CARBOHYDRATE ANALYSIS.

Plant gums are used as binders, adhesives, and emulsifiers in artists' materials. Historically, plant gums have been used as binders in Egyptian wall paintings. Later, they were used as the paint binder in illuminated manuscripts. Gums, such as gum Arabic, are found in watercolor and gouache paints. Gum tragacanth is used as a binder for pastel crayons. Simple sugars like honey are sometimes used to retard drying of paints. Starch, another carbohydrate, is often used as an adhesive or size.

Plant gums are carbohydrates, a class of chemicals that occur in natural products, and are often exuded by plants. Monosaccharides are the chemical building blocks of carbohydrates. If monosaccharides are found singly as monomers, they are considered to be simple sugars. If they are chemically bound together in a polymeric network, they are considered to be complex sugars, also called polysaccharides. Both types of sugars are found as binding media. Honey is an example of a simple sugar made up of fructose. Gum Arabic, on the other hand, is a complex sugar containing arabinose, rhamnose, galactose, glucuronic acid, and galacturonic acid in a polymeric structure.

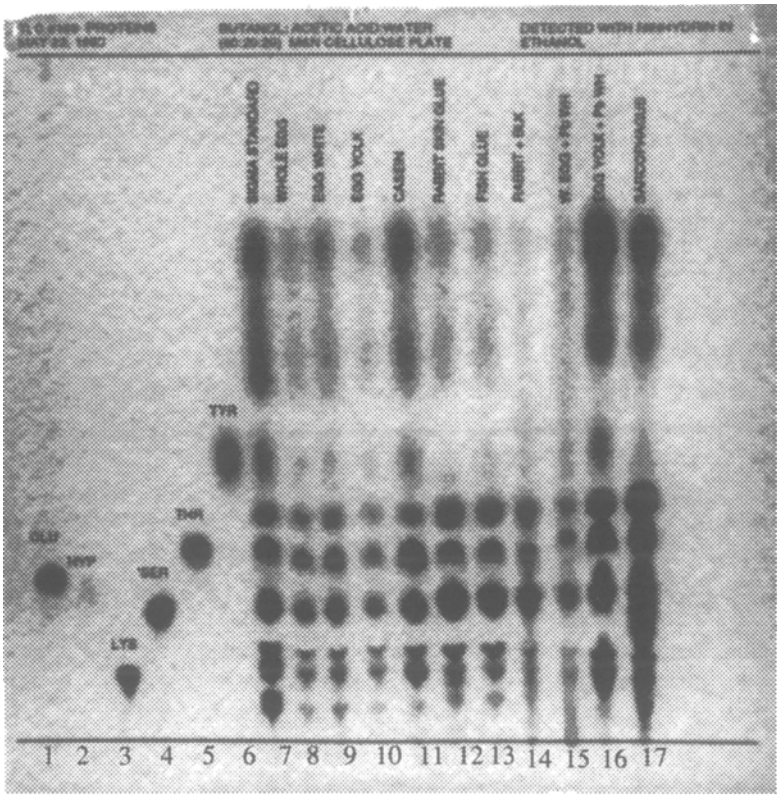

Figure 5. TLC analysis of amino acids, hydrolyzed reference proteins and unknown sample taken from Romano-Egyptian sarcophagus. Stationary phase: Macherey-Nagel MN300 cellulose. Mobile phase: butanol: acetic acid: water (80:20:20). Detection Reagent: 0.2% Ninhydrin in ethanol. Lanes: (1) glucose, (2) hydroxyproline, (3) lysine, (4) serine, (5) threonine, (6) tyrosine, (7) Sigma standard, (8) whole egg, (9) egg white, (10) egg yolk, (11) casein, (12) rabbit skin glue, (13) fish glue, (14) rabbit skin glue + vine black pigment, (15) whole egg + lead white pigment, (16) egg yolk + lead white pigment, and (17) sarcophagus sample.

4.1. Analytical Methodology

Carbohydrates are identified by the presence or absence of monosaccharides within the carbohydrate. The carbohydrate is broken into monosaccharides by dilute hydrochloric acid. Hydrolyzed samples, monosaccharides solutions, and hydrolyzed reference materials are analyzed on a HPTLC silica gel plate. The plate is developed in an acetonitrile and water solvent system in a sandwich chamber. The individual sugars are visualized by spraying with aminohippuric acid detection reagent, heating the plate, and examining under ultraviolet light. A variety of fluorescent colors are observed, ranging from pink for arabinose to orange for glucuronic acid.

4.2. Sample Preparation

The samples needed for this carbohydrate analysis included nine monosaccharide solutions, 4 reference carbohydrates (gum Arabic, gum tragacanth, gum guar, and gum ghatti), and the unknown sample. The paint sample was a blue pigmented paint from the wall painting of the Tomb of Nefertari. Approximately 1 mg of each sample was used.

Each sample was weighed directly into a 1 ml vacuum hydrolysis tube. Reagent grade methanol (200 µl) was added to each sample and allowed to stand for 12 hours to swell the carbohydrate. Next, 200 µl of 2N HCl was added to each sample. Air was evacuated from each hydrolysis tube using a portable vacuum pump. The hydrolysis tubes were tightly sealed, then thoroughly mixed using a mini vortex mixer. The samples were heated to 110 °C in the reacti-therm sample incubator for 12 hours, then cooled to room temperature. The supernatant was decanted into a 1 ml conical vial. The gas manifold was fitted over each conical vial with the needles placed 2-3 mm above the solution. The samples were evaporated to dryness at 40 °C under a stream of high purity nitrogen, then reconstituted in 50 µl of reagent grade methanol. The conical vials were tightly capped and stored in a refrigerator until analyzed.

Monosaccharide solutions of arabinose, fucose, galactose, galacturonic acid, glucose, glucuronic acid, mannose, rhamnose, ribose, and xylose (Sigma Chemical Company) were prepared in a 1 mg/ml concentration. Approximately 2 g of each monosaccaride were dissolved in 2 ml of HPLC grade water (Burdick and Jackson) to obtain this concentration.

4.3. Procedures

HPTLC silica gel plates (Merck silica gel 60 F254) were used in the analysis of carbohydrates. The plates were first washed in methanol, then activated at 100 °C for one hour, before cooling and storage in a dessicator. The plates were activated within 24 hours of use. Glass micro pipettes were used to spot sample solutions on a baseline 1 cm from the bottom of the plate. Monosaccharide solutions were spotted at a 0.5 µl volume. Reference solutions and paint samples were spotted at a 1.0 µl volume.

The chromatogram was developed in a acetonitrile: water (85:15) solvent system using a sandwich chamber. Five milliliters of the solvent system was added to the trough of a sandwich chamber. The chromatographic plate was attached to the backing plate with clamps and inserted into the trough. The entire unit was placed inside a tightly sealed cylindrical chamber to prevent air drafts that can affect the travel of the solvent front. The plate was developed to a distance of 8 cm in 20 minutes.

After development, the plate was dried in the fume hood for 30 minutes, then it was sprayed with an aminohippuric acid reagent. The detection reagent was a 0.3% solution of aminohippuric acid with 3% phthalic acid in ethanol. The plate was again dried for 30 minutes before heating at 110 °C for 10 min.

The plate was evaluated and photographed under ultraviolet light (264 and 366 nm) using both black and white print, and color slide film. The ultraviolet lamps were placed at 45 degrees to the sample on each side. A 35 mm camera with a 50 mm macro lens was used to document the plate. Fujichrome 400 ASA daylight balanced slide film was shot at 800 ASA with Kodak wratten gel filters (2E, 10R, 10M, and 20Y). The exposures, which ranged from 7s to 1m 20s, were based on trial and error. Kodak T-Max 400 ASA black and white slide film was shot at 800 ASA with a Kodak wratten 2E filter for black and white documentation.

4.4. Results

Thin layer chromatography was used to identify simple sugars found in hydrolyzed samples of carbohydrate binders. The binders were identified based on the similarity of chromatographic patterns. Figure 6 shows the thin-layer chromatogram for carbohydrate analysis.

Lane 17 in of the chromatogram contains a standard mixture of nine simple sugars including arabinose, rhamnose, galactose, glucose, mannose, xylose, fucose, glucuronic acid, and galacturonic acid. Five of the nine sugars are completely resolved with this system. The chromatographic system allows complete separation of galacturonic acid, glucuronic acid, galactose, arabinose, and rhamnose. Other simple sugars, such as xylose, fucose, and ribose (not in mixture), or glucose and mannose, are not completely resolved. The ascending order of Rf values for sugars is galacturonic acid < glucuronic acid < galactose < glucose ≈ mannose < arabinose < fucose ≈ xylose ≈ ribose < rhamnose.

From this chromatogram, the reference materials can be distinguished by location and intensity of their spots. However, the paint sample does not provide a recognizable pattern. This chromatogram illustrates the limitation of the method when very little binder is present in the original sample.

5. WAX ANALYSIS

Waxes were used by Egyptians as waterproofing, adhesives, and binders. The encaustic technique uses pigments suspended in a wax binder to create a painting. Waxes are also used in metal casting techniques, and in conservation practices, such as the relining of paintings.

Waxes are chemically complex materials that contain long chain hydrocarbons, acids, alcohols, and esters. They may contain plant sterols, triterpenoids, and their esters. Waxes are products originating from several sources including animals, insects, plants, and minerals. Insect and animal waxes include beeswax, spermaceti wax, and lanolin, among others. Plant waxes include carnauba wax, candelilla, and Japan wax. Other waxes are associated with fossilized materials. They include ceresine wax, earth wax, and paraffin.

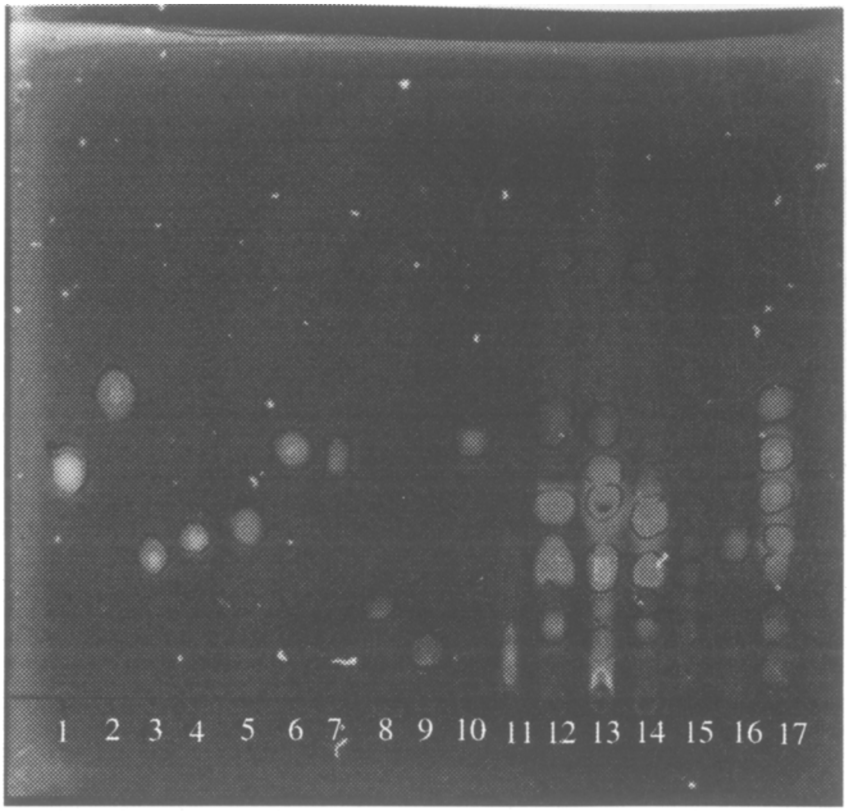

Figure 6. TLC analysis of simple sugars, hydrolyzed reference carbohydrates, and unknown sample taken from the wall painting of the Tomb of Nefertari. Stationary phase: Merck HPTLC silica gel 60 F264. Mobile phase: acetonitrile: water (85:15). Detection Reagent: 0.3% aminohippuric acid + 3.0% phthalic acid in ethanol. Lanes: (1) arabinose, (2) rhamnose, (3) galactose, (4) glucose, (5) mannose, (6) xylose, (7) fucose, (8) glucuronic acid, (9) galacturonic acid, (10) ribose, (11) wall painting, (12) gum Arabic, (13) gum tragacanth, (14) cherry gum, (15) gum ghatti, (16) guar gum, and (17) mixed standard.

5.1. Analytical Methodology

A phenomenological approach is taken for the identification of waxes by TLC. The chromatographic patterns of reference and unknown materials are studied. The number, location, and color of spots are noted. The identification is based on how closely the patterns match.

The wax samples are dissolved in chloroform, then spotted on a HPTLC silica gel plate. The plate is developed in a sandwich chamber containing a petroleum ether, diethyl ether, and acetic acid solvent system. The components of each material are visualized by spraying with an anisaldehyde detection reagent. The plate is heated after spraying, then examined under ultraviolet light where the components are seen as fluorescent spots.

5.2 Sample preparation

Reference and unknown sample solutions are prepared in a concentration of 10 µg/µl. The reference sample solutions are made by dissolving 800 µg of a reference material into 80 µl of chloroform. The reference materials include the following waxes: candelilla, carnauba, ceresine, earth, Japan, montan, paraffin, rice, spermaceti, bleached beeswax, white beeswax, and yellow beeswax.

One sample came from an encaustic facsimile painting made for testing the analytical techniques under development. The sample was taken from the edge of the panel. For this sample a solution of 16 µg/µl was made by dissolving 810 µg of the sample in 50 µl of chloroform.

A second unknown sample was taken from a relining material on the Waterlilies by Claude Monet, circa 1920. The painting is in the collection of the Museum of Modern Art, New York. When the painting was brought into the conservation laboratory for routine maintenance, a sample was taken. The material was thought to be a wax/resin mixture. The unknown sample solution, whose concentration was 26 µg/µl, was made by dissolving 1.3 mg of the sample in 50 µl of chloroform.

All solutions were stored in 250 microliter insert vials inside Teflon® capped vials. These vials were optimum for preventing evaporation of the solutions. The samples were heated at 40 °C for one half hour before they were applied to the chromatographic plate.

5.3. Procedures

All samples were prepared in reagent grade chloroform. The samples were analyzed on 10 cm x 10 cm HPTLC silica gel plates (Merck silica gel 60 F254). The plates were washed with reagent grade methanol and activated for 1 hour at 100 °C. The plates were used within 24 hours of preparation. A 0.5 µl volume of each known sample and a 1.0 µl volume of each unknown sample were spotted on the baseline 1 cm above the bottom of the plate.

The wax analysis uses a petroleum ether: diethyl ether: acetic acid (90:10:1) solvent system in a sandwich chamber for development of the chromatographic plate. Five ml of the solvent system were placed in the trough of the chamber. The chromatographic plate was clamped to the backing plate and placed in the trough. The unit was inside cylindrical chamber that was tightly capped to prevent the solvent front from being affected by air drafts. The plate was developed for 8 cm, which took 10 to 15 minutes.

The plate was removed from the chamber and allowed to dry in the hood at room temperature for 30 minutes. The patterns for the individual samples were visualized by spraying the plate with an anisaldehyde detection reagent. The detection reagent was made by combining 0.5 ml of anisaldehyde, 10 ml of acetic acid, 84.5 ml of methanol, and 5 ml of concentrated sulfuric acid. The plate was dried in the hood for 30 minutes, then placed in the oven and heated at 110 °C for 10 minutes. The plate was examined and documented under ultraviolet light similar to procedures described for sugars.

5.4. Results

Wax binders were identified by comparison to known materials. Unknown samples included material from the encaustic facsimile painting, and relining material from the Monet Waterlilies. The latter sample was a complex wax/resin mixture. Twelve reference waxes were analyzed on the same chromatographic plate with the unknown samples. Figure 7 shows the thin-layer chromatogram for the identification of wax binders.

Identification of the individual components of each wax was not attempted. Instead the chromatographic patterns of the unknown samples were compared to the reference waxes. Separation of at least nine spots was seen for three types of beeswax (white, yellow, and bleached) spotted in lanes 11, 12, and 13. This distinct pattern is also seen in lanes 9 and 10, which contain the encaustic and Monet samples, respectively. No other reference material displays this pattern, although each has a characteristic pattern of its own.

The encaustic facsimile painting was manufactured for the scientific program as a study piece for the validation of analytical methods. The binder used in the portrait was beeswax, as confirmed by this analysis. Also, the relining material of the Monet Waterlilies was identified as beeswax.

6. RESIN ANALYSIS

Natural resins are most often used as varnishes for paintings or furniture. The resin coating provides an increase in the gloss and translucence of a paint or surface. Mastic from the Greek islands and dammar from Southeast Asia are high quality natural resins used as picture varnishes. Also, paint media complexes can be made from oil, mastic, and wax. Other resins, such as dragon's blood, are used as a colored varnish for musical instruments or as a glaze for gold or silver leaf. Shellac, made from the secretions of lac insects, is used for furniture finishing and primers on the grounds of paintings. (Kuhn 1986)

Some natural resins are water insoluble by-products exuded from plants and trees. Others are natural lacquers that are water/oil emulsions tapped from trees. Most resins are from a class of chemical compound known as terpenoids. Terpenoids are compounds made up of isoprene units (Mills and White 1986).

6.1. Analytical Methodology

Of the types of binding media studied in this research, resins are the most difficult to identify and differentiate by thin layer chromatography. The resin solutions are prepared by dissolving samples in ethyl acetate. The analysis is performed on silica gel plates, in a sandwich chamber, using a benzene and methanol solvent system. The separation of components with the resin samples improves with multiple developments. The chromatographic plates are usually developed two or three times in the same solvent system

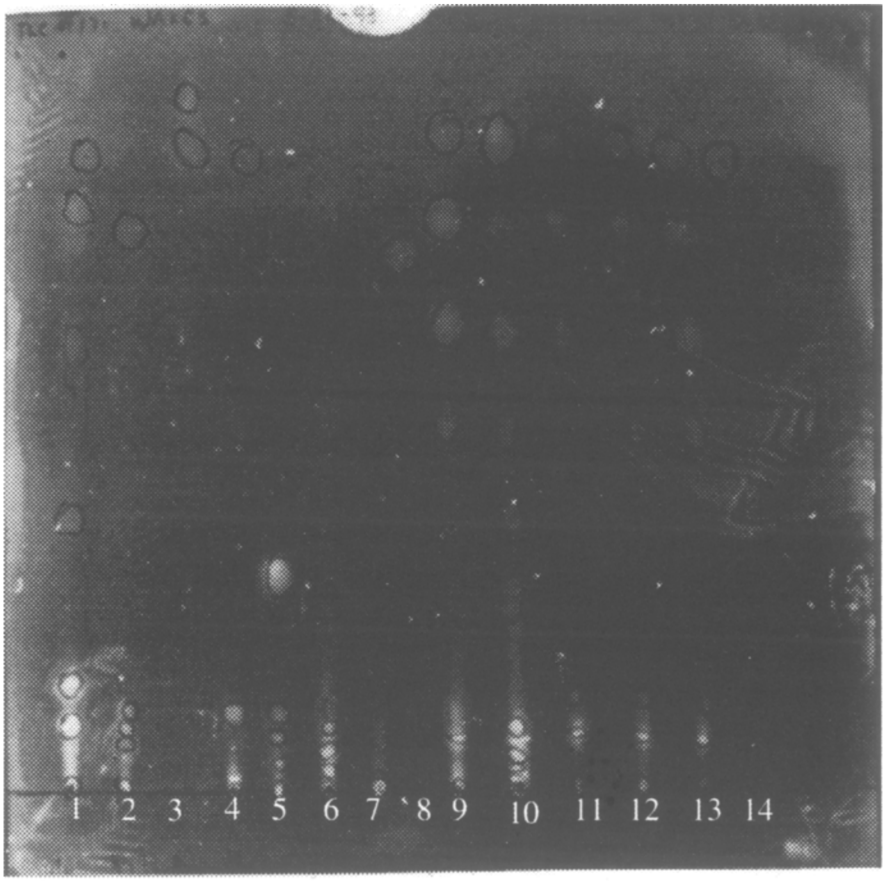

Figure 7. TLC analysis of reference waxes, a sample taken from the encaustic facsimile, and an unknown sample of relining material taken from Monet's Waterlilies. Stationary phase: Merck HPTLC silica gel 60 F254. Mobile phase: petroleum ether: diethyl ether: acetic acid (90:10:1). Detection reagent: anisaldehyde in acidifed ethanol. Lanes: (1) candelilla wax, (2) carnauba wax, (3) ceresine wax, (4) earth wax, (5) Japan wax, (6) montan wax, (7) rice wax, (8) synthetic spermaceti wax, (9) encaustic facsimile, (10) Monet painting, (11) bleached beeswax, (12) white beeswax, (13) yellow beeswax, and (14) paraffin wax.

to improve the resolution of the spots. The plate is sprayed with an antimony trichloride detection reagent and examined under ultraviolet light to visualize the pattern of fluorescent spots for each sample.

6.2. Sample preparation

All reference resin samples were prepared in a concentration of approximately 3 µg/µl or less, by placing 6 mg of the material in 2 ml of reagent grade ethyl acetate. The soluble portion of the resin goes into solution in ethyl acetate while the insoluble portion settles to the bottom of the vial. The reference resins included the following: amber, benzoin, colophony, Congo copal, dammar, dragon's blood, elemi, gamboge, Manila copal, mastic, myrrh, sandarac, and shellac. Four unknown resin samples were analyzed, including the sample taken from the Monet relining, mentioned earlier in the section 5.2. The second sample was from the Pietre Dure Portrait of Pope Clement the VII, in the collection of the J. Paul Getty Museum (92.SE.67). The third was a varnish sample on a late 19th century urn from the Mathew's workshop in the collection of the Oakland Museum. The fourth sample was a finish from a German roll top desk, circa 1785 attributed to David Roentgen and in the collection of the J. Paul Getty Museum (72.DA.47). All unknown sample solutions were made at a concentration of 10 µg/µl in reagent grade ethyl acetate. Both the known and unknown resin solutions were swelled at least 24 hours before analysis.

6.3. Procedures

HPTLC silica gel plates (Merck, 10 cm x 10 cm silica gel 60 F254) were used to analyze resins. The plates were prepared, cleaned and activated following the same procedure used for carbohydrates and waxes. Sample solutions were spotted at a 0.5 or 1.0 µl volume using glass micro pipettes.

Resin analysis uses a benzene: methanol (95:5) solvent system in a sandwich chamber. The chamber setup procedure is the same used for carbohydrates and waxes. A multi-development technique is used in the analysis of resins. The chromatographic plate is developed once to a distance of 8 cm, which usually takes 30 minutes. Then it is removed and dried for 30 minutes in the hood. The plate is placed in the same sandwich chamber a second time, and the solvent front travels up the plate again (in the same direction) for the same distance. The plate may be dried and developed a third time.

The chromatographic plate is sprayed with antimony trichloride detection reagent (Sigma Chemical Co.). The plate is dried, heated at 110 °C for 10 minutes, and examined under ultraviolet light.

6.4. Results

Two resin analyses by thin-layer chromatography are shown. Figure 8 shows the thin-layer chromatogram for analysis of the resin component of the Monet relining material. Figure 9 shows the thin-layer chromatogram for the analysis of the finishes of a Mathews urn and a Roentgen desk, as well as an adhesive used on the Pope Clement portrait. The unknown samples, thirteen reference resins, and two resin paints were run on each plate. The resulting chromatograms contain a large number of spots that fluoresce in a variety of colors. Both the locations of the spots and the colors are significant. Identification is based on comparison of the unknown to the reference materials.

The first chromatogram (Figure 8) was developed twice, while the second (Figure 9) was developed three times. The first eleven lanes of both chromatograms are spotted

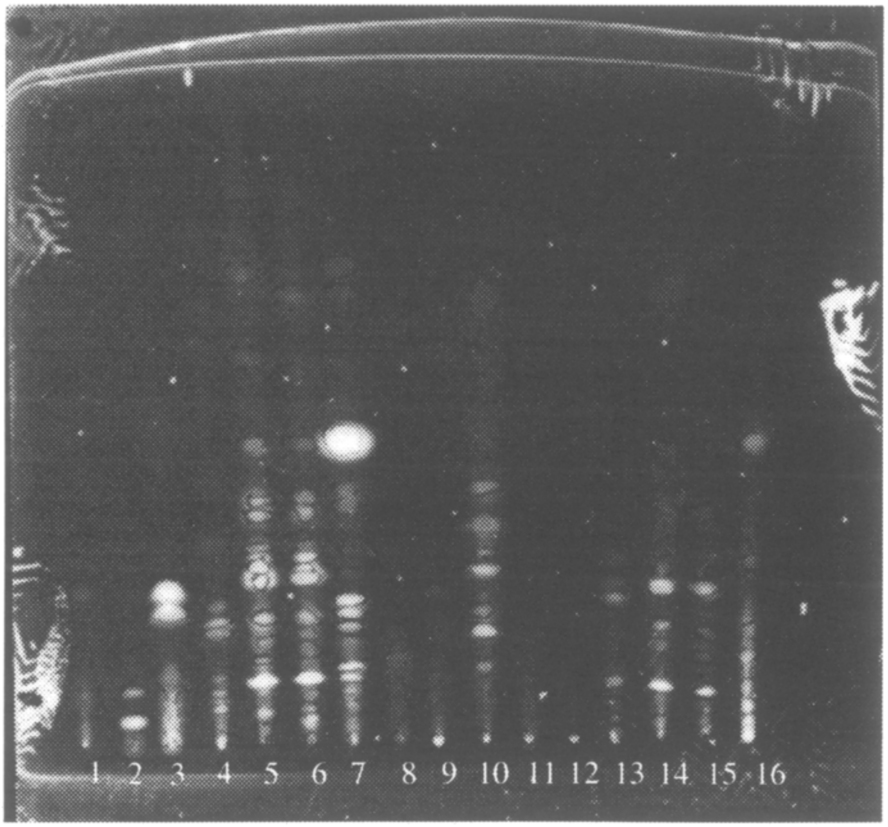

Figure 8. TLC analysis of reference resins, pigmented resins, and an unknown sample of relining material taken from Monet's Waterlilies. Stationary phase: Merck HPTLC silica gel 60 F254. Mobile phase: petroleum ether: benzene: methanol (95:5). Plate was developed twice before detection. Detection reagent: Sigma Chemical antimony trichloride reagent. Lanes: (1) amber, (2) benzoin, (3) colophony, (4) Congo copal, (5) dammar, (6) dragon's blood, (7) elemi, (8) gamboge, (9) Manila copal, (10) mastic, (11) myrrh, (12) shellac, (13) sandarac, (14) dammar + vine black, (15) dammar + yellow ochre, (16) Monet painting.

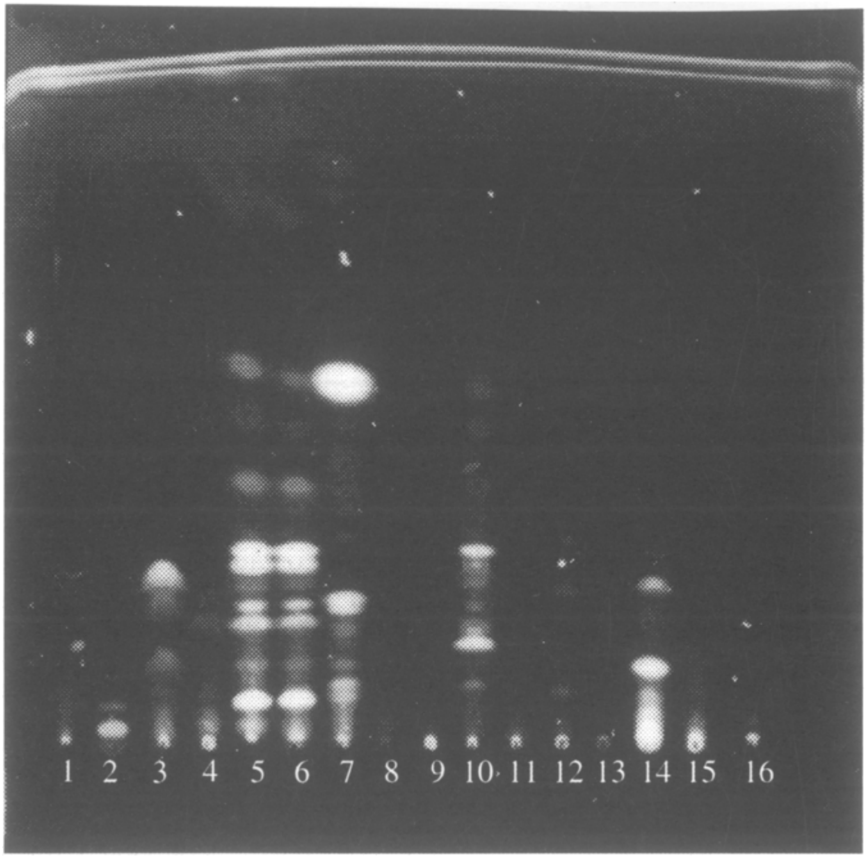

Figure 9. TLC analysis of additional resin samples. Stationary phase: Merck HPTLC silica gel 60 F254. Mobile phase: petroleum ether: benzene: methanol (95:5). Plate was developed three times before detection. Detection reagent: Sigma Chemical antimony trichloride reagent. Lanes: (1) amber, (2) benzoin, (3) colophony, (4) Congo copal, (5) dammar, (6) dragon's blood, (7) elemi, (8) gamboge, (9) Manila copal, (10) mastic, (11) myrrh, (12) shellac, (13) sandarac, (14) Pope Clement adhesive, (15) Mathews urn finish, and (16) Roengten desk finish.

with the same reference resins. Three-fold development improves the separation of the components within each sample, but the solvent front shows more curvature than in the two-fold development. Depending on the nature and the need for resolution within the sample, two- or three-fold development can be used. In many situations, an identification of the resin can be made after two developments.

The chromatogram shown (figure 8), contains pigment/resin mixtures that are located in lanes 14 and 15. These mixtures include dammar resin with vine black (lane 14) or yellow ochre (lane 15) pigment. Unlike the pigment/binder mixtures of proteins, the chromatograms of dammar are not affected by the presence of pigments. The dissolution of the resin binder into ethyl acetate may limit the amount of pigment present in the sample once it is spotted on the chromatographic plate and minimizes any possible interference by pigments on the chromatogram.

The Monet sample is located in lane 16 of the chromatogram of Figure 8. The chromatographic pattern of this sample shows eleven or more spots, most of which have Rf values less than 0.244. This pattern most closely resembles that of elemi, located in lane 7 of figure 8. Most obvious is the intense yellow spot located at Rf of 0.438 in each lane. Some differences between the two samples are seen, which may be due to concentration differences, or to the presence of beeswax, which was also identified in this sample. Gum elemi is known to be a component of wax/resin relining mixtures (Heller 1993). The resin in the Monet sample is identified as elemi.

The Pope Clement sample in lane 14, of figure 9 contains some spots similar to that of colophony (a balsam) in lane 3. The intense blue spot seen in the sample is not analogous to any material on the plate. It may be due to an impurity or an additive in the resin. Alternately, the reference material may not be a good match because there are multiple types of balsams or pine tree resins that can vary in their composition due to source and type of tree. While the analysis of the sample by FTIR microscopy confirms that the material is a balsam, there is also the possibility that the blue spot is due to an added component that was below the detection limit of the IR.

The finish on the Mathews urn cannot be identified by comparison to the reference materials on this plate. Thesolubility of the material and the chromatogram has characteristics of a resinous material, but does not match any reference. Information supplied by the conservator of the piece indicated that the resin may be bitumen. Further analysis with bitumen or other reference materials may identify the finish.

The chromatograpm for the Roentgen desk finish sample, lane 16, resembles the pattern seen in lane 12 for shellac. It shows two spots that are distinctive of a shellac located near the origin of the plate. The first, at the origin, has a distinctive orange color associated with a shellac resin. Other spots seen in the Roentgen desk sample may be due to waxes or other impurities present in the sample since waxes can also be detected with the antimony trichloride detection reagent. The presence of shellac was confirmed by FTIR microscopy.

7. CONCLUSIONS

Our work demonstrates the wide range of binding media that can be analyzed by thin-layer chromatography, including proteins, carbohydrates, waxes, and resins. Table 1 summaries our methodology. This technique provides an inexpensive, simple alternative to more technologically advanced methods, such as gas chromatography (GC) or high performance liquid chromatography (HPLC).

Table 1. A summary of the thin-layer chromatography technique for binding media.

Binding Media	Sample Preparation	TLC Plate	Solvent System	Detection Reagent
Proteins	Acid Hydrolysis 6N HCl	Macherey-Nagel 200 Cellulose	Butanol: Acetic Acid: Water (80:20:20)	Ninhydrin
Carbohydrates	Acid Hydrolysis 2N HCl	Merck HPTLC Silica Gel 60 F254	Acetonitrile:Water (85:15)	Ammino-hippuric Acid
Waxes	Dissolution of sample in Chloroform	Merck HPTLC Silica Gel 60 F254	Petroleum ether: Diethyl ether: Acetic Acid (90:10:1)	Anisaldehyde
Resins	Dissolution of sample in Ethyl Acetate	Merck HPTLC Silica Gel 60 F254	Benzene: Methanol (95:5)	Antimony Trichloride

Thin-layer chromatography provides a qualitative method for identifying binders within paint samples. It is easy to use and can be learned in a short time. Minimal equipment is necessary for analysis. Basic TLC starter kits containing a conventional development chamber and lid, tank liners, sample spotters, TLC plates, a reagent sprayer, a disposable spray box, and a spotting template, can be purchased from suppliers for less than $250. A linear development chamber for HPTLC analysis is $50-100. Solvents, detection reagents, and references are needed for analysis. Multiple samples can be analyzed on one chromatographic plate.

This method offers an intermediate level of identification between a screening method, such as the GCI binding media identification kit (Stulik and Floresheim 1992), and more advanced instrumental methods that provide quantitative analyses.

The interpretation of thin-layer chromatograms requires development of an "eye" for pattern recognition. Work is in progress to develop and improve the simple, low cost computer methods of interpreting TLC plates, discussed in Appendix A.

We have attempted to identify and use environmentally safe reagents whenever possible throughout this method. Unfortunately, to maintain the integrity of identification, some solvents or reagents could not be eliminated. It is important to note that, when working with any thin-layer chromatography method, it is necessary to become acquainted with material safety data sheets for all reagents and to practice safe and responsible laboratory procedures. We will continue to search for alternate solvents and reagents as our work continues.

ACKNOWLEDGMENTS:

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APPENDIX A. COMPUTER AIDED ANALYSIS OF THIN-LAYER CHROMATOGRAMS

Often the identification of binding media by thin-layer chromatography requires the recognition and differentiation of subtle differences in chromatographic patterns. In some cases, identification can be based on the presence or absence of a particular component. In other cases, it is both the presence and concentration ratios of particular components that lead to an identification. One way to approach the problem is to quantitatively determine the amount of each component in the sample. Quantitative analysis by thin-layer chromatography can be performed using scanning densitometry (Szepesi 1990), which requires expensive equipment and a dedicated computer. Less expensive video densitometers are available that can be used for quantitative methods (Touchstone 1993), but may still be out of the price reach of the average conservation laboratory.

A second approach is to use computer aided analysis to match chromatographic patterns between known and unknown samples. This approach assumes that a computer is available to the conservator. An image of the chromatographic plate is digitized using a full page or hand scanner. A density plot of each chromatographic lane of the digital image is determined using NIH Image public domain software on a Macintosh computer. Further analysis results in a series of peak areas associated with the spot locations for each chromatographic lane. This data is statistically compared using Statview statistical software. The identification of the unknown binder is made by comparison to a series of known references and finding the pattern that most closely matches.

We present the results of our preliminary experiments with this second approach to show both the promise of this technique and the direction of our research at the present time.

A1. Experimental Methods

The test chromatogram was a protein analysis run on a 20 cm x 20 cm cellulose plate. Samples on this plate included six amino acids, six reference materials, and two "unknown" samples. The reference materials included whole egg, egg white, egg yolk, rabbit skin glue, fish glue, and casein. One unknown sample was taken from a casein facsimile painting, the other from an egg tempera facsimile painting. The references and unknowns were hydrolyzed using the protocol described in section 3.2. The samples were analyzed according to procedures described in section 3.3. The resulting patterns for the facsimiles were weak due to a low yield upon hydrolysis. Identification of the binding media in the unknown samples was not readily discernible by visual inspection of the plate.

The chromatographic plate was placed on a Hewlett Packard Scanjet Plus, a full page scanner, and digitized using Ofoto software on a Macintosh Quadra 950 computer. The plate was scanned at a 300 dpi scan, and saved as a non compressed TIFF file. The file was then opened in NIH Image, v. 1.43, a public domain software package for the analysis of images. A specialty macro developed for electrophoresis, called the Gel Plotting Macro, was used to determine the location and peak area of each spot in each lane of the chromatogram. The results were tabulated as a series of locations (defined as distance from the original baseline) and peak areas for each sample. Rf values were calculated from the locations. The peak areas for each sample were then ordered by increasing Rf value.

A2. Results and Discussion

These results were analyzed using Statview v.4.0 software. A correlation matrix for the unknown and reference materials was calculated based on the observations of nine peaks. A correlation matrix is a statistical method that provides information on the probability that one pattern matches another. Table 2 shows the correlation matrix of the protein samples analyzed. In this matrix each material is compared to all the other materials on the plate. A 1.000 indicates a perfect match of the materials and, in this case, is found only when the material matches itself on the table. It is important to note that unknown sample #1 most closely matches the casein standard material, and unknown sample #2 most closely matches the egg yolk reference material. Indeed, sample #1 was taken from the casein facsimile painting. Sample #2 was taken from the egg tempera facsimile painting.

Table 2. Correlation Matrix of nine peak obesrvations for each sample. The correlation matrix is a tool to compare patterns, and determine the identification of the unknown protein samples.

	#1	#2	Whole Egg	Egg White	Egg Yolk	Rabbit Glue	Fish Glue	Casein
#1	1.000	0.535	0.245	0.583	0.584	0.226	0.192	0.691
#2	0.535	1.000	0.481	0.793	0.879	0.625	0.703	0.693
Whole Egg	0.245	0.481	1.000	0.411	0.214	-0.103	0.068	0.039
Egg White	0.583	0.793	0.411	1.000	0.835	0.600	0.558	0.659
Egg Yolk	0.584	0.879	0.214	0.835	1.000	0.622	0.603	0.841
Rabbit Glue	0.226	0.625	-0.103	0.600	0.622	1.000	0.911	0.289
Fish Glue	0.192	0.703	0.068	0.558	0.603	0.911	1.000	0.277
Casein	0.691	0.693	0.039	0.659	0.841	0.289	0.227	1.000

A3. Conclusions

These results show promise for analyzing thin-layer chromatographic plates using digitized images. Personal computers found in conservation laboratories for word-processing may be useful for this type of analysis. A hand scanner capable of 300 dpi resolution, scanner software, and statistical software are needed. Further research in this area is under investigation. Developments may include methodology for either Macintosh or IBM compatible systems and further validation experiments.

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