The AIC Painting Specialty Group

POSTPRINTS

VOLUME TWENTY-TWO 2009

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American Institute for Conservation of Historic and Artistic Works

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POSTPRINTS

VOLUME TWENTY-TWO 2009

Papers Presented at the 37th Annual Meeting of the American Institute for Conservation and Historic Works
Los Angeles, California, May 21 – 22, 2009

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Barbara Buckley and Meg Newburger
P O S T P R I N T S
VOLUME 22 2009 ANNUAL MEETING

Papers Presented at the 37th Annual Meeting of the American Institute for Conservation of Historic and Artistic Works
Los Angeles, California, May 21 - 22 2009

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May 21, 2009

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JOHN K. DELANEY

Advances in Computer-Assisted Canvas Examination: Thread Counting Algorithms
C. RICHARD JOHNSON, JR., ELLA HENDRIKS, PETRIA NOBLE, AND MICHEL FRANKEN

The Use of Spectral Imaging as an Analytical Tool for Art Conservation (Abstract)
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PAINTINGS SPECIALTY GROUP
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ABSTRACT

Immunological methods of analysis hold great potential for applications within art conservation. In particular, the method of enzyme-linked immunosorbent assay (ELISA) is emerging as a valuable complement, or in some instances an alternative, to well established analytical methods such as gas chromatography-mass spectrometry and Fourier transform infrared spectroscopy. Until recently, the reliability of ELISA to detect target molecules as they exist in art materials and the effects that aging and pigment interaction have on their antigenic properties received little attention. This article offers a brief overview of a larger study that evaluates the ability of several antibodies to recognize specific proteins within various proteinaceous binding media before and after aging. The binding media examined include; egg-, collagen-, and milk-based preparations from a variety of species, as well as selected natural gums with glycoprotein components such as gum arabic, gum tragacanth, ghatti gum, and cherry gum. Extensive investigations using mock-ups of traditional paint formulations were conducted to evaluate the impact of increased heat and light exposure on the antigenic detection of each protein. In addition, the potential inhibitory effects of 21 different pigments on the antigenic detection of each proteinaceous binding medium were compared before and after aging. Results from serial dilution assays of paint samples suggest that ELISA is indeed a robust and highly sensitive method for analysis of pigmented art materials. Despite findings that indicate accelerated aging, in particular UV light exposure, decreases detection sensitivity, the technique still exhibits extremely sensitive limits of detection (LODs) for binders in aged paint samples. These LODs range from less than 1 µg to 2 µg of paint depending on the type of protein-pigment combination analyzed. The present study also offers an improved ELISA protocol that integrates a signal amplification step involving biotinylated secondary antibodies and streptavidin–alkaline phosphatase, a technique previously unused in the field.

INTRODUCTION

The application of immunological methods to the analysis of artistic works has been sporadic in the past. However within the last two decades, such applications have received increased attention. Kockaert et al. (1989) and Ramírez-Barat and de la Vina (2001) published research on the analysis of paint cross sections using immunofluorescence microscopy (IMF). In 1999, Hodgins conducted dissertation research involving the application of immunological methods to detect collagen-based adhesives from a variety of species and included analysis of collagen-based paint with seven different pigments. More recently, the work of Heginbotham et al. (2006), introduced a wider portion of the conservation community to the principles behind both IMF and ELISA, proposing them as complimentary techniques, and demonstrating their successful application in a case study involving the identification of an egg-based coating within the layered structure of a 17th-century French cabinet attributed to André-Charles Boulle. Mazurek (2007) and Mazurek et al. (2008) built extensively on this research at the Getty Conservation Institute by testing several commercially-available antibodies on a number of proteinaceous materials from a range of species sources and published an improved ELISA protocol capable of detecting egg-, collagen-, casein-, and several natural gums. At present, additional studies involving the use of ELISA are underway in a number of conservation laboratories both in the US and abroad. The research presented in this article is part of a larger doctoral study completed through Clark University and conducted in large part at the University of Massachusetts Medical School.
Despite the growth in amount of research, the immunological methods best suited for analysis of art materials remain largely unfamiliar to many in the conservation field and as such merit further introduction. At the center of all immunological methods is the large family of complex globular glycoproteins, known as antibodies, which are the mediators of the humoral immune response. Antibodies fulfill their function within the immune system due to their remarkable ability to discriminate subtle structural differences among a multitude of complex biopolymers, thereby differentiating ‘self’ from ‘non-self’ molecules. Schematics often depict the antibody molecule as Y-shaped and illustrate how the molecule consists of two identical copies of a polypeptide known as the heavy chain, and two identical copies of a polypeptide called the light chain (fig. 1).

Highly variable regions at the end of each heavy and light chain define the antigen-binding site and give antibodies their specificity for binding infectious organisms and other foreign molecules. These highly variable regions are referred to as the antigen binding fragment or the Fab region. The sites on the antigen to which Fab regions bind are referred to as epitopes (fig. 1b). Epitopes typically consist of 5–8 amino acids that occur either in a linear sequence on the antigen polypeptide chain, or in conformational clusters formed by the antigen’s unique structure.

Antibodies occur in a variety of classes (IgG, IgA, IgE, IgD, and IgM) that define their function in vivo (fig. 2). The classifications are based on the amino acid sequence found in the Fc, or constant portion of the antibody molecule. IgG antibodies, a class used extensively throughout this research, have two identical antigen binding sites and therefore are considered bivalent. Antibodies are typically referred to as either monoclonal, meaning a population of identical antibodies recognizing one specific amino acid or polysaccharide sequence on an antigen, or polyclonal, meaning many different antibodies that react to different regions of an antigen.

Relative to a number of other analytical methods currently in use for paint binding media analysis, the instrumentation required to conduct ELISA analysis is comparatively simple, inexpensive, and the data produced does not involve statistically-intensive analysis. Equipment needs include microtitre plates, a hand-held multi-channel pipet and a plate-reading spectrophotometer that measures the optical density of the
chromophores produced in a positive reaction (fig. 3a-d). Though the relative volumetric expense of antibodies is high, the number of analytical tests possible using such volumes makes the method relatively cost effective.

RESEARCH GOALS

One of the overarching goals of this research was to evaluate the effect of aging on the antigenic properties of proteins used in art materials. Antibodies are known to recognize conformational and linear epitopes on antigens, however when a protein is denatured, as is typically the case with proteinaceous materials used in art making, conformational epitopes are largely lost. Therefore, when dealing with denatured and degraded proteins such as occur in art materials, the use of conformational dependent antibodies is often not an option.

Another goal of this research was to identify antibodies that are broadly reactive across various species sources, but highly selective for the particular type of antigen. In a sense, the fewer antibodies required to identify the type of material present (e.g. egg, milk, collagen, and plant gum), regardless of species source, the better. This would be a desirable property for future applications in the analysis of paint cross sections using immunofluorescence microscopy. Although the potential exists for developing species specific ELISA assays, species specificity within particular types of proteins was considered in this research to be of secondary importance to first developing reliable and highly-specific ELISA assays that are type specific.

In addition to the above goals, another central goal throughout this study was to determine what pigments interfered with antibody binding. Since various metals present in the pigments could potentially complex with the proteins, the possibility exists for epitopes on the target protein to be masked and thereby prevent antibody binding from occurring. To evaluate this, dilution assays were conducted on each of the 21 different pigmented paints from each of the four types of proteinaceous paint sets, including samples from both the accelerated aged paint sets and the identically prepared naturally aged paint sets.

METHODS AND MATERIALS

There are several ELISA formats from which to choose, however the indirect method (fig. 4) has been used most in our field. The essential steps of this method consist of first introducing a buffered solution containing the extracted sample into the plate wells and incubating for a period during which

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Figure 3a-d.

a) 96-well polystyrene microtitre plate, b) a developed plate showing positive colorimetric reactions in some wells, c) the type of multi-channel pipet commonly used in the varied stages of plate development, and d) a plate-reading spectrophotometer.
any marker protein present in the sample is allowed to adhere to the well surface. The plate is then washed and remaining binding sites on the surface of the wells are blocked with a blocking buffer typically consisting of a neutral protein in order to prevent unspecific binding of antibodies added later. After blocking, a solution of the primary antibody, specific to the marker protein, is added and allowed to bind to any marker protein adhered to the plate wells. Later, a secondary antibody is introduced that binds to the constant region of the now marker-bound primary antibody. Typically, the secondary antibody is conjugated to an enzyme, which in the final step reacts with an added substrate to produce a chromophore. Since more than one secondary antibody can bind to the constant region of the primary antibody, the indirect method effectively amplifies the signal by providing an increased number of color-producing enzymes per antigen-antibody complex.

Since one of the central goals of this research was to evaluate the effect of aging and pigment interaction on the antigenic properties of proteins, it was necessary to prepare an extensive number of test samples. Four major types of proteinaceous materials were included in the study including; egg-, milk-, collagen-, and gum-based materials (fig. 5). In addition, several other unrelated art materials were prepared in order to test for cross-reactivity. Unpigmented samples of the various proteinaceous materials were coated onto glass slides and allowed to dry for over 18 months. Duplicate paint sets consisting of 21 different pigments and various binders from the four protein types were also prepared on panels. With assistance from colleagues at Getty Conservation Institute, one set from each of the duplicated paint sets was subjected to accelerated aging.

Although various components of the ELISA method were evaluated over the course of this research and improvements integrated where possible, the most significant modification involved the use of biotinylated secondary antibodies. Unlike the standard indirect method, which uses secondary antibodies directly conjugated to an enzyme (fig. 6a), the method used

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**Figure 4.** Step-by-step diagram of the indirect ELISA method
in this research incorporates biotinylated secondary antibodies that provide multiple binding sites for streptavidin bound enzymes to attach (fig. 6b). Essentially, the more enzymes attached to each secondary antibody the more signal produced.

RESULTS AND DISCUSSION

OVALBUMIN
Ovalbumin was targeted as a marker protein for the presence of egg in art materials. Technically, ovalbumin is an egg white protein, not an egg yolk protein, therefore an antibody specific to phosvitan, a protein found in yolk, has been used by Mazurek et al. (2008) in addition to an antibody specific to ovalbumin in order to ensure detection in cases where yolk alone was used [5]. However, this research suggests that the use of both anti-ovalbumin and anti-phosvitan antibodies to test for the presence of egg as a binder in paint is not necessary, due in part to the sensitivity of the ELISA method used. The results from multiple serial dilution assays (fig. 7) indicate that an anti-ovalbumin antibody can be used successfully to react with samples of not only egg glair and whole egg, but also samples of egg yolk, and all at nanogram levels or below.

Meticulous care was taken to avoid cross-contamination of any egg white into egg yolk samples during preparation, therefore an alternative explanation for the positive reactivity to ovalbumin within yolk samples is considered necessary. There is general agreement that ovalbumin functions as a nutrition source for developing chick embryos, but the migration of the ovalbumin molecules from the egg white through the egg yolk membrane and into the yolk was once thought to occur...
only in fertilized eggs. However, recent studies have shown that during storage, ovalbumin undergoes a shape change from N-ovalbumin to S-ovalbumin, which allows the ovalbumin molecule to pass through the yolk membrane into the yolk, even in unfertilized eggs. The rate of change from N-ovalbumin to S-ovalbumin is said to increase with temperature. The eggs used to prepare the samples in this research were purchased fresh and under constant refrigeration prior to use. Therefore, it seems reasonable to conclude that if ovalbumin is detectable in yolk samples carefully prepared using refrigerated eggs, that egg yolk binding media prepared by artists in times prior to modern refrigeration would have even more opportunity for the N- to S-ovalbumin change to occur and as such ovalbumin can be expected in cases where egg yolk binder was used. This phenomenon has two obvious implications for analysis of paint media using ELISA; 1) it enables the analyst to recognize egg-white, whole-egg, and egg yolk binders using just one antibody, and 2) it precludes analysts from making the determination that paint found to contain both phosvitin and ovalbumin was formulated using a whole egg binder, since it could also be an egg yolk binder.

At first glance, the slightly improved detection of whole egg (indicated by the green curve in fig. 7) over that of egg glair (red curve), appears proportionally inconsistent with the percentage of ovalbumin present in egg white and an equal amount of whole egg until one considers the variety of factors at work that help explain this. Firstly, the strong protein-protein bonds that occur within the egg glair as it dries down to form a coating contribute to decreased solubility and reduce the accessibility of antibodies to the ovalbumin molecules. It is noteworthy that samples of egg glair used throughout this.

Figure 7. Serial dilution curves for hen egg glair (red circles), whole egg (green squares), and egg yolk (black triangles). Each curve is the average of five separate serial dilution assays. The blocking buffer was 2% AgHS, the primary Ab was Chemicon ab1225 at 1:1000 and the secondary Ab was 1:2000. The X-axis is nanogram of sample, and the Y-axis is optical density after 30 minutes.
research exhibited decreased solubility in the elution buffers relative to that of whole egg and egg yolk samples.

The impact of traditional preparation techniques may also play a role. The act of whisking egg whites when preparing egg glair effectively introduces a degree of denaturing that the whole egg and egg yolk samples do not undergo. When quail egg samples were prepared, the egg white was not whisked and subsequently the samples yielded dilution curves more consistent with the relative amounts of ovalbumin expected in each sample (fig. 8).

Lastly, the relatively high degree of reactivity observed with whole egg and egg yolk samples may also be due to a preserving effect on ovalbumin of the additional carbohydrate and lipid components of egg yolk as the sample dries. Research has shown that direct sugar-protein hydrogen bonding and not entrapment of water at the protein surface is responsible for retention of a high level of native protein structure in dried samples (Allison, 1999).

Table 1. LOD for ovalbumin in unpigmented hen and quail egg samples using ChemIcon ab1225 at 1:1000 and the secondary Ab was 1:2000.

<table>
<thead>
<tr>
<th>Antigen with ~18 months of natural age</th>
<th>~ LOD using rbt-anti-hen-ovalbumin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ovalbumin Standard</td>
<td>0.05 ng</td>
</tr>
<tr>
<td>Hen Egg glair</td>
<td>0.3</td>
</tr>
<tr>
<td>Hen Whole Egg</td>
<td>0.2</td>
</tr>
<tr>
<td>Hen Egg Yolk</td>
<td>8.0</td>
</tr>
<tr>
<td>Quail Egg white</td>
<td>0.25</td>
</tr>
<tr>
<td>Quail Whole Egg</td>
<td>0.6</td>
</tr>
<tr>
<td>Quail Egg Yolk</td>
<td>24</td>
</tr>
</tbody>
</table>

With each group of proteins analyzed, efforts were made to test a variety of source species. Limits of detection (LOD) for each of the various samples tested were determined in order to facilitate comparisons between the reactivity of antigen-an-

Table 1 lists the LOD values for both hen and quail eggs. Unlike that seen with the hen egg samples, the serial dilution results from the quail egg samples show that when non-whisked egg white is used instead of egg glair, ovalbumin detection is greater than that of whole egg, as one would expect. As is the case with hen yolk, ovalbumin is detectable in the nanogram range in quail yolk samples.

Figure 9 shows a representative example of reactivities for a pigmented whole egg paint sample. The blue curve corresponds to the sample with ~18 months of natural age, the green curve corresponds to the same paint subjected to thermal aging, and the red curve corresponds to the same paint after accelerated aging with both heat and light. Clearly, photodegradation contributes most to a reduction in reactivity. However, in this case even after accelerated aging with both heat and light, ovalbumin is detectable at dilutions equivalent to 2 nanograms of paint. This pattern of limited change due to aging with heat exposure, as opposed to a clear reduction in reactivity for samples aged with UV-containing light was the general pattern seen in all the paints. However, the extent of reduction in reactivity varied depending on binder and pigment.

Table 2 shows the abbreviated results for protein assays and ELISA assays done on each paint in the whole egg paint set and ranks the paints from most reactive to least reactive. In addition, the table records the changes in reactivity before and after aging, and reports the difference in terms of Δ and %Δ. The order of pigments is based on decreasing reactivity after accelerated aging. The results show that the top three pigments in which ovalbumin was most reactive are verdigris, malachite, and yellow ocher. The two pigments in which ovalbumin exhibited the lowest reactivity are bone black and burnt sienna.
It is noteworthy that the LOD for bone black after aging is substantially higher than the average LOD of all samples. Furthermore, two pairs of pigments with identical metal cations occur far apart. In one case, the iron oxides, yellow ocher and burnt sienna, are at opposite ends of the scale. In the other, the copper carbonates malachite and azurite also have a significant disparity in reactivity after aging: the malachite paint sample exhibits the second best reactivity after aging, whereas the azurite paint sample is in the bottom half on the reactivity scale. It is possible that in both cases, the reason for the disparity is attributed to the amount of coordinated water the iron oxide or copper carbonate molecule contains; it appears that the more coordinated water present in the pigment the less likely

<table>
<thead>
<tr>
<th>Whole Egg &amp; Pigment</th>
<th>Pigment Chemistry</th>
<th>Average protein assay in mg/mL for naturally aged samples</th>
<th>Average protein assay in mg/mL for accelerated aged samples</th>
<th>LOD in ng of paint for naturally and accelerated aged samples w/ ab1225 rbt-anti-ovalbumin</th>
<th>Δ LOD after artificial aging</th>
<th>%Δ LOD after artificial aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verdigris</td>
<td>Cu(CH3•COO)2 • 2Cu(OH)2</td>
<td>2.4</td>
<td>2.4</td>
<td>1.3</td>
<td>0.8</td>
<td>-0.5</td>
</tr>
<tr>
<td>Malachite</td>
<td>CuCO3 • Cu(OH)2 XRF shows trace Ca</td>
<td>1.1</td>
<td>1.2</td>
<td>2.1</td>
<td>1.1</td>
<td>-1.0</td>
</tr>
<tr>
<td>Yellow Ocher</td>
<td>Fe₂O₃ • H₂O, clay, etc. largely goethite (Fe³⁺ O(OH)) XRF shows trace amt. of Si, S, and Ca</td>
<td>2.0</td>
<td>2.4</td>
<td>0.7</td>
<td>1.3</td>
<td>0.6</td>
</tr>
<tr>
<td>(skip nine pigments)</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
</tr>
<tr>
<td>Azurite</td>
<td>2CuCO3 • Cu(OH)2</td>
<td>2.1</td>
<td>1.8</td>
<td>1.1</td>
<td>2.5</td>
<td>1.4</td>
</tr>
<tr>
<td>(skip six pigments)</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
</tr>
<tr>
<td>Burnt Sienna</td>
<td>Fe₂O₃</td>
<td>1.2</td>
<td>1.3</td>
<td>1.0</td>
<td>8.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Bone Black</td>
<td>10% C, 84% Ca₃(PO₄)₂, and 6% CaCO₃</td>
<td>1.5</td>
<td>1.3</td>
<td>2.3</td>
<td>17.0</td>
<td>14.7</td>
</tr>
<tr>
<td>Average values</td>
<td></td>
<td>1.73</td>
<td>1.77</td>
<td>3.48</td>
<td>4.49</td>
<td>4.49</td>
</tr>
</tbody>
</table>

Table 2. Results from protein assays and ELISA serial dilutions for ovalbumin in paints with whole egg binder. LOD values are reported in nanograms of paint before and after accelerated aging.
the pigment is to complex with the ovalbumin protein. Coordinated water within yellow ocher and malachite allows for greater charge dispersion and thus may cause weaker attractive forces between the pigment and the ovalbumin present in the binder. The coordinated water may even sterically hinder the pigment from complexing to ovalbumin. For these reasons, azurite, which contains less coordinated water than malachite, and burnt sienna, which contains no coordinated water, are likely more tightly bound by ovalbumin and as such cause a reduction in reactivity.

COLLAGEN

In the case of collagen, a protein that is highly conserved over a wide range of species and known to be far less antigenically reactive than the other proteins considered in this research, the scale of reactivity is noticeably weaker than that of ovalbumin. Furthermore, the host species in which the antibody was raised and the phylogenetic relationship between the collagen source species and the antibody host species, must be carefully considered in terms of their effects on reactivity. Since a defining property of antibodies is the ability to discriminate self from non-self, it is advisable when conducting analysis of an unknown sample to use at least two different primary antibodies, each from hosts that differ widely in their phylogenetic relationship. In total, seven different collagen antibodies were tested. The two which proved to be most reactive with the range of different collagen samples tested are ab19811 and ab6577, both anti-collagen type I, and raised in goat and rabbit hosts respectively. These results are consistent with research previously conducted by Mazurek (2008) in which the same two antibodies were first identified as effective for such an application.

Table 3 shows the LOD values determined for a set of paints bound in cow gelatin when tested with the anti-collagen antibody ab-6577. It is worth noting that just as in the paints

![Figure 10. Reactivity of two anti-collagen antibodies. Samples representing a wide range of collagen sources were plated at 100 ng/well. Results are arranged in decreasing order of reactivity for ab19811. Both antibodies were at 1:1000. Samples for which the source species is not known with certainty appear in quotations.](image-url)
bound with whole egg, bone black is among the pigments with the least reactivity in the cow gelatin paints. However, unlike with ovalbumin, the data suggests that collagen shows no susceptibility toward reduced reactivity from any iron-based pigments; in fact, burnt sienna has one of the best reactivities.

The three opaque white pigments lead, titanium, and zinc white are associated with the least reactivity with the gelatin-bound paints. Given the chemical differences within this group, the increase in LODs among the three white paints may be unrelated to the formation of metal complexes, and instead may be the result of the strong UV absorbing properties of these paints and possible degradation which takes place

### Table 3. Results from protein assays and ELISA serial dilutions for collagen in paints with cow gelatin binder. LODs are reported in nanograms of paint before and after accelerated aging.

<table>
<thead>
<tr>
<th>Cow Gelatin &amp; Pigment</th>
<th>Pigment Chemistry</th>
<th>Solubility* of naturally aged samples and average protein assay in mg/mL</th>
<th>Solubility* of artificially aged samples and average protein assay in mg/mL</th>
<th>LOD in ng of paint for naturally and accelerated aged samples w/ ab-6577</th>
<th>Δ LOD after artificial aging</th>
<th>%Δ LOD after artificial aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indian Yellow -synthetic</td>
<td>coal-tar derivative (XRF shows minor Cl, S, Al, and trace Ca)</td>
<td>Complete 2.4</td>
<td>Complete 2.6</td>
<td>30</td>
<td>85</td>
<td>55</td>
</tr>
<tr>
<td>Burnt Sienna</td>
<td>FeO3</td>
<td>Partial 3.6</td>
<td>Complete 2.4</td>
<td>66</td>
<td>95</td>
<td>30</td>
</tr>
<tr>
<td>(skip fifteen pigments)</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Bone Black</td>
<td>10% C, 84% Ca3(PO4)2, and 6% CaCO3</td>
<td>Complete 2.2</td>
<td>Complete 2.2</td>
<td>(730)</td>
<td>(870)</td>
<td>140</td>
</tr>
<tr>
<td>Lead White</td>
<td>2PbCO3 • Pb(OH)2</td>
<td>Complete 2.6</td>
<td>Complete 2.1</td>
<td>302</td>
<td>(1000)</td>
<td>698</td>
</tr>
<tr>
<td>Titanium White</td>
<td>TiO2</td>
<td>Partial 1.9</td>
<td>Complete 2.7</td>
<td>332</td>
<td>(1155)</td>
<td>823</td>
</tr>
<tr>
<td>Zinc White</td>
<td>ZnO</td>
<td>Complete 2.4</td>
<td>Complete 2.3</td>
<td>388</td>
<td>(1200)</td>
<td>812</td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td></td>
<td>2.18</td>
<td>2.26</td>
<td>191</td>
</tr>
</tbody>
</table>

Table 4. LOD values for casein in various milk-based samples using GTX-77267.

<table>
<thead>
<tr>
<th>Antigen – after ~18 months natural age on glass slide</th>
<th>LOD in ng/well using GTX-77267 at 1:2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bovine Casein Standard (Sodium Salt Sigma C-8654)</td>
<td>0.06</td>
</tr>
<tr>
<td>Ammonium Casein (pH 8.5-9.0)</td>
<td>0.10</td>
</tr>
<tr>
<td>Farmers Cheese</td>
<td>0.11</td>
</tr>
<tr>
<td>Borax Casein (pH 7.5-8.0)</td>
<td>0.13</td>
</tr>
<tr>
<td>Half-and-Half</td>
<td>0.22</td>
</tr>
<tr>
<td>Cow's Milk 1%</td>
<td>0.24</td>
</tr>
<tr>
<td>Skim Milk</td>
<td>0.26</td>
</tr>
<tr>
<td>Water Buffalo Yogurt</td>
<td>0.29</td>
</tr>
<tr>
<td>Sheep Yogurt</td>
<td>0.41</td>
</tr>
<tr>
<td>Goat's Milk</td>
<td>0.67</td>
</tr>
<tr>
<td>Lime Casein (pH 12.5)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table is arranged from lowest to highest LOD value. All samples appeared completely soluble in extraction buffer, except sheep yogurt, which exhibited a number of small insoluble aggregates, and lime casein, which appeared turbid and had larger insoluble aggregates.
in the surrounding collagen binder when the absorbed UV energy is dispersed. Zinc white in particular has been used in a number of applications due to its photovoltaic properties, e.g. solar voltaic cells and LCD screens.

**CASEIN**

Because the casein molecule has a lack of disulfide bonds between cisteine residues and consequently a general lack of tertiary structure, it is not susceptible to denaturation and its high stability results in excellent detection using ELISA. The LODs for casein in a variety of casein preparation as well as milk-based samples from different species is shown in Table 4. All samples were detected at sub-nanogram levels except lime casein, which has an LOD of 2 ng. The slightly higher LOD for lime casein is likely the result of the high alkalinity that the casein is exposed to during preparation.

The high stability of casein was also evident with the paint samples assayed. Lime casein, the least reactive of the three casein preparations tested, was the binder in a full set of paints assayed before and after aging (Table 5).

Curiously, the LODs were lower in many cases for the lime casein paint samples than that determined for unpigmented lime casein samples. This may be the result of either a slight buffering property on the part of the pigment itself when mixed with the lime casein, and/or a screening effect on the part of the pigment that effectively protects the casein from photodecomposition. The fact that the LODs for both iron oxide pigments were at the low end of reactivity suggests that casein complexes with iron regardless of how much coordinated water is present. The paint with the lowest reactivity was again bone black.

**Figure 11.** Anti-casein serial dilution of lime casein paint with malachite pigment. The blue circles correspond to samples with ~18 months of natural age, the green triangles correspond to the samples after accelerated aging with heat only, and the red squares correspond to samples after accelerated aging with heat and light. Each curve is the average of three separate serial dilution assays. The blocking buffer was 2% AgHS, the primary Ab was Genetex rbt-anti-bovine casein 1:2000, and the secondary Ab was biotinylated goat anti-rabbit 1:2000. The X-axis is nanogram of paints, and the Y-axis is optical density after 30 minutes.
Table 5. Results from protein assays and ELISA serial dilutions for casein in paints with lime casein binder. LOD values reported in nano-grams of paint before and after accelerated aging.

<table>
<thead>
<tr>
<th>Lime Casein &amp; Pigments</th>
<th>Pigment Chemistry</th>
<th>Solubility* of naturally aged samples and avg. protein assay in mg/ mL</th>
<th>Solubility* of artificially aged samples and avg. protein assay in mg/ mL</th>
<th>LOD in ηg of paint for naturally and accelerated aged samples w/ GTX-77267</th>
<th>Δ LOD after artificial aging</th>
<th>%Δ LOD after artificial aging</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Indian Yellow</strong></td>
<td>-synthetic</td>
<td>coal-tar derivative (XRF shows minor Cl, S, Al, and trace Ca)</td>
<td>Complete 1.3</td>
<td>Complete 0.9</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Malachite</td>
<td></td>
<td>CuCO₃•Cu(OH)₂ XRF shows trace Ca</td>
<td>Complete 1.1</td>
<td>Complete 1.2</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Verdigris</td>
<td></td>
<td>Cu(C₂H₃O₂)₂•2Cu(OH)₂</td>
<td>Complete 2.2</td>
<td>Complete 1.4</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Azurite</td>
<td></td>
<td>2CuCO₃•Cu(OH)₂</td>
<td>Incomplete 1.4</td>
<td>Complete 1.2</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>(skip fourteen paints)</td>
<td></td>
<td>✧</td>
<td>✧</td>
<td>✧</td>
<td>✧</td>
<td>✧</td>
</tr>
<tr>
<td><strong>Yellow Ocher</strong></td>
<td></td>
<td>Fe₂O₃•H₂O, clay, etc. largely goethite (Fe³⁺O(OH)) XRF shows trace amt. of Si, S, and Ca</td>
<td>Incomplete 0.9</td>
<td>Complete 0.7</td>
<td>2.1</td>
<td>4.3</td>
</tr>
<tr>
<td><strong>Burnt Sienna</strong></td>
<td></td>
<td>Fe₂O₃</td>
<td>Incomplete 1.3</td>
<td>Incomplete 1.2</td>
<td>2.3</td>
<td>4.3</td>
</tr>
<tr>
<td><strong>Bone Black</strong></td>
<td></td>
<td>10% C, 84% Ca₃(PO₄)₂, and 6% CaCO₃</td>
<td>Incomplete 1.9</td>
<td>Complete 1.8</td>
<td>12.</td>
<td>11.0</td>
</tr>
<tr>
<td><strong>Average values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 5. Results from protein assays and ELISA serial dilutions for casein in paints with lime casein binder. LOD values reported in nano-grams of paint before and after accelerated aging.
The Effect of Accelerated Aging and Pigment Interaction on Antigenic Detection of Proteinaceous Binding Media Using an Improved Protocol for Enzyme-linked Immunosorbent Assays

Table 6. Optical density results for JIM19 and JIM13 on a variety of samples at 50 ng and 5 ng.

<table>
<thead>
<tr>
<th>Sample</th>
<th>OD at 50 ng JIM19</th>
<th>OD at 50 ng JIM13</th>
<th>OD at 5 ng JIM19</th>
<th>OD at 5 ng JIM13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum Arabic</td>
<td>3.6</td>
<td>3.8</td>
<td>2.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Gum Ghatti</td>
<td>3.5</td>
<td>3.8</td>
<td>3.6</td>
<td>3.7</td>
</tr>
<tr>
<td>Gum Tragacanth</td>
<td>3.6</td>
<td>0.2</td>
<td>3.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Pectin</td>
<td>2.2</td>
<td>1.6</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Cherry Gum</td>
<td>0.1</td>
<td>0.6</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>Karaya Gum</td>
<td>0.1</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carrageenan</td>
<td>0.1</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Soya Flour</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Funori</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Guar Gum</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Larch Arabinogalactan</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Yucca Starch</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Wheat Starch</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Rice Starch</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Corn Starch</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Xanthan Gum</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Kauri Gum</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Rosin</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>Gum Elemi</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dammar</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Egg White</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Egg Yolk</td>
<td>0.2</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Honey</td>
<td>0.2</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Milk</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7. LOD values for various gums and pectin using JIM13 And JIM19.

<table>
<thead>
<tr>
<th>Antigen</th>
<th>JIM13</th>
<th>JIM19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum Arabic</td>
<td>0.2 ng</td>
<td>0.6 ng</td>
</tr>
<tr>
<td>Ghatti Gum</td>
<td>0.2 ng</td>
<td>0.2 ng</td>
</tr>
<tr>
<td>Gum Tragacanth</td>
<td>44.0 ng</td>
<td>0.5 ng</td>
</tr>
<tr>
<td>Cherry Gum</td>
<td>7.2 ng</td>
<td>28.8 ng</td>
</tr>
<tr>
<td>Pectin</td>
<td>8.3 ng</td>
<td>6.3 ng</td>
</tr>
<tr>
<td>Karaya Gum</td>
<td>17.0 ng</td>
<td>68.0 ng</td>
</tr>
</tbody>
</table>

Primary Abs were diluted 1:100. Secondary Abs were diluted 1:2000. The extraction buffer was EB1 and the blocking buffer 2% AgHS.
amino groups often occur in antigenic sequences and thus charged amino groups on the protein. Charged carboxyl and as well as negatively charge phosphate ions and positively and negatively charged carboxyl groups present on the protein, do with interactions between positively charged calcium ions structural ordering of both collagen and casein has much to do. The unique role that calcium phosphate plays in higher ordering of casein into larger structures known as casein micelles. phosphate plays an essential role in higher ordering of casein almost entirely of tricalcium phosphate. Additionally, calcium derived from the powdered remains of charred bone consists orders. Because the pigment bone black, a.k.a. ivory black, is the structural matrix of bone, hydroxyapatite binds to and packs between collagen fibers in order to make higher structural orders. Because the pigment bone black, a.k.a. ivory black, is derived from the powdered remains of charred bone consists almost entirely of tricalcium phosphate. Additionally, calcium phosphate plays an essential role in higher ordering of casein molecules by essentially helping to bind individual submicelles of casein into larger structures known as casein micelles.

The unique role that calcium phosphate plays in higher structural ordering of both collagen and casein has much to do with interactions between positively charged calcium ions and negatively charged carboxyl groups present on the protein, as well as negatively charge phosphate ions and positively charged amino groups on the protein. Charged carboxyl and amino groups often occur in antigenic sequences and thus play a critical role in epitope recognition. By complexing to such groups, bone black may effectively be masking charged amino and/or carboxyl containing epitopes.

It is noteworthy that there is in fact a protein separation technique based on hydroxyapatite known as HA chromatography that exploits the tendency for nonspecific interactions of the charged carboxyl and amino groups on proteins with the positively charged calcium and negatively charged phosphate ions on the hydroxyapatite-infused stationary phase resin.

Serial dilution assays were also conducted to determine LODs using JIM13 and JIM19 against a number of gums and polysaccharides (Table 7)

**BONE BLACK INDUCED REDUCTION IN IMMUNOREACTIVITY**

Clearly bone black is implicated in causing a reduction in the immuno-reactivity of ovalbumin, collagen, and casein. It yielded the highest LOD in whole egg, egg yolk, and lime casein paints, and along with the opaque whites had the highest LOD in cow gelatin paints. The LOD for bone black started out relatively high in both lime casein and cow gelatin paints even before accelerated aging. The higher LOD values cannot be explained simply as a function of black being absorbent to light energy, since vine black had a relatively low LOD among all paints tested.

The reason for the reduction is likely found in the chemistry and biological origins of bone black. Bone is made up of 70% hydroxyapatite, a calcium phosphate mineral. Within the structural matrix of bone, hydroxyapatite binds to and packs between collagen fibers in order to make higher structural orders. Because the pigment bone black, a.k.a. ivory black, is derived from the powdered remains of charred bone consists almost entirely of tricalcium phosphate. Additionally, calcium phosphate plays an essential role in higher ordering of casein molecules by essentially helping to bind individual submicelles of casein into larger structures known as casein micelles.

In each of the mixed sample assays described below, a combined approach was used that included a blocking buffer of 0.2% Tween-20 for the anti-collagen Abs and 2% AgHS for the other Abs. This combined approach proved successful; however, some of the background values were still fairly high with the mixed samples. The use of a milk-based blocking buffer for antibodies other than the anti-casein antibody is an investigational option for assays that seek to identify the presence of milk in unknown samples. However, less obvious non-specific binding can also occur with other blocking buffers, for example 2% AgHS proved an effective blocking buffer when used for assays involving the JIM IgM antibodies, but when used with gt-anti-collagen IgG ab19811 lead to unacceptably high background values. The possibility of cross-reactivity between ab19811 and other constituents of AgHS is a valid consideration and a review of the results from the collagen assays (fig. 10) offers some clues that may help explain the comparatively lower background values observed with other antibodies used in combination with AgHS blocking buffer. The collagen assays clearly demonstrate that of the two antibodies, the gt-anti-collagen (ab19811) was much more reactive with horse collagen than the rbt-anti-collagen. The fact that background values are significantly higher when using ab19811 in combination with the horse serum blocking buffer than when using any of the other antibodies (all of which were raised in either rabbit or rat) suggests a parallel between the species reactivity observed with the two anti-collagen antibodies and the degree of cross-reactivity between primary antibodies and serum-based blocking buffers.
Klausmeyer, Albertson, Straehle, Woodland, and Schmidt  *The Effect of Accelerated Aging and Pigment Interaction on Antigenic Detection of Proteinaceous Binding Media Using an Improved Protocol for Enzyme-linked Immunosorbent Assays*

option; however, when included on the same plate great care must be taken to avoid any cross-contamination of wells since the anti-casein antibody is extremely sensitive. It may prove useful therefore that for future multi-antibody ELISA assays of unknown samples, a multi-plate approach be adopted. Using this format, the simplest approach to blocking would be to segregate Abs such as ab19811, ab6577, and ab1225 to one plate and block them with a milk-based blocking buffer, and the other Abs in the series, including the anti-casein antibody, could go on another plate and be blocked with a different buffer.

The final comparative study of blocking buffers conducted within this research evaluated the performance of SEA BLOCK blocking buffer (no.37527, Pierce, Rockford, IL) relative to 0.2% Tween-20, and 2% AgHS blocking buffers. SEA BLOCK blocking buffer contains steelhead salmon serum, which is said to have no substantial interaction with mammalian antibodies. Though SEA BLOCK did not entirely eliminate background values, it did produce lower average background values than the 2% AgHS when used with GTX77267, ab1225, JIM13, and JIM19, without an associated decrease in signal strength. For the two anti-collagen Abs, the performance of SEA BLOCK was evaluated against that of 0.2% Tween-20, which had already been shown to be more effective than 2% AgHS when used with the anti-collagen Abs. In the case of ab6577, the background from SEA BLOCK was much improved over that of 0.2% Tween-20, however for ab19811 the average background value with SEA BLOCK value was slightly higher than that of 0.2% Tween-20 (0.149 and 0.115 respectively).

Regardless of the specific blocking buffer used, evidence suggests that incubating the blocking buffer at RT rather than 37°C, brings about a slight reduction in background values. Elevated temperature may in fact cause kinetically unfavorable conditions for binding of the blocking proteins to the well plates. Although the vast majority of ELISAs conducted in this research included an hour-long incubation period of the blocking buffer at 37°C, this practice was discontinued in later assays without a concomitant loss in detection sensitivity. Evidence from identical assays involving ab6577 indicates that after the initial plating step, conducting the rest of the ELISA at RT actually leads to improved detection.

It seems likely that due to the extremely sensitive nature of the assay and the additional signal amplification component incorporated into this particular ELISA protocol, that background signal will continue to be present to some degree regardless of the block used. However, as mentioned previously, stopping development earlier in the processing step is an effective and obvious option.

**PAINT SAMPLES WITH MIXED BINDERS**

Although the ELISA method repeatedly proved to be highly reliable and sensitive on paint samples with a single binder, it

![Figure 12. Detection of gum arabic in paint samples containing a mixture of proteinaceous binders.](image)
remained to be seen how the method would perform on samples consisting of more complicated mixtures. Therefore, assays were conducted to evaluate the ability of ELISA to identify proteinaceous components within varied mixtures of egg, collagen, casein, and gum arabic bound paints. The paints assayed were pigmented with either yellow ocher or lead white pigment. Samples of these mixed paints were tested with and without accelerated aging. Figure 12 shows the dilution curves for gum arabic from a related set of mixed samples. In each sample, gum arabic was detected from among all the other proteins. The same mixed samples were tested for the presence of each of the other proteins using their corresponding antibodies and similar successful detection occurred with all. Figure 13 shows the results for casein.

BIOTINYLATED SECONDARY ANTIBODIES

The ELISA method used throughout this research, which incorporates biotinylated secondary antibodies as a means of signal amplification, offers significant improvements over ELISA methods used thus far for the analysis of art materials. Although this method involves an extra processing step, its adoption appears merited due to the gains in detection sensitivity over those reported using more traditional indirect ELISA methods in which the secondary Ab is directly conjugated to alkaline phosphatase or HRP. Additionally, the improved signal strength allows for shorter development time and provides clearly interpretable results.

The use of biotinylated secondary antibodies does raise questions regarding the possibility of cross-reactivity between either the biotin moiety complexed to the secondary antibody and endogenous biotin-binding proteins such as avidin (0.05% of egg white proteins are reported to be avidin), or the streptavidin-alkaline phosphatase and any endogenous biotin present in the sample. However, throughout the course of this research, no indication of such cross-reactivity was observed. Were cross-reactivity a problem with any of the multiple samples examined in this research, corresponding signals of sample cross-reactivity would be evident in the serial dilution control assays that involved plated samples but did not include the use of the primary Ab. Similarly, signals from non-specific binding would be consistently evident with antigens assayed for, but not included in, mixed samples, but this was not the case.

The lack of cross-reactivity seen with the samples assayed in this research, suggests that endogenous biotin-binding proteins that may be present such as avidin, are not prone to binding with the biotinylated secondary antibodies used, and also that SA-AP does not cross-react with any endogenous biotin. Four possible explanations are offered; (1) although the avidin-biotin complex is known to be extremely stable even under extreme chaotropic conditions, endogenous biotin-binding proteins may incur a loss of binding affinity due to denaturation from age, (2) the binding sites on the native biotin-binding protein are already fully occupied and exchange of biotin with streptavidin does not occur, (3) steric hindrance of
biotinylated secondary Abs prevents binding to native biotin-binding proteins, or (4) the amount of biotin-binding protein present in the samples is so small as to be a non-factor.

As a non-protein water-soluble B-group vitamin, biotin by itself does not bind well to the ELISA plates and any biotin residue present is readily washed away. Research has shown that a small amount of biotin is present in egg yolk and to a lesser extent in egg white, however in both cases this biotin is tightly bound to biotin-binding proteins (in the case of the less abundant egg white biotin the protein is avidin), and that the biotin is essentially non-exchangeable at RT (White et al. 1976, 1987). When present as a native biotinylated protein, the biotin apparently is either present in such small amounts or in a form that does not facilitate binding with the SA-AP as easily as the SA-AP binds to the biotinylated secondary Ab. With egg in particular, the latter may be explained by the known higher binding affinity to biotin of avidin than streptavidin, thus making exchange unfavorable and as such avoiding the potential for cross-reactivity between endogenous biotin and the SA-AP. Furthermore, the biotinylated secondary Abs do not bind to the biotin in the same way as native biotin-binding proteins such as avidin, and as such enables the binding of SA-AP to readily occur when added later.

Since milk is known to contain biotin, one might suspect a potential for cross-reactivity, however none was evident in any of the milk-based samples assayed. In fact, some researchers use milk blocking buffer in western blots and ELISA even when using biotin/streptavidin systems, preferring the excellent blocking properties of the milk blocking buffer and avoiding problems with cross-reactivity by thorough washing with either a TBS or PBS and Tween-20 wash buffer.

CONCLUSIONS

This research, along with that of other researchers, demonstrates that ELISA can be an extremely effective method for identifying specific proteins and glycoproteins used in art materials. Furthermore, this research indicates that immunological detection of these proteinaceous materials remains possible even after they are mixed with various pigments and subjected to accelerated aging. Although degradation of the materials, particularly light-induced degradation, does have a deleterious effect on antigen maintenance, sensitivity of detection after accelerated aging remains very good for all but a few protein-pigment combinations. Whole egg, casein, or gum arabic binders were all detectable at levels less than 10 µg of paint sample, whereas paints prepared with cow gelatin binder (chosen due to its low antigenic activity on the scale of collagen samples analyzed) were detectable with 2 µg or less of paint sample. Despite the relatively high level for cow-gelatin paints, this sensitivity of detection is likely more than sufficient for use in conservation.

While pigment interference does not preclude immunological detection, bone black, and to a lesser extent burnt sienna, zinc white, titanium white, and lead white cause reduced detection of some proteinaceous materials and therefore, when alternative sampling sites are available, it is better to avoid these pigments. In general, the greater the extent of coordinated water in similar oxides or carbonates, the less likely it appears they are to cause interference.

This research also indicates that serial dilution assays provide reliable data for interpreting ELISA results through direct evaluation of the dilution curve. Elevated base lines seen in many of the dilution curves, even after the background is subtracted suggests that one runs the risk of false positives when interpreting results based solely on optical density values from single dilutions assays.

Improved detection sensitivity over previously published results was achieved primarily through the use of biotinylated secondary antibodies to amplify detection signal. The use of biotinylated secondary antibodies and streptavidin-alkaline phosphatase does not lead to any discernable cross-reactivity in any of the samples tested.

Preliminary tests on paint samples containing a mixture of binders indicate that ELISA is effective at making specific determinations of individual components within complicated mixtures.

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The Effect of Accelerated Aging and Pigment Interaction on Antigenic Detection of Proteinaceous Binding Media Using an Improved Protocol for Enzyme-linked Immunosorbent Assays

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Optimization of Infrared Reflectography

ABSTRACT

Infrared reflectography (IRR) utilizes the decrease in optical scattering and absorbance of paints in the infrared to render visible preparatory sketches and paint changes. Advances in application methods and instrumentation offer conservators a wide array of choices. In this paper a review of the IRR phenomena, cameras and methods will be given to help conservators optimize instrumentation and methods for their specific applications.

The optimization is determined from spectral reflectance measurements of artist materials as well as optical modeling and measurements of the various cameras available (Si CCD, InGaAs, PtSi, and InSb). The reflectance spectra from 350 to 2500 nm of the artist materials (paints, grounds, and underdrawing material) and test panels to help to determine the best spectral region to image a given paint-underdrawing-ground combination as well as the required spectral sensitivity camera. IRR examples showing the level of improved clarity obtained by limiting the spectral band (i.e., 1100 to 1400 nm versus 1500 to 2000 nm) will be given. Detailed modeling and measurements of image sharpness (limiting resolution and modulation transfer function) of various camera and camera lenses with and without spectral filters are also given. Results of controlled sharpening, based on measured modulation transfer function, show level improvements possible by image processing. Experimental results of recent studies into using multi-spectral (3 spectral bands), and hyperspectral (100 spectral bands) infrared camera are given and show promise to provide further improved visualization of preparatory and paint changes for challenging paintings. By using optimized working methods, spectral filters, and post capture image processing good IRR are possible with a variety of cameras.

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Advances in Computer-Assisted Canvas Examination: Thread Counting Algorithms

ABSTRACT

Techniques from computer-based image processing offer new tools to conservators for canvas examination. From the periodic pattern of intensity values exhibited by the x-ray of a painting, various signal processing algorithms can be applied to count the nominal light to dark and back to light fluctuations exhibited in moving along the centerline of a thread from one crossing thread to the next. Computer-assisted thread counting produces a much larger archive of thread count data than can be accumulated in the same time period by traditional manual methods. Moreover, weave density and thread angle maps provide powerful new tools for determining bolt mate status and visualizing cusping.

THREAD COUNTS FROM X-RAYS IN ART HISTORY

Scanning along the vertical and horizontal threads in a simple plain weave canvas and counting the number of crossing threads within 1 or 2 centimeters, results in descriptive data often collected by conservators or researchers in their technical study of canvas supports. Since the original canvas is hidden by paint layers on the front and, invariably a lining canvas on the back, x-rays are commonly used for thread counting.

As the initial ground layer fills the interstices in the canvas weave providing a smoother surface for the subsequent paint layers, its thickness can fluctuate being thicker in the valleys between threads, and thinner where the threads overlap. Furthermore, this ground layer often contains radio-absorbent pigments, e.g. lead white. Consequently, the ground-filled grooves between the threads absorb more x-ray energy, and the regions where the threads overlap absorb less energy. The resulting periodic variation in the x-ray image can, depending on the nature of the ground, reveal the light-to-dark-to-light transition corresponding to a count of one thread.

Over forty years ago, this thread count data obtained from x-rays was used in posing a technical art historical question. The issue was whether or not there was a relationship between thread counts (i.e. weave density) and the size of paintings. The resulting examination of Dutch paintings up to 1700 in the collection of the Centraal Museum in Utrecht did not reveal a strong correlation.

A more comprehensive approach to the collection of thread count data by the Rembrandt Research Project, as reported in the 1980s [2], identified several paintings by Rembrandt and assistants in Rembrandt’s workshop from the same bolt, including portraits which were painted as companion pieces. The average, maximum, and minimum thread counts form the “standard” data collected for a painting. The decision to declare two paintings as “probably from the same bolt” requires that average canvas densities in one direction, the warp, differ by very little, and the average densities in the other direction, the weft, differs by less than 1 th/cm. It also requires that the ranges from minima to maxima are similar.

In a recent study, thread counts together with the analysis of preparatory ground layers helped to place paintings by Gauguin or Van Gogh that were cut from the same bolt of coarse jute fabric. [3] From Van Gogh’s letters, we know that Gauguin purchased a 20m bolt of jute, persuading Vincent this once to paint on such coarse canvas. Identifying paintings with average thread counts of ca. 5.2 x 6.5 th/cm revealed 28 paintings that were cut from this 20m bolt of jute, some of which had been doubted as being painted by Vincent van Gogh. Thus, matching average thread counts can also support investigations of authenticity.
The standard procedure for taking manual thread counts (using a light box and a magnifying eyepiece) is time-consuming, tedious, and sometimes beyond the scope of the human eye. Techniques developed in the field of computer-based image processing offer new tools to conservators. When processing a scanned image of a painting, the computer can call on a wealth of digital signal processing algorithms to assist in image analysis. From the periodic pattern of intensity values exhibited by the x-ray and related to the original canvas threads, various signal processing algorithms, such as a Fourier transform, can be applied to infer the nominal period of light to dark and back to light fluctuation exhibited in moving along the centerline of a thread from one crossing thread to the next. [4]

MOTIVATION: INVESTIGATION OF MAJOR PAINTINGS FACING TREATMENT

Current investigation of two important paintings preceding decisions regarding conservation treatment raised questions concerning canvas densities. In order to try and answer these questions (automated) accumulation of massive amounts of thread count data was necessary.

One of these two paintings is in the collection of the Mauritshuis in The Hague. At some point in the past this seventeenth-century painting depicting Saul and David (1655/60) by Rembrandt and/or Studio (Bredius no. 526, Mauritshuis inv. no. 621) was cut-up and reassembled (the joins are indicated by the white hatched lines in fig. 1). Petria Noble has shown that the painting now consists of ten separate pieces of canvas and that it was originally made up of two horizontal strip-widths of canvas from the same bolt most likely with a central horizontal seam. [5] In the 1800s when the painting was reassembled – using an unusual notched (crenellated) join – several other canvas segments were also added to the upper, lower and right edges and upper right corner (labeled A, B, C, D, E and F in fig. 1). Manual thread counts by Michiel Franken of each of the canvas segments demonstrates that the narrow strip B at the bottom right below the figure of David, has a thread density of H:14 x V:14 th/cm, identical to that of the figure segments both above and below the horizontal seam. This strongly suggests that strip B was once part of the original painting. If strip B was indeed part of the original composition, it is important to try and determine what its original orientation and location was in the composition. Was it vertically between the two figure segments, horizontally above the current David segment or in a vertical orientation above the David segment?

The second painting raising questions on thread count to be considered in this paper is The Bedroom by Vincent van Gogh (F482 [6], illustrated in fig. 2. A question of art historical interest involves a second painted version of the subject in the Art Institute of Chicago (F484). [7] From Vincent’s letters we know that the first study was painted on 16–17 October 1888 and subsequently water-damaged in his studio. In September 1889 the (possibly repaired) original was copied by the artist. Some experts have questioned which version is which. One way to answer this question is to locate other pictures with secure dating originating from the same bolt of linen as F482.
These questions regarding issues of adjacent placement on the same canvas bolt of two now-separated pieces of canvas motivate the search for a technique that facilitates, not just comparison of average thread densities, but assessment of weave density pattern match. The direct approach of assembling full-coverage weave density maps for paintings that can be compared for continuity/similarity in their individual weave patterns is not feasible if the data is to be assembled with manual spot counts. A first attempt at automating a spot count is described by an example at the start of the next section. Subsequently, this automated counting procedure will be extended to counting in closely-packed spots across the entire painting, thereby generating the desired weave density maps.

**SPOT THREAD COUNT**

Consider *The Fall of Leaves* by Vincent van Gogh (F651) November 1889, illustrated in fig. 3. The x-ray of the upper left corner of F651 is shown in fig. 4. The tree trunks are visible in the negative as inhibiting the passage of the x-rays more than adjacent parts of the painting.

A magnified swatch of a 600 dpi scan of the x-ray of the upper left corner of F651 is shown in figure 5. [8] The same swatch but with the greyscale reversed (so white becomes black, black becomes white) in figure 6 provides a quite readable image with regard to thread count. This swatch is approximately 430 horizontal pixels by 330 vertical pixels. Counting 21 vertical threads across the top edge of this swatch results in approximately $21/430 = 0.0488$ th/pixel. Since a 600 dpi scan corresponds to approximately 236 pixels/cm, the vertical thread count for the swatch in fig. 6 is approximately 11.5 th/cm. Similarly, for the 24 horizontal threads crossing the right edge of the swatch in fig. 6 the thread count is approximately $24(236)/330 = 17.2$ th/cm.

Figure 7. plots the intensity levels of the approximately 430 pixels in row 50 of fig. 6. Starting at the first peak on the left near index 0, counting “one” with the next peak at approximately index 25, and continuing to count produces an integer count of 21 gaps (or thread widths) between peaks. Attempt-
ing to repeat this peak-counting procedure for the column 180 data in fig. 8 proves problematic. Due to the much darker/lower “peaks” of every other thread, a convincing count is difficult, though 24 seems close.

As the intensity pattern is roughly periodic its Fourier series composition can be expected to have a strong term that corresponds to the average period of this particular signal. For a set of sampled data, the Discrete Fourier Transform (DFT) can be used to numerically determine the strengths of sinusoidal components of the data across a range of frequencies. [9]

In June 2007, this realization spawned a simple semi-automated procedure involving the following steps:

- Draw horizontal/vertical line across scanned x-ray image.
- Compute discrete Fourier transform (DFT) of horizontal/vertical intensity curve.
- Ascertain frequency location -- within suitable range -- of DFT magnitude maximum.
- Convert to threads/cm.

Using this crude automated procedure on the three swatches from F651 in figs. 6, 9, and 10 produces table 1. The average of the three measurements from different areas of the x-ray of F651 compares quite favorably with the museum hand count record of 11.5 x 17 th/cm. To accelerate the development of more sophisticated algorithms accommodating weave tilt relative to the x-ray image and varying weave clarity across an x-ray, a competition was organized for a more sophisticated spectrum-based algorithm.

To provide an accurate dataset of thread counts to be used to determine the relative performance of candidate algorithms, a graphical user interface (gui) was built that prompts the user to draw a line along a thread and records end coordinates of the test line and then queries the user for a manual count of crossing threads. Using this gui, a team of Cornell University students counted over 900 spots (with verification) in over 20 paintings by Vincent van Gogh as a test base for candidate algorithms. Each spot was counted independently by two students, and was considered verified when their answers agreed.
Candidate algorithms were created by researchers in electrical and computer engineering departments at Rice University, University of Wisconsin, and Worcester Polytechnic Institute and were tested on this database in May 2008. The best algorithms achieve 95% of counts within ±1 th/cm of verified spot count. From the museum records of average manual thread counts compiled by Ella Hendriks for the paintings in the test set, 83% of the average counts for paintings were within ±1 th/cm of average of the verified spot counts for that painting. This suggests that the automated techniques are of comparable quality to the traditional manual methods.

WEAVE DENSITY AND THREAD ANGLE MAPS

With this evidence of satisfactory accuracy, we set up our best-performing algorithm to provide the average count inside any 1/2 inch square swatch. Then we wrote a program that would repeat this calculation for every 1/2 inch square on 1/4 inch centers across an entire x-ray film. These values can then be color-coded to indicate the deviation in the local thread count from the average measured across the painting. The resulting color values could be assembled into a map of the weave density deviation variation, and superimposed, if desired, over the corresponding portion of the x-ray.

Let us consider Head of an Old Man by Vincent van Gogh (F205), painted in Antwerp on 7 or 8 December 1885, as shown in fig. 11. The scanned (600 dpi) x-ray of this painting is shown in fig. 12. The superimposed colors indicating the deviation in horizontal threads/cm from the painting average of 13.3 th/cm appear in fig. 13. This figure also includes a color bar for interpreting the horizontal thread density values. A similar plot for the vertical threads is shown in fig. 14.

The first things to notice in the two weave density maps are the stripes. fig. 13, which illustrates the density of horizontally oriented threads exhibits horizontal stripes of the same color. Fig. 14 exhibits similarly stripy behavior, but with vertical stripes.

This is to be expected. The weaving process is such that the closeness of small groups of threads to each other continues across the entire piece of fabric. The expectation is that the variation in the density pattern of the horizontal (vertical) threads down (across) a piece of canvas would be matched by a horizontal (vertical) neighbor.

A byproduct of our calculations of average thread densities in each small square is a calculation of the average angle of these threads relative to the horizontal (or vertical) orientation of the x-ray. Using a similar color coding to that in the weave density maps produces thread angle maps, as shown in fig. 15. The two images in fig. 15 illustrate the deviation from horizontal and vertical of the (nearly) horizontal and (nearly) vertical threads, respectively. The associated color bar indicates a range of +8 to -8 degrees from the associated horizontal or vertical. The most obvious feature is the variation in the horizontal thread angle across the top of F205. The horizontal threads are oriented down (blue), then flat (yellow), then up.
Advances in Computer-Assisted Canvas Examination: Thread Counting Algorithms

Johnson, Hendriks, Noble, and Franken

Thread Counting Algorithms

This repeated variation from blue through yellow to red and back through yellow to blue is an indication of a particular sort of scalloped deformation known as primary cusping caused by the pull of the canvas edges where these are nailed or otherwise fixed to the priming frame. The vertical thread map for F205 in fig. 15 illustrates less pronounced cusping down its right side. The other noteworthy feature of the horizontal weave density map for F205 is that the right edge is predominantly red, which indicates an upward tilt to all of the horizontal threads at the right edge.

There is documentary, but also, physical evidence to support this idea, including similar average manual thread counts and the comparable build-up and composition of ground layers. Its horizontal weave density map appears in fig. 17 and its vertical weave density map in fig. 18. The thread angle maps for F260 are provided in fig. 19. While there is no primary cusping in the horizontal threads across the top of F260, there is mild cusping in the vertical threads along its right side. The horizontal threads show an upward tilt at the right edge, though less so than with F205.

The current method of determining whether pieces of canvas originate from the same bolt is to decide if the basic descriptors (maximum, minimum, average, and standard deviation) of the average thread counts in the 1/2 inch squares covering each painting are sufficiently similar. This data is provided in

![Figure 13. Horizontal weave density deviation map for F205](image1.png)

![Figure 14. Vertical weave density deviation map for F205](image2.png)

The painting *Backyards in Antwerp* by Vincent van Gogh (F260), painted in Antwerp between December 9 and late February 1885, Van Gogh Museum (Vincent van Gogh Foundation) illustrated in fig. 16 is suspected as being cut from the same piece of ready-primed canvas as that used for F205.

![Figure 16. Vincent van Gogh, Backyards in Antwerp (F260), 1885, Oil on Canvas, 44.0 x 33.5 cm, Amsterdam, Van Gogh Museum (Vincent van Gogh Foundation)](image3.png)
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Table 2. The average thread counts for horizontal threads are within 0.1 th/cm of each other. For vertical threads, the average values are separated by only 0.3 th/cm and the respective minimum and maximum values are no more than 0.6 th/cm apart. The corresponding standard deviations are within 0.1 th/cm of each other. The close similarity of these thread count descriptors provides support for the contention that F205 and F260 are from the same canvas bolt.

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Table 2. Weave density map count data for F205 and F260

Given the weave density maps, we can attempt to line up their characteristic patterns to provide even stronger evidence that these two paintings come from the same bolt of canvas. While the side-by-side alignment of F205 and F260 does not produce a convincing match, their vertical alignment one above the other, as shown in fig. 20, does.

Furthermore, the thread angle maps provide evidence that F205 and F260 are neighbors on the stub end of the canvas bolt, as illustrated in fig. 21. Both F205 and F260 show an

Figure 17. Horizontal weave density deviation map for F260

Figure 18. Vertical weave density deviation map for F260

Figure 19. Thread angle maps for F260

Figure 20. Vertical alignment of the vertical weave density deviation maps for F205 and F260 reveals a match
upward tilt of the horizontal threads towards their right edge. This is more marked for F205, which is located closer to the edge of the canvas as primary cusping is evident along its top edge. It appears that this warp edge [12] of the canvas bolt was tensioned and fixed to the priming frame before the weft edge was, causing the uneven pull visible in the corner of the horizontal thread angle map.

CONCLUDING REMARKS

Automatically generated weave density maps and thread angle maps offer powerful new forensic tools. These maps and the associated statistics of the accumulated data can offer assistance in determining warp and weft directions of the canvas threads, visualizing cusping, and evaluating bolt mate status. Motivation for our development of thread counting tools used to produce weave density and thread angle maps was provided by our study of Rembrandt and/or Studio, Saul and David and Van Gogh’s The Bedroom. However, more work is needed before the problems associated with these works can be resolved.

Thorough manual and computer-assisted thread counts for the figure segments and strip B in the Saul and David confirm that strip B with its average thread count of H:14.03 x V:13.98 th/cm closely matches the average weave densities of the original canvas portions:V:13.98 x H:14.06 th/cm. However, the narrowness of strip B together with its weave irregularities (i.e. aperiodicitie), along with the potentially large missing portion of canvas between strip B and the remaining original canvas portions, complicate matching the weave density patterns of strip B and the figure segments, leaving it inconclusive (so far).

For the Amsterdam version of The Bedroom (F482) a unique identifier, i.e. a denser than average (by 2 th/cm) horizontal stripe, was discovered with the composition of the weave density maps. [13] However, no convincing weave match has yet been found with the few paintings now in museums that date from exactly the right fall 1888 or fall 1889 time frame. The search continues.

In this paper, we have presented a case study (of two paintings by Vincent van Gogh) using automated thread counting software that can provide extensive information useful in canvas research. This case study demonstrates that this new computer-based tool will allow conservators to gain deeper insight from canvas examination than traditional manual thread counting procedures allow.

Computer-assisted spot-counting software is available for free distribution to interested museums. Software to be used by conservators for automatically generating full weave density and thread angle maps and performing weave match tests is currently under development.

ACKNOWLEDGEMENTS

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ENDNOTES

6. All F numbers in this paper refer to the catalog numbers in Faille 1970.
7. Vincent van Gogh, The Bedroom, 1889, Oil on canvas, 73.6 x 92.3 cm., Chicago, The Art Institute of Chicago, Helen Birch Barlett Memorial Collection, accession# 1926.417.
8. All X-ray greyscale scans used in this paper were collected at 600dpi by Frans Stive, Technical Documentalist, Conservation Department, Van Gogh Museum.


12. The warp direction is aligned with the longer dimension of the original canvas bolt and the weft with the shorter one. Typically, due to the method of manufacture, warp threads have less variation in their local weave density values than weft threads. In our case, comparison of the vertical and horizontal standard deviations in Table 2 indicates that the difference in weave density regularity is noticeable for F205, with the horizontal threads showing less variability with a lower standard deviation, but not apparent for F260.

   The presence of primary cusping across the top of F205 is a more convincing marker of warp designation of the horizontal threads.


REFERENCES


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ABSTRACT

During the 1970s and early 1980s, visible reflection spectro-photometry was introduced as an analytical tool for art conservation by pioneers W.D. Wright and R.M. Johnston-Feller. During the 1990’s, this was extended to imaging where from five to 31 spectral bands were captured using a monochrome sensor and either absorption or interference filters. Initially, the imaging goal was improved color accuracy. With time, the goal expanded to include obtaining spectral data. In our research, we have used an RGB color-filter array sensor with its NIR blocking filter removed and two optimized absorption filters used sequentially, resulting in a pair of RGB images. Through a learning-based calibration, visible spectra are estimated at each pixel. Such a system has cost and resolution advantages. We have used this system for pigment identification, pigment selection for restorative inpainting, pigment mapping (decomposing a work of art into its constituents), lighting design, and digital rejuvenation where images are simulated where pigments that have undergone undesirable color changes (e.g., fading or darkening) are replaced with chromatically stable pigments. This system and these applications will be described in this paper. In particular, we will focus on the analysis of Vincent Van Gogh’s *The Starry Night* [Saint Remy, June 1889; oil on canvas, 29 x 36 ¼' (73.7 x 92.1 cm); acquired through the Lille P. Bliss Bequest].
ABSTRACT

Vincent van Gogh is best known for his vivid colours, his vibrant painting style and his short, but highly productive career. His productivity is even higher than generally realized, because the artist would often re-use the support of an abandoned painting and paint a new or modified composition on top. These hidden paintings offer a unique and intimate insight into the genesis of his works. Yet, current museum-based imaging tools are unable to properly visualize many of these hidden images. Here, we present the first-time use of Synchrotron radiation based X-ray Fluorescence mapping, applied to visualize a woman’s head hidden under the work Patch of Grass by Van Gogh. We recorded decimeter-scale, X-ray fluorescence intensity maps, reflecting the distribution of specific elements in the paint layers. In doing so we succeeded in visualizing the hidden face with unprecedented detail. In particular, the distribution of Hg and Sb in the red and light tones respectively, enabled an approximate colour reconstruction of the flesh tones in the hidden face. This reconstruction proved to be the missing link for the comparison of the hidden face with Van Gogh’s known paintings. This approach opens up new vistas in the nondestructive study of hidden paint layers, which applies to the oeuvre of Van Gogh in particular and to Old Master paintings in general.

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Simply White: The Diverse Painting Materials of Robert Ryman

ABSTRACT

Within the confines of a very limited color palette, Robert Ryman has experimented with almost every conceivable type of paint medium on a wide range of supports. As part of a larger project investigating the ageing properties and conservation implications of Ryman’s different paint media, samples from key works at Dia Art Foundation and the Solomon R. Guggenheim Museum have been analyzed and the results compared to documentation available from the artist.

INTRODUCTION

Robert Ryman (born 1930) began painting predominantly white paintings in the mid-1950s, utilizing materials, light and context to create works of extraordinary subtlety. Although his early work sometimes incorporated brightly colored and partially obscured underlayers, white has dominated his palette for practically his entire career. His mostly monochromatic body of work (cf. fig.1) may prompt associations with minimal or conceptual art, but Ryman does not describe his work in those terms. His discussions about his work and process reveal that he has focused intently on the subtleties of his materials and techniques, distinguishing him from many of his contemporaries. Robert Storr writes “From the outset, Ryman’s painterly ‘approach’… simply consisted of seeing how his tools and raw materials would behave.” [1] The choice of white corresponds to the search for a color that “doesn’t interfere”: Ryman has said, “It’s a neutral color that allows for a clarification of nuances in painting. It makes other aspects of painting visible that would not be so clear with the use of other colors.” [2] In a 1971 interview he said: “I don’t think of myself as making white paintings. I make paintings; I’m a painter. White paint is my medium.” [3]
The care with which Ryman systematically labeled and documented his paintings testifies to the importance of materials in his work. Many of the paintings bear labels on the back, where the artist recorded what he used in great detail. Figure 2 shows the label on the back of Tower I, 1976, which even gives the percentage for the binding media mixture and the type of fasteners used. The artist has also demonstrated great concern for the conservation of his paintings during a number of interviews, including those with Carol Mancusi-Ungaro in 2003 [4] and with two of the authors, Carol Stringari and Julie Barten, in 1999. [5]

However, even with this extensive documentation, and notwithstanding the possibility of errors in some of Ryman’s labeling, some questions still remain unanswered. Some of the labels give vague or generic designations and many use proprietary names of products that might not be manufactured anymore, or for which the formulations may have changed over time. For example, the label on the back of Tower II, 1976, indicates that the “Paint is polymer emulsion on black ‘acrylivin’” (cf. fig. 3); the term “polymer emulsion” could include practically any vinyl based or acrylic based emulsion products.

This paper reports on the initial, analytical phase of a long-term study into the materials used by Robert Ryman conducted by the Getty Conservation Institute, in collaboration with Dia Art Foundation and the Solomon R. Guggenheim Museum, in which samples from key works at each institution have been analyzed and the results compared to documentation available from the artist. This phase was also considered an excellent test for the analytical procedures that have been developed for modern paint analysis, given the wide range of media likely to be present in these paintings.

SAMPLES

The selection of 22 works by Ryman at Dia Art Foundation and 25 works at the Guggenheim [6] conveniently complement one another. Many of the works at the Guggenheim date from the late sixties and early seventies and are documented as including products such as “enamel” [7], Enamelac, Gripz and Swansdown Enamel. The Guggenheim Museum’s conservators expressed curiosity regarding the chemical composition of these products, as they noticed differences in their optical and ageing properties. The works at Dia cover a later period and a broad time frame, from the mid seventies to 2003. Only one piece (Cord, 1994) is documented as including Enamelac, the other works being in oil, acrylic, vinyl acetate emulsion, encaustic, and Varathane.

Seven paintings were sampled at the Guggenheim Museum, yielding a total of thirteen samples. Eleven works were sampled at Dia, some comprised of multiple panels, producing a total of twenty-nine samples. In addition, one of the authors, Francesca Esmay, visited Robert Ryman’s studio for a preliminary assessment of the reference materials available (cf. picture of shelves in Ryman’s studio, fig. 4), and sampled some of the most immediately relevant materials, including a Lascaux 575 clear varnish, a Lascaux white paint pigmented with titanium dioxide, and Enamelac in two different dilutions.
All samples were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and pyrolysis-Gas Chromatography/Mass Spectrometry (py-GC/MS). The experimental details are listed in appendix I.

RESULTS

A summary of results can be found in Table 1 (paint samples) and 2 (reference samples).

Acrylic and vinyl based paints
At least four different types of acrylic paints, varnish and primers were detected. A copolymer of methyl methacrylate (MMA) and n-butyl acrylate (nBA) detected in *Factor*, 1983, seems identical to the Lascaux paint reference. In contrast, a copolymer of MMA and ethyl acrylate (EA) was found in *Tower II*, 1976, which would indicate another acrylic brand, possibly Liquitex, as it has been very commonly used in the United States [8, 9]. Both are heavily loaded with calcium carbonate, acting as an extender/filler. In Transfer, the paint is also a p(MMA/ nBA) copolymer containing calcium carbonate, but the dark acrylic primer proved to have a different composition, a MMA / n-butyl methacrylate (nBMA) copolymer with small amounts of p(nBA) and dimethyl phthalate, the latter probably being a plasticizer.

An acrylic varnish based on a p(MMA/nBMA) copolymer was used to varnish *Third Prototype* 2003, Dia:Beacon, 2003 and *Factor*, 1983. Both varnishes appear identical to the Lascaux 575 varnish sampled in Ryman’s studio in 2009: not only is the copolymer the same in all three samples, they all contain the same fairly unusual additive, tri(butoxyethyl) phosphate (TBEP), probably present in the formulation as a plasticizer. Figure 5 shows the pyrograms of the paint from *Factor* and the varnish from *Third Prototype* 2003, Dia:Beacon. In *Third Prototype* 2003, Dia:Beacon (fig. 6) the varnish serves an unusual function: it actually holds the fourteen vinyl panels to the wall without the aid of any additional hanging device. The artist has applied a new coat of varnish to fix the panels to the wall every time they have been installed and the work’s title is adjusted in relation to the location and date of installation. It is interesting to note that the two works were varnished twenty years apart. Although Ryman was not absolutely positive...
Rivenc, Barten, Esmay, Learner, and Stringari *Simply White: The Diverse Painting Materials of Robert Ryman*

Table 1. Paint samples, summary of analytical results

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<th>Date</th>
<th>Institution</th>
<th>Paint media (documented)</th>
<th>Support (documented)</th>
<th>Analytical results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard sampled</td>
<td>1967</td>
<td>Guggenheim</td>
<td>Swansdown Enamel</td>
<td>cold rolled steel</td>
<td>Alkyd paint with large amounts of plasticizers. Primer is also an alkyd. Calcium sulfate anhydrite</td>
</tr>
<tr>
<td>Untitled (panel 2 of 4 sampled)</td>
<td>1969</td>
<td>Guggenheim</td>
<td>Enamelac</td>
<td>corrugated cardboard</td>
<td>Shellac-based, drying oil likely. Calcium sulfate anhydrite; probably amorphous quartz</td>
</tr>
<tr>
<td>General 53 ½ x 53 ½</td>
<td>1970</td>
<td>Guggenheim</td>
<td>Enamelac</td>
<td>cotton canvas</td>
<td>Enamel: alkyd paint containing p-(ter-butyl) benzoic acid. Not identified</td>
</tr>
<tr>
<td>Lenox</td>
<td>1971</td>
<td>Guggenheim</td>
<td>Enamelac</td>
<td>linen canvas</td>
<td>Shellac-based, drying oil likely. Calcium sulfate anhydrite</td>
</tr>
<tr>
<td>Aneta</td>
<td>1972</td>
<td>Guggenheim</td>
<td>Enamelac</td>
<td>cotton canvas</td>
<td>Shellac-based, drying oil likely. Calcium sulfate anhydrite; probably amorphous quartz</td>
</tr>
<tr>
<td>Emprise 2</td>
<td>1973</td>
<td>Guggenheim</td>
<td>Gripz</td>
<td>cotton canvas</td>
<td>Shellac-based, drying oil likely. Talc (magnesium silicate); additional unidentified silicate mineral</td>
</tr>
<tr>
<td>Capitol</td>
<td>1973</td>
<td>Guggenheim</td>
<td>Gripz</td>
<td>unprimed linen canvas</td>
<td>Shellac-based, drying oil likely. Not identified</td>
</tr>
<tr>
<td>Varese Wall</td>
<td>1975</td>
<td>Dia</td>
<td>Vinyl acetate emulsion</td>
<td>Wood door panels, with metal bar, five foam blocks</td>
<td>Probably at least two different paints, the bottom layer being an acrylic-styrene, the upper layer possibly a PVA-acrylic paint. Bottom layer contains talc (hydrated magnesium silicate), and probably montmorillonite; upper layer contains kaolin.</td>
</tr>
<tr>
<td>Tower II</td>
<td>1976</td>
<td>Dia</td>
<td>Acrylic</td>
<td>black acrylic, (acrylic/PVC) sanded Plexiglas fasteners</td>
<td>p(MMA/ p(EA)) Calcium carbonate</td>
</tr>
<tr>
<td>Phoenix (8 units)</td>
<td>1979</td>
<td>Dia</td>
<td>Varathane</td>
<td>steel panels, fasteners with bolts</td>
<td>Alkyd paint Calcium carbonate and talc</td>
</tr>
<tr>
<td>Factor</td>
<td>1983</td>
<td>Dia</td>
<td>oil over acrylic (recto) and acrylic with varnish (verso)</td>
<td>Fiberglass with epoxy edge, metal rod with oval attachments</td>
<td>Verso: p(MMA/nBA)primer; p(MMA/nBMA) varnish. Calcium carbonate</td>
</tr>
<tr>
<td>Transfer</td>
<td>1987</td>
<td>Dia</td>
<td>Acrylic</td>
<td>Gatorboard (multilayer composite polystyrene foam) and four steel bolts</td>
<td>p(MMA/nBA); p(MMA/nBMA) primer with small amounts of nBA, and dimethyl phthalate. Calcium carbonate</td>
</tr>
<tr>
<td>Consort</td>
<td>1988</td>
<td>Dia</td>
<td>Acrylic</td>
<td>Fiberplate</td>
<td>p(MMA/nBMA) with large amounts of dimethyl phthalate; shellac markers. Calcium carbonate</td>
</tr>
<tr>
<td>Cord</td>
<td>1994</td>
<td>Dia</td>
<td>Oil and Enamelac</td>
<td>Lumaste (acrylic) panel</td>
<td>Drying oil; the very thin layer of Enamelac was hard to sample. Results show markers for shellac and pMMA from the Lumaste panel. Baryum sulfate (in the oil paint), unidentified component</td>
</tr>
<tr>
<td>Third Prototype</td>
<td>2003</td>
<td>Dia</td>
<td>Acrylic and varnish</td>
<td>14 vinyl panels</td>
<td>p(MMA/nBMA) varnish, in the white paint mostly MMA was identified. Calcium carbonate</td>
</tr>
</tbody>
</table>

1 For the Guggenheim paintings, the documentation corresponds to the copies of Robert Ryman's original records for these works that were given to the Solomon R. Guggenheim Museum by the artist when the Guggenheim acquired the works. Dia's documentation corresponds to database entries for each artwork in preparation for a catalogue raisonné of paintings and drawings.
about it, he thinks it is quite likely that he re-used the same product that he had bought in 1983. [10]

Consort, 1988, is also documented as acrylic, although analysis of the white paint yielded a composition of a p(MMA/nBMA) copolymer that contained a significant quantity of dimethyl phthalate – i.e. quite similar to the dark primer from Tower II – but, which also contained two peaks that correspond to the shellac markers detected in both Enamelac and Gripz (cf. below). To date, it has not been possible to completely interpret this finding, although some level of mixing would be suspected.

Only one vinyl acetate based medium was detected, in Varese Wall, 1975 (fig.7). Varese Wall is a large work, painted with a latex house paint. The support for the painting consists of five wooden door panels which are braced with metal bars on the verso and sit on five small blocks of blue foam that are evenly spaced. differs from other examples of Ryman’s works in that the entire surface is repainted as the need arises. The repainting occurs when the work is transported since, given its size and construction, disfiguring cracks develop at the junction between the individual door panels. The work has been repainted each time it has been installed and, according to Dia’s documentation, it was repainted in 2003 under Ryman’s supervision by Dia’s preparators during installation at Dia:Beacon using a flat interior latex house paint per Ryman’s instructions. Although many layers seem to be present, it proved challenging to separate them and Py-GCMS analysis was therefore performed on the entire cross-section of the sample. Py-GCMS analyses detected mostly PVA, styrene, and a plasticizer, diethyl phthalate. Very small amounts of nBMA were also detected. Because of the small sample size required for FTIR, it was possible to perform two different runs, one on the top of the flake and one on the bottom, and the two spectra show some clear differences. The inorganic content is markedly different. The bottom layer contains talc (hydrated magnesium silicate) and another type of clay or silicate, the best library match for it being a type of clay called montmorillonite. The upper layer, on the other hand, contains kaolin. There is evidence that the organic content is also different, in spite of the CH regions of both spectra being very similar. Specifically, the upper layer shows an intense peak at 1240 cm-1, which is one of the most distinctive features of PVA paints [8]. In contrast, this peak is absent from the spectrum of the bottom layer. The latter shows aromatic vibrations around 3030 cm-1 and a peak at 701 cm-1, both quite characteristic of styrene, which are not present in the upper layer. The CH stretching region in both cases is similar to that of a p(MMA/nBMA) copolymer, although the similarity could also be the result of a mixture of different components. This confirms that the paint used for the repainting is not the same than the original one; this seems to be of no importance to Ryman, as long as the paint used for the repainting is a good quality flat interior latex house paint. [10]

Enamels and shellac paints (Enamelac and Gripz) Phoenix, 1979, is composed of eight steel panels and was documented as painted with Varathane. The panels are primed with different dark primers and present different levels of gloss. This is not related to the use of different paints but to the fact that the paint in some selected panels was sanded down to obtain matte surfaces. The color of the primers varies from blue/grey to dark red, and as a result the top white layers present subtle variations of shade from cool to warm. Varathane is actually a product line rather than a single paint. It still exists, although it is now distributed by Rust-Oleum and consists of a variety of polyurethane-based wood finish products. The Varathane product used in 1979 by Ryman, however, proved upon analysis to be a classic alkyd formulation, i.e. a polyester resin modified by the addition of a drying oil. It includes glycerol and
pentaerythritol, phthalic anhydride, suberic, azelaic, palmitic and stearic acids.

Two additional alkyd formulations were identified from paints described as enamel, one in *Standard*, 1967 and the other in *General* 53 ½ x 53 ½, 1970, with both formulations presenting some uncommon characteristics. *Standard* consists of thirteen painted cold rolled steel panels. Ryman remembers using a paint called Swansdown Enamel, a matte enamel which he bought “from a place called Baylan’s” in Greenwich Village, choosing it because he “heard it was the best.” [5] Indeed, the paint has been documented by Guggenheim conservators as appearing very stable and resistant. The polyols are glycerol and pentaerythritol, the polybasic acid is phthalic anhydride, and various fatty acids are present, suberic, azelaic, myristic, palmitic and stearic. The oil modifier is therefore likely to be a drying oil. What is unusual about the paint is the abundance of phthalates, presumably acting as plasticizers: diethyl and dibutyl phthalates are present, but mostly very large amounts of di(-2-ethylhexyl)phthalate (DEHP) (See pyrogram in figure 8).

The red primer sampled at the verso of the panels of *Standard* is a straightforward alkyd, composed of glycerol, pentaerythritol, phthalic anhydride and suberic, azelaic, myristic, palmitic, and stearic acids. In both the primer and in one of the two paint samples, abietic acid derivatives were detected. The presence of these compounds might be due to contamination from the commercial lacquer that Ryman used to coat the panels to isolate them and prevent rusting. The DEHP might also come from this isolation lacquer layer, although it was found only in the paints and not in the primer, unlike the abietic acid derivatives. FTIR analysis also indicated that the paint has a low medium content and high levels of calcium sulfate anhydrite, acting as a filler and probably a matting agent. Ryman indeed recalls that Swansdown was a matte paint. [5]

The high gloss enamel paint on *General* 53 ½ x 53 ½ contains glycerol and pentaerythritol (the latter by far predominant), phthalic acid, but also p-(t-butyl) benzoic acid, a monofunctional acid sometimes found in alkyd formulations. [11] Azelaic acid is present in large amounts, perhaps indicating a high level of oxidation, and there are much smaller quantities of many other fatty acids: caprylic, pimelic, suberic, sebacic, myristic, palmitic and stearic. Ryman doesn’t remember what product he used; only that it wasn’t Swansdown. [5]

Ryman stated that he used both enamel and the shellac-based sealant product called Enamelac on *General* 53 ½ x 53 ½. The Enamelac covers the entire surface of the canvas and the enamel comprises a slightly smaller square on top, which leaves the Enamelac visible only around the perimeter (fig. 9). He seemed interested in the differences in optical properties between the two media, remarking during the 1999 interview, “the enamel still has the bounce to it, and the Enamelac is still kind of yellow and has that softness.” [5] In the same interview, Ryman and the Guggenheim conservators discussed the presence of cracks in the enamel section of the painting: Ryman remarked “the cracks, that’s the problem with the enamel on that cotton….I mean it should’ve been on a hard surface rather than on the soft surface of the cotton.”

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**Figure 8.** Pyrogram of “enamel” paint in *Standard* (1967, Solomon R. Guggenheim Museum).

**Figure 9.** *General* 53 ½ x 53 ½ (1970, Solomon R. Guggenheim Museum).
paints tend to increase in brittleness with ageing [12], and so cracking is more likely to occur if it is applied to a flexible support such as canvas, from accidental impacts or the dimensional changes provoked by climate fluctuations. Very sensitive to conservation problems, Ryman subsequently switched to rigid supports when painting with enamel to avoid this cracking problem. [1]

Shellac-based paints were found in six different works, each time in agreement with the documentation from the artist. Ryman’s original records describe Untitled, 1969, General 53 ½ x 53 ½, 1970, Lenox, 1971, and Arista, 1972 as painted with Enamelac, while Emprise 2, 1973, and Capitol, 1973 are documented as painted with Gripz. So far, there is no indication of whether the dates are significant, e.g. Gripz not being available before 1973, or only coincidental. Guggenheim conservators were particularly interested in the differences between these two products, having observed that Enamelac seems noticeably yellower than Gripz. These observations are obviously complicated by the possible interference of other variables, such as the thickness of the paint layers, and underlying substrates, etc.

Upon analysis, however, a few fairly subtle differences could indeed be observed between the two products. The inorganic content is one of the most obvious differences that FTIR detected. The paint in Emprise 2, documented as Gripz paint, includes talc (magnesium silicate) as a filler and probably another type of clay or silicate mineral. By contrast, the paints in Untitled 1969, Lenox and Arista, documented as Enamelac, all contain calcium sulfate anhydrite. Arista and Untitled 1969 seem to also contain an additional inorganic component, probably a form of amorphous quartz. The reason why these paints differ in inorganic content from Lenox is unclear but might be due to slight variations in the Enamelac from batch to batch or a small compositional change introduced in 1971.

Other possibly significant differences among the shellac-based paints include discrepancies observed in the carbonyl region of the FTIR spectra of the paints. The spectra of Lenox, Arista and Untitled 1969 (Enamelac) consistently present two main peaks in this region, one at 1731 cm⁻¹ and one at 1716 cm⁻¹. The first one corresponds to ester bonds and the second to free carboxylic acids. The spectrum of Emprise 2 (Gripz) shows a broader overall carbonyl peak and presents a third peak at 1699 cm⁻¹. A comparison between the Py-GCMS analysis results of General 53 ½ x 53 ½ (Enamelac) and Capitol (Gripz) shows, in addition, that both paints contain a drying oil, since glycerol and fatty acids including azelaic acid are present. The Gripz paint from Capitol also contains some extra shellac markers eluting between 17 and 21 minutes (cf. a comparison of both pyrograms in fig. 10).

One possible explanation for the alleged difference in yellowing between the two paints could be a difference in the processing of the resins, in particular if either of the resins, most likely the Gripz, underwent a bleaching process. Shellac is naturally orange and can therefore be subjected to whitening or bleaching, a procedure that involves an alkali treatment. One of the likely consequences of that treatment is to create additional sesquiterpenoid compounds [13]. In FTIR spectra, the modifications caused by the alkali treatment typically result in a broader carbonyl band, with the peak at 1716 cm⁻¹ being more intense than the peak at 1731 cm⁻¹. In orange shellac, the two peaks are normally of fairly equal intensity and the free carboxylic acid peak at 1716 cm⁻¹ only becomes predominant upon ageing (fig. 11). The spectrum of Emprise 2 does have a broad carbonyl band; the extra peak at 1699 cm⁻¹ might be related to the formation of additional alicyclic sesquiterpenoid compounds upon bleaching, as might be the extra shellac markers seen in the pyrogram. It would be interesting to compare unaged references of Enamelac and Gripz, to determine if the shape of the carbonyl band before ageing is consistent with orange and white shellac, however no reference of Gripz has been made available to date.

Another difference observed that might partially account for the observed greater yellowing of Gripz might be found in

![Figure 10. Pyrograms of General 53 ½ x 53 ½, (Enamelac, 1970, Solomon R. Guggenheim Museum) and Capitol (Gripz, 1973, Solomon R. Guggenheim Museum).](image-url)
the degree of oxidation of the drying oils used to prepare the shellac-based media; the oil present in General 53 ½ x 53 ½ (Enamelac) has an azelaic acid to palmitic acid ratio (A/P ratio) of 3.5 while the oil in Capitol (Gripz) has an A/P ratio of 0.7. This does not explain, however, why one oil would be more oxidized than the other; this could be due to processing, environmental conditions, or history of exposure, for example. In addition, this trend could not be confirmed with other samples as the sample sizes were insufficient. Further work on the references, if both can be made available, would be needed to interpret the differences in ageing properties more conclusively.

ANALYTICAL TECHNIQUES

Both analytical techniques used for this study proved useful, but brought different levels of information. FTIR allows rapid discrimination of the paints but does not give a detailed paint composition. FTIR gives information on the inorganic content of the paint, but this might sometimes turn into a disadvantage as the vibrational features of inorganic fillers can often overwhelm the spectra and make identification of the organic binder difficult. PyGCMS analyses are more time-consuming and require a larger sample size, but give detailed information on the organic composition of the paint. However, PyGCMS provides no information about the inorganic content. The choice of whether to derivatize the samples in preparation to pyGCMS analyses or not has a significant bearing on the results. It is indispensable for alkyds and oil based paints, as the polar compounds would be hard to detect without derivatization, but not for vinyl or acrylic paints, which exhibit more complicated programs when derivatized. In cases where the samples are completely unknown, derivatization if probably safer, but a preliminary FTIR analysis can help to determine the best sample preparation method by giving a broad indication of the composition. On the whole, FTIR and pyGCMS are complementary, and provided a fairly holistic characterization of the samples.

CONCLUSION

The analytical study of an artist’s materials, complemented by interviews and documentation, often gives an invaluable insight into that artist’s creative processes. Eighteen of Robert Ryman’s paintings from Dia Art Foundation and the Solomon R. Guggenheim Museum were sampled for this preliminary study, and for each work, good analytical results were obtained. On the whole, these results agreed with the documentation available from the artist about these paintings, but they also provided additional information and some necessary clarifications on some of the binder terms used, perhaps most importantly the group of paints labeled “enamel”. The results also confirmed the amazing diversity of painting media used by Ryman: for the eighteen paintings analyzed so far, at least eleven different binding media were detected, and it was encouraging to observe that all these media could be detected using a combination of the same two analytical techniques: FTIR and PyGCMS. Some questions remain unanswered, of course, and others arose from the analyses, and these will be addressed during the next phase of the project, which will include a more detailed interview with Ryman on his painting materials and the sampling of a much larger group of reference products that remain in his studio. Finally, the combination of the extremely limited pigment range with the diversity of binding media used, presents a unique opportunity to monitor and compare the handling, aesthetic and aging properties of a wide range of modern binding media.

APPENDIX I: EXPERIMENTAL

FTIR

Selected particles of each samples were placed on a diamond window and flattened using a metal roller. The samples were analyzed using a 15X Cassegrain objective attached to a Bruker Optics, Inc. Hyperion 3000 FT-IR microscope housing a liquid nitrogen cooled mid-band MCT detector, and purged with dry air. The spectra are the sum of 64 scans at a resolution of 4 cm⁻¹. Reference spectra from the infrared spectral database were utilized in the identification process.

pyGCMS

A Frontier Lab PY-2020D double-shot pyrolyzer system equipped with a CGS-1050E carrier gas selector, SS-1010E
selective sampler, and MJT-1030E microjet cryo-trap was used for pyrolysis. The pyrolysis interface was maintained at 320°C. The pyrolyzer was interfaced to an Agilent Technologies 5975C inert MSD/7890A gas chromatograph/mass spectrometer. A Frontier Ultra ALLOY-5 capillary column was used for the separation (30 M x 0.25 mm x 0.25 µm), with helium carrier gas set to 1 ml/minute. The split injector was set to 320°C with a split ratio of 50:1 and no solvent delay. The GC oven temperature program was 40°C for 2 minutes, then ramped to 320°C at 20°C /minute, followed by a 9 minute isothermal period. The MS transfer line was at 320°C, the source at 230°C, and the MS quad at 150°C. The mass spectrometer was scanned from 33-600 amu at a rate of 2.59 scans per second. The electron multiplier was set to the autotune value. Samples were placed into a 50 µl stainless steel Eco-cup fitted with an Eco-stick, and three microliters of a 25% methanolic solution of tetramethyl ammonium hydroxide (TMAH) were introduced for derivatization. After three minutes, the cup was placed into the pyrolysis interface where it was purged with helium for three minutes. Samples were pyrolyzed using a single-shot method at 550°C for 6 seconds.

ENDNOTES

4. Interview with Robert Ryman, Dia Art Foundation, Dia Beacon, October 2003, Carol Mancusi-Ungaro.
5. Interview with Robert Ryman, Solomon R. Guggenheim Museum Conservation Department, July 1, 1999, Carol Stringari and Julie Barten.
6. Most of the Ryman works in the Guggenheim’s collection were acquired in 1991 as part of the Panza Collection.
7. “Enamel” is a term used generically by Ryman. The analyses revealed that it refers to different types of alkyd paints.
10. Verbal communication with two of the authors, Rachel Rivenc and Francesca Esmay, November 11, 2009.
A Closer Look: Condition Issues in Abstract Expressionist Ground Layers

ABSTRACT

In the middle of the 20th-century, experimentation in house paint formulation crossed paths with the experimentation of artists with house paint. A brittle and ineffective white house paint was being marketed during a period when the Abstract Expressionists were using house paint as a ground layer material. Paintings created during this brief period have the potential for hidden problems. This research examines a group of paintings from the collection of the Hirshhorn Museum and Sculpture Garden, and highlights a possible relationship between zinc oxide oil grounds and condition problems observed in these paintings. The goal of this research is to encourage discussion related to the preservation of works from this important period.

INTRODUCTION

In 2007, the Hirshhorn Museum and Sculpture Garden (HMSG), Smithsonian Institution, completed an inventory and condition survey of their paintings collection. During the review of approximately 4,600 paintings, a pattern of condition issues was observed within HMSG’s mid-century holdings. In collaboration with the Museum Conservation Institute (MCI), Smithsonian Institution, a research fellowship was proposed to take a closer look at the situation. The project was initiated with funding through the Smithsonian Institution’s Conservation of Museum Collections program, and completed with assistance from the Samuel H. Kress Foundation.

STUDY GROUP SELECTION

HMSG’s permanent collection reflects Joseph Hirshhorn’s close relationships with renowned mid-century artists. A list of potential candidates for this study was created following a review of conservation and survey records, and inspection of the works. This research project focuses on paintings from what is now called the Abstract Expressionist School, a group of artists known for their innovative techniques and materials. Paintings in this study group include works by New York-based artists Willem de Kooning (1904-1997), Hans Hofmann (1880-1966), Franz Kline (1920-1962), and Jackson Pollock (1912-1956), as well as contemporaneous works by European colleagues Karel Appel (1921-2006) and Antonio Saura (1930-1998). Artists were chosen based on similarities in technique and palette, as well as the potential for shared information regarding materials. Several paintings by each artist were chosen for inclusion in this study: some early works by de Kooning, on fabric and board, works by Hofmann, mostly from the period when his NY school was active, two early 60s paintings by Kline, some early work by Pollock, a number of paintings by Appel, including works that highlight the shift in his pallet inspired by his first trip to NY, and three late 50s paintings by Saura, one each from his female portraits, crucifixion, and self-portrait series. Damaged and undamaged works by each artist were included in the final study group of 20 paintings.

CONDITION

Early attention was paid to repeating condition patterns. Many of the works exhibit blind cleavage and lifting, which appears to be associated with an intralayer failure of the ground layer material. This failure is lamellar in appearance; a layer of ground material is attached to the lifting paint, while another layer of ground material remains attached to the primary support. There are examples of this type of failure in cleaving cadmium colors in several of the works by Hofmann and Appel (fig. 1). In the case of Kline and Saura, we see a location-specific cracking of carbon blacks. Works by both...
artists contain multiple whites (visible to the unaided eye); the black remains intact where it is painted over one of the whites, but exhibits widespread cracking when it passes over a second white (fig. 2). During XRF analysis, zinc was consistently found in the damaged areas in these paintings. Samples from several works were examined to obtain further information about the composition of the artists’ painting materials.

ANALYSIS

Microscopy of samples from damaged areas of the paintings indicated the presence of zinc particles in the white layer beneath the damaged cadmium and black paints; the distinctive auto-fluorescence is visible under UV illumination when viewed with the appropriate UV filter. Scanning Electron Microscopy–Energy Dispersive Spectroscopy of the samples confirmed the presence of a zinc oxide white layer under a layer of either cadmium red or carbon black (figs. 1 and 2).

Based on the SEM results, paint samples from a select number of the works were sent to the National Gallery of Art for Pyrolysis-Gas Chromatography–Mass Spectrometry analysis. Py-GC-MS results indicated an oil-based binder for all samples. The chromatogram plots also exhibited unusually high peaks related to unsaturated fatty acids. For comparison, Py-GC-MS analysis was performed on a range of oil-based white paint samples from the Materials Study Collection at MCI. The zinc oxide comparison samples exhibited the same excess fatty acid peaks visible in the zinc oxide-containing study group paints. These samples include a 30-year-old drawdown sample of Grumbacher zinc white, a 20-year-old control sample of zinc white (prepared by Gamblin Artists Oils), and a 10-year-old drawdown sample of Speedball zinc white (fig. 3). The zinc oxide-free comparison samples showed no excess unsaturated fatty acid peaks.

Fourier Transform Infrared false color imaging (performed at the Institute for Atomic and Molecular Physics in Amsterdam) of zinc oxide layers from both the study group paintings and the Materials Study Collection comparison samples also revealed an unexpected, widespread distribution of unoxidized fatty acids throughout the zinc oxide paint layer.

A large amount of extant unsaturated fatty acids is unexpected in paintings that are nearly 60 years old. This phenomenon is the result of the unique drying process of zinc oxide oil paint. In an oil medium, zinc oxide forms a tightly packed crystalline structure, but with a highly ordered lamellar distribution that orients layers of unsaturated fatty acid chains between layers of the fatty acid carboxyl groups and the zinc matrix. This layered structure makes the paint very stiff, and the highly ordered packing of the hydrocarbon chains makes the unsaturated
bonds more difficult to oxidize. The excess unsaturated fatty acids in zinc oxide paint remain trapped within the paint layer years after oxidation of the paint should have been completed. It is as if the paint has prematurely “frozen” into position, without the structural stability afforded by the cross-linking that would accompany the natural drying process. Shortly after application, zinc oxide has formed an unusually stiff and brittle oil paint. [1]

Recent research has hypothesized that anomalous bond formation within the zinc matrix further disrupts the structure. This weakness, along with the zinc – hydrocarbon – zinc layering, may explain the plate-like intralayer cleavage present on the paintings.

**INDUSTRIAL LITERATURE**

There is generous documentary and anecdotal evidence of the Abstract Expressionists’ use of house paints in their work. Due to similarities in formulation during this period, in the absence of alkyds, there is little that can be done analytically to determine if a mid-century artist was using an oil-based house paint or a similar, commercially-prepared artists’ paint. Yet this similarity in formulation can work in the conservator’s favor. Before the introduction of titanium dioxide substitutes, the commercial paint industry struggled to fashion a zinc oxide paint that could replace lead white, and fill the need for an opaque and durable white coating. Industrial literature from the period directly addresses the behavior and characteristics of zinc oxide oil paint.

Frustrations from within the industry can be found as early as a 1907 treatise on the merits and defects of zinc white that begins: “Zinc white covers poorly. It dries poorly. It stands the weather badly.” From the earliest articles, zinc oxide oil paint is acknowledged as reactive, brittle, and difficult to use.

There is a wealth of industrial literature from the same period as the study group paintings, including a 1949 Oil & Colour Chemists’ Association symposium devoted entirely to the discussion of zinc oxide. One presenter at the symposium noted that “zinc fails by checking and cracking with flaking… and erosion which seems fairly severe,” but added the optimistic comment that “paints containing zinc pigments have, however, a natural useful life of at least three and a half years.” With its regular anticipated repainting, it is clear that the industry definition of “useful” differs significantly from that of the artist and conservator considering the long-term stability of a work of art.

The industrial literature is particularly useful when it addresses the use of zinc oxide oil-based house paint as a priming layer. The author of a 1935 article from the *Official Digest of the Federation of Paint & Varnish Production Clubs* states that “it is possible that too little thought has been given as to how a primer might work under different paints…. In some cases there is a marked increase in checking and cracking of the finishing coats and in others an actual decrease in adherence of the whole system… for satisfactory durability, adjacent applications must not differ too greatly from one another.
in distensibility or hardness.” A 1941 article in *Industrial and Engineering Chemistry* notes that “complete elimination of zinc oxide from primers is recommended by one school of thought on the subject and is opposed by another… Conclusions about the use of zinc oxide in primers must be subordinated to the more fundamental problem of compatibility between primer and finish paint… Leaders of both schools of thought concerning the place of zinc oxide in primers agree that compatibility is a dominant consideration.” The authors of a 1936 study in the same journal conclude that “there is a direct relationship, in terms of performance, between relative hardness of undercoat and top coat, and that certain combinations are incompatible.”

**MECHANICS**

One way to examine issues of compatibility within the layered structure of the study group paintings is to compare the mechanical properties of each individual layer. For this portion of the project, representative data were culled from previous mechanics research performed over a period of 30 years, on control samples from the Materials Study Collection at MCI. Control samples from the collection were chosen based on similarity in pigment composition and analytical testing profile. In addition, the simple formulation of the control samples limited the potential effect of anomalous materials.

Stress-strain plots from a series of tensile tests highlight the stiffness and brittleness of zinc oxide oil paint. This is especially significant when compared to the tensile test results for other types of oil paints found in the study group paintings, such as cadmium red and lamp (carbon) black. At even the small amount of strain created by keying out a painting, the zinc oxide layer has failed before any significant strain is placed on the other pigmented layers (fig. 4).

Customized force-strain projections (based on stress-strain data) were created for the materials found in the study group paintings. The first set of projections was calculated using the average thicknesses of the materials in one of the Kline paintings, including the canvas and size layers. In those areas of the artist-primed canvas where the ground layer is thicker, the force on the zinc oxide layer increases (fig. 5).

It is also worth remembering that many of these paintings are on hygroscopic supports. Though the glue and canvas respond to changes in relative humidity, the zinc oxide oil paint layer is practically non-responsive to changes in humidity, and cannot adapt to dimensional changes in the other materials.

Mechanical stresses and forces throughout the layers of this painting structure can result in widespread cracking and delaminations throughout the ground layer. Resultant fissures within the ground layer will increase the potential for subsequent damage.

**CONCLUSIONS**

Abstract Expressionist compositions often include thick layers of paint. The brittle and inflexible characteristics of zinc oxide oil paint are not ideal properties for an intermediary layer between a thick oil paint composition and a flexible and hygroscopic support. The mechanical properties of the zinc oxide oil paint are incompatible with the requirements of a ground layer for these works. The mid-century artist’s choice of an oil-based house paint ground may have compromised the painting structure.
Rogala, Lake, Maines, and Mecklenburg A Closer Look: Condition Issues in Abstract Expressionist Ground Layers

The study group artists did not use zinc white oil paint as a ground layer for all of their paintings; it is recommended that collections from this period be reviewed to determine which paintings might contain zinc oxide oil grounds or underlayers. Works with zinc oxide oil grounds should be carefully observed, particularly during periods of mechanical stress, or changes in the environment. Areas of flaking paint in these works may indicate a compromised ground layer, and should be closely examined. The possibility of blind cleavage and delamination should be considered.

QUESTIONS AND ANSWERS

Have you seen examples of paintings extruding excess fatty acids (as has been reported in some works by van Gogh)? No, I have not seen any examples of extruding materials in the study group paintings. This may be due to the high pigment volume concentration in zinc oxide oil-based house paints. Not only does this create an extremely strong matrix that restricts the movement of the materials, but it also supplies an excess of pigment material for any reaction. Even if the fatty acids could move, they wouldn’t need to.

Are you familiar with the zinc-related problems in pre-Raphaelite paintings? As I understand it, pre-Raphaelite painters covered their lead white grounds with a layer of zinc oxide white, in order to create a brighter foundation for their compositions. From a mechanics perspective, this would create essentially the same problem that we’re seeing in the AbEx works: a brittle, ineffective support layer. The zinc is the weak layer in the painting structure.

Did the use of zinc oxide phase out in Europe at the same time as in the U.S.? The U.S. industrial literature seems to link the replacement of zinc oxide in house paint with its poor performance in weathering tests. Several of the articles mention that while weathering conditions vary across the U.S., these are generally worse than conditions in Europe. DuPont introduced titanium dioxide commercially in the U.S. in the mid-1950s, but I don’t know when titanium white became generally available in Europe. It’s something to keep in mind when reviewing mid-century collections.

ACKNOWLEDGMENTS

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Bottom: similar projection, with increased thickness of ground layer (zinc oxide failure point highlighted in both examples)

Figure 5. Force-strain projections, calculated from tensile testing data
A Closer Look: Condition Issues in Abstract Expressionist Ground Layers

Colors, Inc.; Mark Gottsegen, Materials Research Director, Intermuseum Conservation Association; Michael Skalka, Art Materials Collection and Study Center, National Gallery of Art. Funding: The Samuel H. Kress Foundation, and The Smithsonian Institution Fellowship Program.

ENDNOTES

1. In a similar manner, the matrix restricts the movement of the zinc soaps, which have remained distributed throughout the paint layer in the study group paintings. While fatty acids will typically saponify in the presence of metal salts, it is unusual to find such high concentrations of unreacted unsaturated fatty acids, which is directly related to the unique failure characteristics of zinc oxide paints.

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ABSTRACT

At the 2008 AIC Meeting in Denver, an introduction to the life and work of the American Abstract Expressionist painter, Clyfford Still, was presented along with a glimpse into the artist's little known paintings of the 1930s through 1950s. Still's mysterious art collection and the various conservation efforts that have been centered around it over time were described. Many of the oil paintings from the Clyfford Still Estate have been undergoing examination and treatment in the ARTEX Conservation Laboratory since 2004. Barbara A. Ramsay has directed the work of the ARTEX conservators who have carried out conservation treatment of the Still paintings: Kristen Loudermilk, Pamela Betts, and Peter Nelsen.

In the AIC Los Angeles presentation in 2009, specific conservation concerns and some of the challenges inherent in preserving these complex modern paintings were elaborated upon. Results of the condition surveys and establishment of priorities were described. The conservation philosophy of minimal intervention that has been adopted by the team of conservators at ARTEX was discussed. Most of the close to 200 paintings examined to date appear to be in astonishingly good physical condition, but those with conservation problems have required treatment of various kinds.

Specific examples of conservation treatment were presented, for example: the reduction of pronounced planar deformation of the previously rolled cotton duck canvases; mounting of the paintings (many oversized canvases) onto stretchers; local consolidation of lifting, flaking, and/or powdery paint (often matte, weakly bound oil paint); and lessening of the appearance of disfiguring surface grime, debris, or paint efflorescence.

Our approach was presented in terms of resolving issues such as: which of the multiple fold lines should be used for mounting of the paintings on stretchers (and what type of stretchers to use) ; whether or not to remove, reduce, or otherwise treat severely reticulated and discolored varnishes applied by the artist; whether or not to enhance the saturation of very matte paint according to instructions provided by the artist; whether or not to infill and inpaint losses in these hitherto untouched paintings and, if so, to what extent; and how to best protect these paintings during handling, storage, and travel.

Mention was made of the technical research being conducted into the materials of Clyfford Still, by ARTEX in collaboration with Dr. Susan Lake of the Hirshhorn Museum and Dr. Tom Learner of the Getty Conservation Institute.

The entire collection of 825 Still paintings will soon reside in the new Clyfford Still Museum, scheduled to open in Denver in 2011.

ENDNOTES


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Barbara A. Ramsay earned a B.Sc. in Biology and studied Art History and Studio Art at the University of Toronto. In 1976, she graduated with a Master of Art Conservation degree (Paintings and Paper) from Queen’s University. Barbara practiced painting conservation at the National Gallery of Canada from 1977 through 1995, the last five of those years as Senior Conservator of Fine Art. Barbara has been Director of Conservation Services at ARTEX DC since 1999 when she established the ARTEX Conservation Laboratory.
ABSTRACT

The treatment was a response to a damage sustained by an Ed Ruscha painting. Due to the nature of the support and to the artist's technique, alternative techniques of tear mending and inpainting were needed. Minimal use of adhesive was advised considering the characteristics of the painting. A system of Gore-Tex sutures was used to provide the strength and stability. The inpainting could not penetrate the canvas. The paint layer was therefore prepared on a substrate and affixed onto the damage. Although not yet time-tested, the methods may offer solutions to some problems presented by contemporary paintings of similar construction.

INTRODUCTION

Technique and painting description

The painting that is the subject of this article belongs to the “City Plans” series, a group of works created by Ed Ruscha in the late 1990s and early 2000s. Consistently preoccupied with certain aspects of the American life, culture and imagery, this body of work uses simplified Los Angeles map sections, projected from a sharp angle as if seen in bird’s eye view and painted in grades of black and white. The result is what the artist calls “Metro Plots”, seemingly abstract, synthetic and isolated spaces, in fact illustrating widely known spots on the Los Angeles road map.

The distinct technique of the artist this time involved lightly placing the stencils of letters and outlines of sections of city plans against the stretched, unprimed cotton canvas and spraying over them black acrylic paint. In some of the paintings from the series, including this one, Ruscha followed with a spray-applied acrylic varnish, using first gloss and subsequently matte varnish.

Gentle handling of the canvas surface, precise distance of spraying and assorted paint and varnish qualities made the spatters cling to the raised tendrils of the canvas rather than get embedded in it, creating the non-static, foggy surface the artist aimed for, vibrant yet extremely uniform. Their quality “spontaneous and quick”, quoting E. Ruscha was achieved in a process that combined expert knowledge of the materials and absolute control of their application, allowing some accidental results but no mistakes.

“Portland to Memphis” was painted by Ed Ruscha in 2000. The painting is in the format of a horizontal rectangle, 42 1/8” by 84”. Its primary support is a plain weave one-ply cotton canvas, medium weight, very tightly woven. The canvas bears a reed mark pattern in the form of a tiny gap between every third warp yarn. The direction of the warp is vertical. The canvas may have been sized by manufacturer, however no sizing is distinguishable. It was neither sized nor primed by the artist. The canvas is stretched on an eight member wooden strainer with the joins reinforced with thin triangular and rectangular plywood braces, and held with staples on the back. The side edges of the painting are covered with a black pressure sensitive tape that extends slightly onto the reverse. The pictorial layer is Liquitex acrylic Ivory Black paint sprayed over the canvas, which produced a uniform but not cohesive film, its continuity varying from almost solid coat to almost bare canvas. The varnish layer is Liquitex Gloss and Matte Soluvar Varnish (comprising of a mixture of Acryloid B-67 and Acryloid F-10 diluted in a mixture of solvents, with an addition of fumed silica for the Matte Varnish). Microscopically, the paint layer has an open-work quality and is made of varied size paint drips (“b.b.sized”, “weird shaped”), some of them minuscule and, of miniature varnish droplets irregular in size, virtually suspended within and on the nap of the cotton, creating a complex three-dimensional structure.
Damages
While in transit, the painting was subject to an event that was extremely short in duration but very far reaching in its outcome. While the crate containing the painting was being moved, a badly aimed fork lift went through it, piercing it front to back (fig.1).

The damage was immediately noticed and the whole cargo transported to the conservation studio as quickly possible. Upon its unpacking, the extent of the damage became clear (fig.2).

A monumental yet elementally constructed work of art, crisp and pristine, was now disfigured, un-exhibitable and structurally unsound (fig.3).

The tear that resulted from the accident was located within 11” to 16” from the top edge and approximately 28” from the right edge. It was vertically oriented, stair-shaped, consisting of two long vertical sections and a short horizontal section, approximately 5” long in all (fig.4). The direction of the warp being vertical meant that the tear went mostly across the weft, breaking about 6 threads of the warp and about 140 threads of the weft. A separate effect of the object’s impact on the canvas was its serious distortion and subsequent gapping of the area (fig.5). Many threads were severely misaligned and pulled out of the weave matrix. The structure of the weave was deformed in some areas by as much as four thread counts. This together with the fact that the canvas remained stretched, meaning under continuous tension caused the edges of the tear to pull apart as much as approximately one half of an inch.

The paint layer damage was limited thanks to its non-continuous character, flexibility and good adhesion to the canvas substrate. Despite that, some of the paint droplets were lost due to the disruption and fraying of the torn canvas threads.

Figure 1. Damaged crate containing the painting.

Figure 2. Tear visible in the upper right quadrant.

Figure 3. Tear area, detail.
TECHNICAL CHALLENGES AND PROPOSED METHODOLOGY

The technique and construction of the painting imposed very strict limitations on available treatment solutions, both for tear reparation and for the inpainting. The double challenge was laid on the one hand by the support unprimed, partly unpainted cotton canvas, on the other by the method of paint application irregular spraying onto the canvas of dilute acrylic paint and synthetic varnish.

Support
The thread by thread mending method most often used at the studio for repairing tears was ruled out as the single solution due to the characteristics of the canvas. Firstly, the concern was that a liquid adhesive used on the raw, absorbent threads would be difficult to control and that upon aging it could subsequently become visible on the surface of the canvas. Secondly considering the size and the shape of the tear, most likely it would be necessary to apply a reinforcement of the mend on the back side of the canvas, which itself would have to be attached with an adhesive. That too presented the risk of an alteration and discoloration of the original canvas. As an alternative, we decided to use a mending solution that would not only eliminate the use of liquid materials but also the need for an added stabilizing reinforcement on the back.

The proposed method consisted of using some aspects of the thread to thread mending in combination with a system of Gore-Tex monofilaments interwoven into canvas. In the first phase the distortion would be eliminated, the pattern of the weave recreated under magnification provided by binocular microscope. During this procedure the use of minimal amounts of humidity was taken into consideration: it would facilitate shaping and positioning of the threads. At this stage some number of Gore-Tex filaments would be introduced, in order to stabilize the recreated weave. Next the weave recreation would be initiated. Simultaneously with reweaving and reconnecting of the threads, monofilaments would be introduced into the entire area of the tear for permanent and stable reinforcement of the canvas.

Paint layer
Facing a combination of the artist’s technique of spray-applying a dispersed non-continuous paint layer, and of the very absorbent cotton canvas support, an alternative had to be proposed to the liquid and semi-liquid paints typically used for inpainting. The assumptions here were that even paint very thick in consistency would be hard to control; it would be at least to some degree absorbed by the canvas threads, therefore staining them, while not providing fully satisfying means of color compensation. In response, we opted for pre-making the missing paint layer elements and subsequently affixing them onto the areas of loss.

TREATMENT

Canvas distortion
The first problem approached was the canvas distortion. After ensuring that the damaged paint layer around the tear was stable and did not require preliminary consolidation, the painting was placed face down on a glassine-covered work surface. In order to facilitate following the weave pattern, the threads were counted and every eighth thread of the weft was marked with a minuscule piece of low-tack drafting tape. Those markers were left throughout the initial phase of reweaving.

Gradual tension was applied to both sides of the tear, by attaching thin strips of masking tape to each side, with the adhesive part blocked over the tear area, and pulling the tapes across the tear to the opposing side. The individual threads were also manually manipulated in the opposite direction of the distortion. The tightly woven canvas was very resistant, and while yielding at first, the deformation tended to quickly reappear. The difficulty of the process was increased by the fact that the canvas could not be removed from the strainer, which meant working against the opposing tension forces. Subsequently the strips of tape were replaced by Treckers (“Pullers”), canvas-tensioning devices equipped with adjustable screws designed and manufactured by Professor Winfried Herber (fig.6).
They were placed around four sides of the tear and secured on one side to the strainer bars and on the other to the canvas with use of pressure sensitive tape (Powerstrip) across from the tear edge. During this procedure the area was gently weighted in order to maintain the canvas planarity. The progress in removing the distortion was checked regularly and the tension gradually increased by adjusting the screws of the Treckers.

This process was done over a period of several months, eventually resulting in an almost full elimination of the approximately half-inch gap separating the vertical sides of the tear, and approximately quarter-inch gap of the horizontal section of the tear.

The extended duration of the procedure allowed the distorted and misaligned matrix of the canvas in the area of the tear to be brought back to its original position in a measured, gradual and even manner, and increased the long-term dimensional stability of the area.

It is worth noting that although it made the mending process a little more difficult, the decision of leaving the painting on the strainer during the procedure was deliberate. It eliminated submitting the canvas and the mend to significant physical maneuvers and to varied degrees of tension, preserved the original finishing of the painting edges, and provided easy access to both front and back of the painting during the entire treatment.

**Gore-Tex monofilament and mending**

After the procedure had been sufficiently advanced – the canvas in the area was planar, its weave conforming almost exactly to the original weave pattern and the sides of the entire tear were very close, the loose threads were preliminarily retwined and realigned with the weave matrix by mechanical manipulations, using surgical tweezers and fine-point hooks. Subsequently the introduction of the Gore-Tex sutures was initiated using a curved non-cutting needle and suture forceps (fig.7).

At first the Gore-Tex monofilaments were interwoven into the entire area of the tear, across the tear, at 1-, 2-, 3-, 4-, 5- and 6-thread increments vertically, reaching a span of between 2 to 3 1/2” horizontally on either side of the tear (fig.8). The sutures were positioned so as to lie alongside the threads and did not pierce the weave. Moving along the threads of the weft, the filament was introduced with its needle under the ends of the warp. Once the end of the line was reached, the thread was doubled back, leaving around 5” floating for further manipulation, and the filament run in the opposite direction at the chosen increment.

A single monofilament usually “served” 4 rows. If at the beginning of a new row the remaining monofilament reserve was not long enough for an entire row, a new suture would be started. The distance from the edge of the tear was irregularly maintained, to minimize the risk of creating a solid line of

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Figure 6. System of Treckers affixed to the strainer.

Figure 7. Mock up of introducing Gore-Tex sutures into the weave of the canvas.

Figure 8. Monofilaments introduced across the tear (image digitally manipulated).
tension in the weave and potentially telegraphing the shape of the sutured area to the face.

A similar method was applied on the horizontal section of the tear, with the exception of the monofilaments’ alignment. They were interwoven along not one but several threads of the warp in order to achieve a more uniform pull (fig. 9).

With the Gore-Tex threads introduced along the whole tear, the entire area was stabilized.

At this point the first phase of reweaving could be executed. Still working on the back side of the canvas, the results were now regularly checked on the face.

Canvas threads torn by the impact were deformed: due to lack of tension, they had become loosened, unraveled and as a result thick and fluffy. Attempts at reweaving them in that condition produced a bulky, fuzzy surface. As a modifying step the threads were very slightly moistened with distilled water and a fine brush. This allowed twisting and smoothing them but the effect was very short lived. As soon as a thread dried and was manipulated it would lose its shape. It was decided to use a sizing agent in order to control and shape the threads. A 1% solution of Methyl Cellulose 4000 in distilled water was chosen as a sizing agent, due to its chemical similarity to the canvas, combined with its very high viscosity and therefore minimal penetration. Methyl Cellulose was applied with a fine brush on one or two unraveled threads at a time, the thread(s) were smoothed with a warm micro-spatula and immediately twisted and rewoven. In the process, care was taken to position threads in a way so that any paint flakes still attached to threads ended up on the face of the painting. Starting at bottom and top ends of the tear and gradually moving towards the short horizontal tear section, all threads were shaped and subsequently interwoven. This prepared them for the final phase of thread reconnection.

At this stage the tear edges were still not as close as necessary. In order to overcome this, two subsequent steps were taken. Firstly, using up the extra lengths at the end of the rows of stitches all the Gore-Tex monofilaments were tightened as much as possible. Secondly, additional sutures were introduced along the weft at larger increments and of 1-2” span in order to pull together the sides of the mend even tighter and to further stabilize the area (fig.10).

These manipulations resulted in ends of broken threads close enough to be reconnected.

Existing overlaps of threads were secured by brush-applying a minimal amount of warm 3% sturgeon glue with a trace of Vinamul 3252, and setting the join with a warm needle point. The threads that were too frayed to connect as end to end attachment were joined by adding a piece of thread taken from the edge of the canvas. The very tight weave and the fact that the warp threads were significantly longer than the weft threads made fitting all threads difficult. It was essential to maintain them maximally twisted and under as much tension as possible and to very frequently check the proper alignment of all threads. Each finished section was weighted down to set and to restrict movement.

After mending was completed, the tear surface was minimally higher on the face of the painting. It was understood that this may have been caused by not using more adhesive to size and set the threads. In order to reduce the surface unevenness, the painting was placed on the table face up, a support platform was placed under the canvas and the area was weighted down. The procedure was repeated several times with good results. The last step was making sure that the weave surface in the area was even. Some additional adjustments were executed also...
on the front side of the mend — single threads were smoothed
and pressed down with a warm micro-spatula.

From that moment on the painting was placed in an upright
position (fig.11).

After having inspected the behavior and visual appearance
of the mend over a period of several weeks, and making sure
that it was sufficiently stable and sound, the painting was once
again placed face down and the Gore-Tex ends were secured
in place by double folding each one and twining it around
three preceding yarns of weave running perpendicular to the
direction on the monofilament.

Excess monofilament was clipped off leaving approximately
2” sections of loose reserve beyond the stitching. The painting
was returned to an upright position.

Inpainting
After the mending some parts of the paint layer were pres-
ent on the face side of the mend, but there were also areas of
paint loss (fig.13). Following the initial treatment outline, the
paint layer comprised of black acrylic paint drips and, varnish
droplets had to be “manufactured”.

Regarding the black paint, the goal was to obtain drops and
dribbles of shape, color and texture similar to the original
ones. Those varied from pinpoint size to ¾ inch in diameter,
and were of irregular shape with semi-gloss sheen and a wavy
texture. As far as driblets of varnish, in terms of size they were
distinguishable only under magnification, of various sizes, of
round shape, clear. Considering the spontaneous and natu-
ral quality of both drips and droplets, following the original
method as closely as possible in manufacturing them seemed
to be the best approach. The materials chosen for casting the
paint layer elements were acrylic paint, and acrylic mediums,
for their physical and visual similarity to the original paint
layer and because of the wide range of visual effects they
can produce.

In the case of paint


drips, the final “prod-
uct” was dependent on
three factors —color and
texture of the paint,
the substrate and the
method of application.
The choices for all of
them were made based
on prior tests (fig.14).

The paint mix was made of Lascaux Artists’ acrylic colors with
the addition of acrylic Lascaux Medium 2 Matt and black
pigment, made up to a consistency of an opaque wash. Two
substrates were a silicone (Silputty) mold taken from a cotton
canvas very similar to the original and silicone paper. The
paint was applied by spritzing with a brush and left to dry.

To obtain clear resin droplets, even parts of acrylic paint medi-
ums Lascaux Transparentlack Matte and Lascaux Transparent-
lack Gloss were combined with water to a low viscosity mix-
ture and spray-applied on a swath of polyester canvas, creating
a structure of clear microscopic spheres three dimensionally
attached to the nap of the canvas, similar to the one covering the surface of the painting.

In the inpainting process an individual drip of paint was delicately detached from the silicone mold and individually pre-matched by placing it on the area of the loss, in some cases cut to appropriate size and shape. Once selected, its back was moistened with a Methyl Cellulose 4000/Vinamul mixture and it was attached onto the area of loss using a warm micro-spatula. Pinpoint drips were applied by gently scraping the dry paint that had been sprinkled over silicone paper and applying it with a damp brush onto the designated area. The raw canvas was a sufficiently rough enough substrate for the dry paint particles to remain in place without use of additional medium or adhesive. Small bunches of fibers covered with acrylic medium droplets were removed with surgical tweezers from the mock-up canvas, applied onto the area of the loss and tacked into position with a heated micro-spatula.

All the above mentioned methods of visual compensation were used simultaneously, and the effect frequently checked at various angles and distances. When the entire area seemed adequately saturated with the paint elements it but remained slightly light in tone. This was rectified by brush-applying minute quantities of refined soil.

After the paint compensation phase was finished, the appearance of the tear varied minimally varied depending on the angle of viewing. It was indistinguishable from the surround when viewed from a forward or moderately angled position, and visible as a slightly brighter spot when viewed from an acute angle. Considering its minimal impact on the overall aspect of the painting and the fragile and exigent nature of the painting surface, the result was considered acceptable.

CONCLUSIONS
The main objectives of the treatment were met with only small modifications. It is assumed that the use of a high centipoise Methyl Cellulose, and of a limited amount of sturgeon glue with a minimal quantity of vinyl acetate/ethylene copolymer as adhesives, although initially ruled out, were peripheral and superficial enough to eliminate the risk of altering the original substrate as the adhesives age.
It is hoped that the Gore-Tex suture system will prove to be a reliable and stable structural reinforcement of the mend. Both the structural and the esthetic parts of the treatment of “Portland to Memphis” were to some degree experimental. Durability and effectiveness of the treatment will in part depend on a stable environment and conditions provided for the painting. At the same time, given the “superficial” nature of the treatment, and in fact thanks to it, most of its procedures can be relatively easily reversed or modified by means of gentle mechanical manipulation, should the need arise.

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MATERIAL INFORMATION

Gore-Tex® Suture, ePTFE nonabsorbable monofilament, PT-9, VV-6, 30”, 1:1 Needle-To-Thread Ratio
W.L. Gore & Associates, Inc.  
Medical Products Division  
P.O. Box 2400  
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(928) 779-2771  
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Methyl Cellulose Powder USP/FCC, 4000 centipoise  
Fisher Scientific  
2000 Park Lane Drive  
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Tesa Powerstrips® Large  
tesa tape, inc.  
5825 Carnegie Boulevard,  
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(800) 426 2181  
http://www.tesa.com/consumer/solutions/tesa_powerstrips

Silputty  
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The Emergence of Brazilian Abstraction and the Conservation of the Leirner Collection at the Museum of Fine Arts, Houston

The Leirner Collection at the Museum of Fine Arts, Houston (MFAH), was acquired in November 2007 and treatment began on the collection in October 2008. The collection has forty-four paintings that required assessment and treatment before two separate exhibitions, one at the Museum of Fine Arts and another in Switzerland, starting in September 2009. The paper discusses the art historical background of the Leirner Collection and the treatment that proceeded from October 2008 through May 2009.

The Collection of Adolpho Leirner, business man and textile engineer from São Paulo, Brazil, represents works of art from the very innovative period in Brazilian Constructivism: Concrete and Neo-Concrete Art. The collection began in 1961 with the initial purchase of a painting by Milton Dacosta, and grew for more than thirty years in the acquisition of sculptures, paintings, works on paper, posters and graphic materials. The collection represents fifty-six artists who have by now gained a recognition that they did not enjoy for much of the 20th century. The Leirner Collection emerged from a self-avowed, deep-seated passion for Constructive Art. In 1953 Adolpho Leirner went to England to study textile engineering and design. There he became acquainted with the International Constructivist movements of the first half of the 20th century developing a love for architecture, the Russian Constructivists, De Stijl, the Bauhaus and Art Deco. With Leirner’s return to Brazil, he was naturally drawn to Brazilian Constructivism. In the early 1960s he saw these works rejected as “outdated” when lyrical, informal abstraction and figuration in art were back in vogue. At this point he purposefully decided to collect Brazilian Constructive Art fully aware he was saving for posterity this singular moment in the history of Brazilian Art. To the extent that the history of the Brazilian Constructive movement has yet to be written, the Leirner collection fulfills the critical function of providing a foundation from which to establish the very field it aims to represent. Leirner did not limit his collecting to well-known avant-garde artists of the period, but included key harbingers of abstraction in Brazil as well as independent artists whose iconoclastic approaches to Concrete Art further amplified the already complex visual and theoretical parameters of the Brazilian Constructive Art project.

Dr. Mari Carmen Ramírez, Latin American Art curator at the Museum of Fine Arts, Houston says “the most outstanding feature of this collection is its focus and cohesion in representing a particular period and for this reason it is the foremost scholarly reference for this as yet little written history of the Brazilian Constructive Art movement.” Because the works range from the earliest manifestations of Geometric Abstractionism (1930 – Cicero Dias) to the experimental proposals of the São Paulo and Rio de Janeiro Concrete and
Neo–Concrete Art groups, the collection plays an important role in the dissemination of the Brazilian reinterpretation of Constructivism. Since the early 1990s works from the collection have been shown in more than 130 national and international exhibitions. The Leirner collection, to paraphrase Dr. Ramírez, “offers an opportunity for reassessing Brazilian and International Modernism. Displaying the collection in close proximity with other European, North American and Latin American artists who explored similar artistic and intellectual issues challenges historical classifications, abolishes automatic pigeon holing and annihilates the worn out assignations of ‘peripheral, derivative, or marginal’ to artworks that were more often than not only superficially studied.” Dr. Ramírez had long been interested in this collection and initiated talks towards its acquisition. Negotiations were finalized in May 2007 when Leirner selected the MFAH to house his collection. He found the MFAH a more advantageous home for his artworks due to the existence of the International Center for the Arts of the Americas (ICAA), part of the MFAH, presided over by Mari Carmen Ramirez. The ICAA serves as both a curatorial department and a research center. Its focus is the formation of a new collection of modern and contemporary art in all media by artists from Mexico, Central and South America, the Caribbean and Latinos based in the US. The center also emphasizes research culminating in major exhibitions, lectures and symposia.

After WWII innovative ideas in the arts in Brazil emerged with the economic boom and surge in modernization. There were extensive and intensive changes in technologies and their attendant alterations in life habits; for example skyscrapers, automobiles, radio, and television. The entire world after WWII was marked in all sectors of activity and thought by optimism that was cut short in the early 1950s by the conflict in Korea and the Cold War. But in Brazil, optimism would endure longer. While Europe was rebuilding what WWII had destroyed, in Latin America the plan was to build a new reality. In Brazil the Constructivist project in art and architecture went hand in hand with similar projects in the economic, political and social spheres, such as the emergence of the steel industry, an auto industry and the exploration of petroleum. In Brazil it was felt that everything had to be rethought such as strategies for economic development, the implementation of democracy and cultural projects. Art was to play an essential part and practiced for social purposes; an art accessible and comprehensible to all, not containing local or regional thematics, or excessive subjectivity. That pictorial art would be Concrete Art: a universal language of formal and geometric lines, substituting the cosmos for chaos, order for disorder. In the words of Swiss Concrete artist, Max Bill, a pivotal figure in the formation of the Concrete art movement in Europe and its emergence in Brazil, “it is better to represent man in his better possibilities instead of fragmented and chaotic.” This cultural and artistic explosion in Brazil produced Neo–Concrete art, a new realist cinema, the terse pure lines of precise architectural surfaces, new music and literature, and a new genre: Concrete Poetry. Well–known examples of this period of creativity were the inauguration of the sophisticated, utopian, futurist capital of Brasilia in 1960, the creation of the Biaxinial of São Paulo in 1951, and Bossa Nova, an offbeat musical genre with new syncopations and rhythmic accentuations sung in a contained voice, in an unaffected, natural singing style. The culmination in 1958, seventeen year–old Pelé. This event seemed to mobilize the country’s can–do mood and spurred then President Juscelino Kubitschek’s accelerated modernization program. These unprecedented achievements of modernization energized and motivated artists from São Paulo and Rio de Janeiro. They thoroughly embraced the legacies of Russian Constructivism, Dutch Neo–Plasticism and the Bauhaus. And despite the thirty year lag that separated them from these movements, they proceeded to transform the legacies into unique projects that centered first on different approaches to Constructivist rules and later, on the potential of non–figurative art to mediate between an individual’s relationship to his/her environment.

In an attempt to establish a tabula rasa and declare their independence from the art of the past, Concrete and Neo–Concrete artists avoided any reference to local artistic developments and instead positioned themselves as non–derivative proponents of the International Constructive art tendencies. Their insistence on this point led art historians to trace the beginnings of Constructive art in Brazil to Max Bill’s presence in the first São Paulo Biennial of 1951. However, the painter Cicero Dias, featured in the Leirner collection, counters the official narrative with his abstract works, dating as early as the late 1930s, by reinserting the debate over Brazilian Constructive Art into the context of the evolution of Geometric Abstraction in Brazil. The question of providing a spiritual or trans–subjective content to a non–figurative language – that is, how to transcend the game of formal relations and mere color that occupied painters Kandinsky and Malevich – was also taken up by Rio Neo–Concrete artists, Lygia Clark and Hélio Oiticica. This question acted as a catalyst in the 1959 formation of the Neo–Concrete movement by the Rio artists. The Concrete artists in São Paolo, such as Alexandre Wollner, remained faithful to the Concrete ideas: the exploration of formal and chromatic variations without seeking any transcen-
dence either symbolic or emotional. The goal was to discon-nect from all subjectivity and simply propose the pleasure of pure seeing as in the work of Waldemar Cordeiro. From a technical standpoint these works are distinguished by their use of commercially available industrial materials, with the paint manipulated into modular elements and an objective rational approach towards structure. Acting as a counterpoint, the Rio Concrete group was more interested in color and the roles of intuition and empiricism in the creative process as in the art of Ivan Serpa. The Rio artists, like Lygia Clark, by contrast, felt that the rationalism of the São Paolo group was excessive. Lygia Clark and Hélio Oiticica would eventually move beyond the two-dimensional limits of the canvas and introduce the participation of the spectator in the work of art which is the particular trait of Neo-Concrete art. In 1960 Hélio Oiticica explored the physical experience of color in a series of hanging painted wood constructions that compelled the viewer to walk around and move among the hanging pieces to discover color as both a physical body and an environment. Both Clark and Oiticica were fascinated by scientific theo-ries of the experience of the space-time continuum. Oiticica wrote, “Color and Structure are inseparable, as are Space and Time, and the fusion of these four elements I consider to be the dimensions of a single phenomenon.” In Lygia Clark’s Bicho, (Critter), 1962, the viewer becomes a participant and co-creator by manipulating the hinged metal plates into another configuration. Neo-Concrete Art not only produced artworks, but theories of art, such as the theory of the Non-Object – that is, the idea that an artwork, though materially conveyed, is not a thing, but a meaning. Neo-Concretism’s emphasis on reincorporation of the subjective dimension and elements of real time and space in the experience of the viewer-as-participant gave rise to daring innovations. In conclusion Neo-Concretism, the Brazilian interpretation of the Constructive project in art, was the first Brazilian contribution to a universal visual language. The artists from São Paolo and Rio de Janeiro of the 1950s-and 60s contributed a highly original chapter in the history of International Modernism.

What is obviously different and new in Brazilian Concrete art are the materials, which are essential to the message here. The spirit of invention appeared stylistically and also in the use of new materials. The new materials in the 1950s and 60s were polymers in varying forms including: alkyd paints and coat-ings, PVA emulsion house paints, acrylic paints, nitrocellulose modified paints and plastic-laminated composite wood panels. The artworks of the Leirner Collection were created with great optimism for the future and all things modern. Although these artworks were constructed of new materials they were housed in the old-fashioned manner. In Brazil, one lived with the windows open at all times and this meant that accretions from car fumes and industrial soot were deposited on these new surfaces. In many cases the non-artist materials used in these artworks reacted to both living conditions and accretions in ways that unexpectedly complicated treatment.

The painting conservation department of the MFAH received the Leirner paintings beginning in September 2008 and the delivery of the paintings was completed by mid-October 2008. The paintings were to be examined and treated by the painting conservation lab by June and September 2009, for two separate exhibits, the latter of which was to be in Swit-zerland. The MFAH conservation department is roughly ten years old and, during these early years, there has been an enormous amount of treatment completed by the conserva-tion staff. So, although the treatment of forty-four paintings in a year was a daunting prospect, it was not a challenge new to Andrea di Bagno, Chief Painting Conservator, and Maite Leal, Associate Painting Conservator.

As Assistant Conservator, Erica ESH James was placed in charge of all initial documentation, including writing condi-tion reports as well as starting the photographic documen-tation including UV-VIS and IR irradiation. As a recent recipient of an IMLS Leadership Grant, the department had purchased the Hasselblad Phase One Camera System with associated computer processing, lighting and printing tech-nology. With so many paintings to assess and treat, the most effective method of initial examination and reporting was to document the basic fabrication of each painting and then, as treatment proceeded, add further details that were noted before treatment, as well as details of analysis. During the initial examination and chemical spot testing for material identification, three main concerns emerged. For many of the paintings, including those by Lygia Clark and Hélio Oiticica, only general medium classes were assigned such as “enamel” or “commercial” paint. Second, the paint layers were often composed of a number of materials. Many presentation surfaces contained visible inclusions and often, presumed surface coatings were in fact exudates from the underlying paint layer. Finally, the substrates that the paintings were executed on were variable, including canvases with very uneven weave counts and Masonite boards, so that the condition of the paintings was seriously impacted by simply the inherent fabrication of the painting.

The primary supports were either a canvas-type material or hardboard. One of the most notable attributes of the canvases
was the fact that the thread counts were very uneven. It was not uncommon, for example, to find 10 more warp threads than weft threads per centimeter. Warp or weft threads often appeared to be two different fibers or, threads from two different lots of fibers. For example, the warp threads might be darker and thicker than the weft threads. In general, the fabric primary supports were generally very thin. In addition, many of these canvases were seriously warped on their auxiliary supports which were, more often than not, artist-fabricated strainers. As the strainer would warp the canvases, also vulnerable to moisture uptake being of variable weave and clearly unsized, would warp as well. The structural vulnerability of the paintings meant that sometimes, but not always, paintings had to be loose-lined and if the strainer was substantially warped (would not sit flush against the wall during exhibition) it had to be replaced. In all structural work, the utmost care was taken to preserve the original intent of the artist. A transparent blind lining material (available from Testa-fabrics in Switzerland) was used that was stiff and transparent enough to see signatures on the verso. If an auxiliary support had to be replaced it was saved, photographed, and the labels were removed and preserved for viewing on the back of the final backing board. Much discussion has been devoted to the preservation of original auxiliary supports. A severely-warped auxiliary support cannot be brought back into plane, especially the light-weight strainers that were originally not strong enough to handle the tension of the canvas. It’s retention in the original configuration jeopardizes the primary support, especially during travel, exhibition and the handling that a painting must endure during those periods. In addition, it is not the original intent of the artist to have a painting sit askew during display so when necessary, when required, the utmost care was made in the replacement of strainers. The ground layers varied from artist-applied to commercially-applied layers. The paint layers varied from the smooth, high-gloss surfaces applied by Hermalindo Fiaminghi to the very matte yet very stable and somewhat coarse black surfaces created by Lygia Clark.

On a painting by Hélio Oiticica, a much more traditional oil paint layer was encountered but even when a treatment of a paint layer seemed straight-forward, there could be issues with the surface coating. A surface such as that of Oiticica required the use of an emulsion to remove grime and debris either embedded in or underneath a matrix of synthetic or natural resins. That, combined with two campaigns of previous restoration, with wax retouches and fills, made for a complicated treatment. The effort to use the newest materials available created artworks that were absolutely current in design and revealed nothing, or very little, of the artist’s hand in its creation.

The following five paintings provide specific examples in how fabrication, intent and environment impacted treatment. The first painting “Puro e diagonal”, by Samson Flexor, was created in 1957 and treated by Erica ESH James. Grime from dirt, debris and soot at-least lightly permeated every portion of air space. For all the paintings, the first treatment concern was the removal of grime. The initial layer of grime was removed with saliva. A secondary layer of grime was removed with an EDTA chelating solution at a pH 8 and then, for the final, more stubborn layer of grime, a chelating gel containing methyl cellulose and citric acid at a pH 8.5 with the non-ionic surfactant Pluronic L-10 was used. It was cleared with saliva and then water. Following the initial application of EDTA and the gel, the secondary application of the EDTA solution swelled the final layer of grime so that it could be removed with the mechanical action of a brush and swab.

Virtual no. 14 was completed by Hermalindo Fiaminghi in 1958 and Andrea di Bagno, Chief Conservator, began treatment of the painting in February 2009. The painting had a dense layer of grime on the image as well as overpaint along the edges. Although readily swollen with the EDTA solution (pH 8), it was softened and then efficiently removed mechanically under the microscope with a small, rounded scalpel. The paint layer was designated as enamel early on by exhibiting galleries, however, analysis revealed alkyd paints were applied by the artist on a commercially-prepared board. The white background was identified as an ortho-phthalic alkyd. The matte grey layer contained a low proportion of alkyd medium compared to the pigment component while the red paint layer was very glossy. From a treatment standpoint, a complete cleaning was only achievable by working under magnification with a scalpel. On Planes on Modulated Surface, No. 5, artist Lygia Clark used ortho-phthalic alkyd paint with the addition of nitrocellulose paint. The white paint layer most likely contains titanium dioxide; the gray includes a mixture of carbon black with titanium dioxide and the black a carbon black with barium sulfate filler. The attempt in the creation of these works to develop a universal message is seen in the modernity of the materials. The lines were inscribed with the mechanical action of a brush and swab.
in sphere-like globules onto which, at a later date, wax had been rubbed. The wax was not removed as time constraints prevented a full removal. There were losses in all the colors and excessive overpaint throughout the surface. Gouache was locally applied through an airbrush to restore continuity and readability to the surface. The next painting is an untitled painting by Alexandre Wollner also completed in 1957. A graphic artist, Wollner completed the painting on a pre-fabricated board trademarked Duratex, a plastic-laminated composite wood panel. The originally white coating turned beige over time and the artist applied a black alkyd-based design layer including what was identified as muscovite filler. What is interesting here is that the filler was used solely as a bulking agent and, as it is transparent, imparted no color to the black design element. A surface coating was then sprayed on top of the paint layer during previous conservation, as visible in UVF photography. Untitled by Mauricio Lima was executed in 1962 in a, relatively speaking, traditional manner, with an oil paint layer on canvas. The grime and soot layer was removed in the first phase with amylase. A more tenacious layer of grime was removed with a NaOH pH 13 solution, rinsed with distilled water, and the wet surface dried immediately with cotton. The thick layer of wax that had been sprayed on over the entire surface was removed with heat from a hot air tool, Naphtha and mechanical action under the microscope along with the retouches covering black transfer marks. Because wax coatings were found on many of the paintings it was first believed they were housekeeping measures as the paintings conservation staff were informed that the collection had never been treated. However, in the retouching and abrasion, there was evidence of prior conservation measures.

As the conservation of the Leirner Collection is carried on in the painting conservation laboratory, the notion that understanding the context in which a collection was created and how this relates to understanding its conservation has become even more apparent. Understanding that the “materials are the message” leads to insights into why a particular material was chosen and why the artist makes certain choices. This is especially relevant here as any addition to a canvas, that could appear not original, could in fact be chosen for a very specific reason. As the conservation continues on, more insights will be gained and hopefully continue to contribute to our understanding of this very innovative time in Latin American art history and this collection in particular.

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American Painters and Varnishing: British, German, and French Connections

ABSTRACT

A study of American painters' techniques sheds light on both American and European varnishing practices. Painters who described European varnishing techniques (as well as their own) include John Singleton Copley, Gilbert Stuart, Thomas Sully, and Rembrandt Peale. In the second quarter of the nineteenth century, some American painters applied overall 'toning' layers to their paintings in the belief that contemporary British painters and the Old Masters did this, while some Americans experimented with a bewildering variety of different varnishes. After 1860, although there are fewer extent notebooks containing detailed recipes, techniques remained varied. John Singer Sargent and Frank Duveneck differed on the proper gloss and thickness of a varnish in 1881. By the 1880s, some Americans influenced by French Impressionism chose to leave their paintings unvarnished altogether, while others continued to varnish—with a great variety of different techniques—well into the twentieth century.

SOURCE DOCUMENT

The Changing Faces of Eva Callimachi Cartagi: A Portrait by Henri Fantin Latour

ABSTRACT

The Portrait of Eva Callimachi Cartagi, painted in 1881 by Henri Fantin Latour is a feature work of the Kröller-Müller Museum’s collection in Otterlo, the Netherlands. The painting arrived at the Getty Museum for conservation treatment consideration in 2003. Such was the extent of the damage of the painting that it was considered to be a portrait without a face.

The disfigurement to the sitter’s face appears to have been caused by large drying cracks which were presumed to result from the use of bitumen. This damage led to several past conservation campaigns that may have exacerbated rather than solved the aesthetic problem. These former treatments allowed for the changing nature of treatment methods and of ethics within the field of conservation to be brought into discussion.

INTRODUCTION

In the field of paintings conservation, it is a prerequisite to attain as much information as possible about the work prior to carrying out any treatment. This research is integral in gaining a deeper understanding of both the artist’s intention and of that which the work has experienced during its life time after being painted.

Investigation into the Portrait of Eva Callimachi Cartagi, painted by Henri Fantin Latour in 1881 revealed a painting that had, in parts, degraded to such an extent that it could no longer be exhibited. In an attempt to render the image more presentable, the painting underwent at least one campaign of conservation and restoration treatment. It is this action that gives rise to an interesting debate over the changing nature of conservation treatments and ethics of a profession that plays an important part in attempting to preserve one’s cultural heritage.

A HISTORY OF THE PORTRAIT

The portrait came into the Kröller-Müller collection in 1913 when Anton Kröller bought it for his wife Helen Müller along with a painting by Vincent van Gogh as a gift for their 25th wedding anniversary. [1] The similarities between the appearance of Eva Callimachi Cartagi with that of Helen Kröller-Müller are quite clear (figs. 1 and 2). The two sitters of similar age stand in a statuesque pose, both dressed elegantly in a white dress; an arrangement of flowers can be found in the bottom right corner. This portrait is a painting that held special interest for Helen and had an important place in her extensive collection of art works. It was given a prime location in her house, Groot Haesebroek, Wassenaar in The Hague, (fig. 3) which was often frequented by art lovers and artists alike. [2]
Eva Callimachi Catargi was not an artist herself but did indeed partake in art classes, Fantin has depicted her in a painting entitled *The Drawing Lesson*. [3] She was a member of the elite artistic society in Paris in the second half of the 19th century being the daughter of Nicholas Callimachi-Catargi, Rumanian minister plenipotentiary to Paris, cousin to Prince Alexandre Callimachi, Prince of Samos and former Turkish ambassador to Paris and later wife to Russian diplomat Alexandre de Basily. [4].

It is fortunate that a complete set of good quality black and white photographs of this painting were taken prior to treatment, probably around the late 1960s early 1970’s (as that is when the first record exists) showing the front and back of the painting (figs. 4a and 4b). The image of the reverse of the painting shows the original stretcher on which the name Mme de Basily rather than Eva Callimachi Catargi can be found on a label indicating that the portrait was probably carried out prior to her marriage to Alexandre de Basily, hence its current title. [5]

**PHOTOGRAPHIC DOCUMENTATION**

The black and white before treatment photographs thought to be from the same time include details of the portrait’s head (figs. 5a and 5b). The fact that these photographs were taken and indeed saved is fortuitous as they provide us with information about the condition of the portrait before conservation treatment was considered that would otherwise not have been available to us.

Confounding these images is a letter from the Kröller- Müller museum’s archives. It was written by M.N van Loon on behalf of Eva’s daughter-in-law, Mrs de Basily, ‘a philanthropist and patron of the arts.’[6] Dated 16th August 1967, the letter describes a visit she made that summer to the Kröller-Müller museum to see this painting in particular. It describes Mrs de Basily’s disappointment when she could not find the portrait of her mother-in-law hanging in the museum’s galleries. She was told that the work was un-exhibitable and that it was being stored in the depot. She was permitted to enter into the

![Figure 3. Photograph of Helen’s salon in Groot Haesebroek, in Wassenaar in The Hague dated by the Kröller-Müller Museum 1931-1937.](image)

![Figure 4a. (left) Photograph presumably taken in and around 1968 showing the front of *The Portrait of Eva Callimachi Catargi* before restoration was carried out.](image)

![Figure 4b. (right) Photograph presumably taken in and around 1968 showing the back of *The Portrait of Eva Callimachi Catargi* before restoration was carried out.](image)

![Figure 5a: Detail of the sitter’s head presumably taken in and around1968 of *The Portrait of Eva Callimachi Catargi*. It is thought this detail shows the painting before invasive treatment was performed by Susijn](image)

![Figure 5b: Detail of the sitter’s head presumably taken after treatment by Susijn in 1973 of *The Portrait of Eva Callimachi Catargi*.](image)
depot to see the work and it is her description of the work in general and the nature of these cracks in particular that later proved to be integral in helping us gain an understanding of the photographic documentation made. She writes:

‘…. the painter used bitumen in his work. This has swollen and formed a thick black crust that has cracked and curled up. The result renders the original intent of the painter largely unrecognizable.’

She goes on to write that she had spoken to a restorer in the Rijksmuseum, Amsterdam who mentioned that treating this problem ‘is not entirely out of the question.’

‘Mechanical action on its own will not work, but the hardened bitumen can be removed from the painting once it is softened (presumably by heat) and removal can then be carried out with knives.’ [7]

Furthermore, the portrait of Eva was recorded in the museum’s catalogue as being under restoration since 1968. The text writes that ‘...(the cracks which have appeared in the hair and in the dark parts of the neck and dark parts of the face are due to an application of bitumen)... an attempt will be made to remove the bitumen as far as possible and to replace it by paints of lasting quality.’ [8] It was Mme de Basily, in the same letter from 1967, who offered to finance the restoration of the painting.

CONSERVATION HISTORY:

A written source suggests that the portrait was treated in 1969 by a restorer called Luitsen Kuiper before undergoing a recorded conservation and restoration treatment of the work in 1973 by J.J. Susijn. [9] Susijn also reports removing the varnish and lining the painting with a wax-resin adhesive of Dammar, beeswax and turpentine. Extensive retouching of the face, in particular the eyes, lips and chin area was then carried out. The materials used for the retouching were not noted and no record is made of how the cracks in the sitter’s face themselves were treated. It is thought that he filled the large traction cracks with a synthetic resin, possible a ketone resin (Talens), over which he then carried out his retouching campaign.

On closer inspection of the photographic documentation, thought to have been carried out prior to treatment, two details taken show an obvious difference in the appearance of the sitter’s face. The detail in Figure 5a taken of the face prior to treatment shows raised cracks rendering the face largely unreadable. This ‘crusty’ and cracked looking surface is located in the areas of shadow in the sitter’s face (i.e. the eyes, the mouth, under the nostrils, the hairline and on the proper left of the sitter’s neck). In the black and white photograph the wide drying cracks appear dark. The detail seen in Figure 5b, shows a much more readable image of the face. The eyes are visible and the drying cracks now appear white in the black and white photograph. The reason for this remained something of a mystery. It was initially thought that the former detail may have been taken in raking light; therefore suggesting the other detail was taken in normal light. However, closer inspection of the images in combination with the description of the painting in the letter written by Eva’s daughter-in-law assisted us in finding a solution to the very different appearance of these two details.

The description of Eva’s daughter in law of the procedure for treating paintings with bitumous cracks by heating up the surface and removing the damage with knives made us look at the details in a new light. In addition, the very flat upper layer of all the paint samples taken from the damaged areas made us question the treatment of the cracks that may have been carried out, but was not recorded. Post prints from IIC Netherland symposium held in December 1990 and entitled ‘Retouching in the Restoration of Artworks’ provided us with insightful information concerning this aspect of the treatment of the disfiguring cracks. In the transcript of the symposium, the restorer J.J. Susijn is recorded as saying the following about treating works with bitumous cracks:

‘Generally speaking, it’s just the wrong use of materials; and this will eventually age badly. It turns out in some cases that by just leveling the surface removes the most disturbing effects. I did that with a portrait of Fantin-Latour in the Kröller Muller Museum. I just smoothed out the surface to the same level as the surrounding layers – not very nice - but it gave an acceptable result; it was better than doing nothing. That is the only time I have done something about this problem most of the time I have just left it.’ [10]

It became clear that the ‘thick black crust that has cracked and curled up’ [11] on the hair and shadowed areas of the face had indeed been scraped off by Susijn, probably in 1973. The detailed photographs now made sense: one was a normal light detail of the head of the sitter prior to the treatment of scraping off the uppermost layer(s), the other a detail after this treatment. As shocking as this seems to us now, it cannot be denied that when we look at the two details of Eva’s face prior to and after this invasive treatment was carried out, her appearance has indeed improved.
SCIENTIFIC INVESTIGATION AND POSSIBLE EXPLANATIONS:

What still remained unanswered, however, is what caused these incredibly disturbing crack patterns to develop. Samples were taken from the damaged brown areas in order to determine if there were any elements present which could indicate the presence of bitumen as previously thought or of a pigment or siccative which could have contributed to the formation of these cracks. A photograph of the work taken by Brame & Laurenceau in 1909/10 shows the absence of cracks. [12] It can thus be deduced that the cracks did not begin to appear until at least 30 years after the portrait was painted by Fantin. The painting was likely to have been in the Kröller-Müller Museum collection when the cracks began to form.

XRF analysis revealed elevated cobalt levels in the hair, which were confirmed by SEM/EDS analysis to be due to cobalt violet pigment (cobalt (II)-phosphate [CO3(PO4)2]). [13] The elements present in the brown areas are similar to those found throughout the painting with the exception that there is a higher amount of cobalt present in these areas than in other sites examined. [14] This could be an indication of a greater abundance of a cobalt-containing pigment. A high concentration of siccative could cause rapid drying of the paint layer and contribute to the ductile cracking of the paint.

Examination of the cross sections of the paint samples taken from the hair showed some interesting results not only with regards to their composition, but also with regards to their appearance. [15] There are many layers in both of these sections. The lower layers appear to be more intact while the upper layers appear somewhat mixed possibly indicating some wet-in-wet technique or softening during lining. The top layer is very flat which was initially thought to have been as a result of the 1973 lining. The restorer said that he ‘levelled’ the surface of the painting but did not describe how he did this. We can only rely on Mme de Basily’s account of how she heard of the paint layer being softened and then scraped off with knives as a solution to treating ‘bituminous’ cracks such as these. Indeed closer inspection of sample # 4 in UV light does reveal a fluorescent layer that does seem to have been sliced rather than squashed by the lining (fig.6). In both sections, the overall paint layer is quite thick (40-50µm) while the individual layers are very thin (< 5µm). There are highly fluorescent, lightly pigmented layers interspersed between more pigmented, less fluorescent layers.

Media analyses (FTIR, GC/MS and PyGC/MS) were carried out in attempt to ascertain the influence of the binding medium on the possible development of the cracks. In some of the samples the layers are very thin so isolation of the individual layers for GC/MS and PyGC/MS analysis was not always possible. [16]

Reflectance FTIR was carried out on mounted cross-sections in order to try to obtain information about individual layers and especially to determine if the medium composition of the medium rich slightly pigmented layers was different from the more pigmented layers. [17] The analysis of various cross-sections indicated the presence of natural resin/oil mixtures in all of the various fluorescing layers. The spectrum from the investigation of the resin matched closely with references dammar type spectra. The layers contained varying concentrations of resin and oil. The medium rich slightly pigmented layers appeared to contain somewhat more oil than the more heavily pigmented layers.

In order to confirm the materials used by Susijn in his 1973 report and to understand the results from binding medium which may have been tainted by the lining adhesive GC/MS analysis was carried out on the lining adhesive. It was identified as beeswax mixed with dammar resin with very little pine resin or Venice turpentine and some oil, which was in keeping with Susijn’s report. The composition of the binding medium for the paint layers was mostly linseed oil, mastic resin, beeswax and some pine resin or Venice turpentine. No bitumous materials were found in any of the samples. It is impossible to irrefutably demonstrate whether the beeswax originated from the lining adhesive or the paint medium. Since the dammar did not penetrate the ground from the lining adhesive it is possible, but not verifiable, that the beeswax did not penetrate the ground or the paint layers as well.

Figure 6: Cross-section #4 taken from the right side of the figure’s head. Ultraviolet illumination. (magnification x20)
The concentration of mastic for the samples from the hair and neck were higher than for samples taken from the rest of the painting. In the hair, the high concentration of resin could cause contraction of the paint layers when drying. Additionally, XRF analysis indicated that the amount of cobalt in the hair followed by the brown shadows was higher than for the samples from the rest of the painting. The cracking in the hair is most likely a result of the elevated concentration of resin (fig. 7).

It has been reported that Fantin is known to have used Roberson’s Medium which is a mixture of one part drying oil, one part copal varnish and two parts ‘Genuine’ mastic varnish. To this was added one ounce of oil of spike’. [18] Fantin wrote to his friend and fellow artists Otto Scholderer, dated July 1880 and stated that ‘to dry them (his paint layers?), I always use Robertson Medium (sic)’. [19] Organic analysis showed that no copal resin was detected and that the binding medium appears to be more similar to that of megilp, a mixture of oil and mastic varnish or a beeswax/mastic varnish/oil medium, both of which have been documented as artist’s materials in the 19th century. [20]

The elevated levels of resin in the neck may be due to the many translucent layers applied in between the paint layers (figs. 8a and 8b). XRF did not indicated elevated levels of cobalt. The cracking in the neck is sharp edged, rather than ductile, as is seen in the hair. This cracking may be due to a combination of mechanics (stiffness of many layers) with the rapid drying of the resin.

The definitive cause of these drying cracks cannot be given, but there are strong indications that it may have been a combination of high levels of resin, the possible development of fatty acids as a result of the presence of cobalt phosphate minerals and artist’s technique.

CONSERVATION TREATMENT

In light of the research carried out, we were able to provide possibilities to how these cracks might have developed. However, a decision concerning the restoration of the painting still had to be made. The 1910 photograph from Brame and Laurenceau played an important part in determining whether or not treatment should go forward.

When comparing the sitter’s face in the 1910 photograph with the current face of the sitter it was clear that the expression of her face had slightly changed. Reconstruction of the face by Susijn in 1973 had been carried out without this valuable source.

After much discussion in the paintings department between conservators and art historians it was decided that the 1973 restoration could indeed be improved. The lighting of the galleries in the Kröller-Müller museum is not sympathetic in allowing the painting to be readable as it comes from above throwing a reflected light on the portrait showing quite hor-
rific surface deformations which are further rendered unreadable as the resin used by Susijn had yellowed substantially (figs. 9 and 10).

In an attempt to overcome this, it was decided to carry out a similar, yet different, approach to that carried out by Susijn in 1973. Similar, in that in order to make the sitter’s face readable, the wide drying cracks could be filled and the lost areas of the face reconstructed such that the and that the painting could be exhibited in the galleries of the museum; different, in that the expression would more closely resemble that of Eva’s based on the 1910 photograph and the choice of more stable materials.

The Talen’s varnish and the retouchings were very easily removed with xylene. An isolation layer of Regalrez 1094 (50% in benzene w/v) was applied to the painting to isolate the fills. [21] This layer succeeded in filling in those minute cracks that were visible between the fill and original surface interface. The large gaping cracks were filled with a mixture of a stable thermoplastic synthetic resin and chalk (Mowiol 4-88 (a poly(vinyl) alcohol 88% hydrolyzed) was used as a binder. [22] After the cracks were filled and textured, the base retouching was carried out using gouache employing an enlarged image of Eva’s face from the 1910 photograph to allow for a more accurate reconstruction. After an isolation layer of Regalrez 1094 (50% in benzene w/v) was applied to the now coloured fills, the final glazes were added using Gamblin Conservation colours. [23] The 1910 image permitted delicate contours to be imitated; the subtle changes in tones and colours were achieved by close and careful examination of the adjacent original paint layers. Multiple thin coats of Regalrez 1094 (25% in Shellsol D-28, w/v) were then applied.

Figure 9: Reflected light detail of the sitter’s face from The Portrait of Eva Callimachi Catargi by Henri Fantin-Latour (2005)
to the painting using a spray gun to even out the gloss of the retouched image with that of the rest of the painting.

CONCLUSION:

The decision to proceed with the restoration of the painting was the result of looking at the function of the work for its original purpose – a portrait of Eva Callimachi Catargi – a work bought by Mr Kröller for his wife and holding an important place in the museum’s collection. Taking into account its conservation history we could see that an attempt was made by the conservator to also achieve this aim. The methods employed in order to make this possible can now be seen as being extremely invasive. It cannot, however, be denied that the treatment could have been seen as being something of a success. The work was again readable and could hang in the galleries to be appreciated for forty or so years.

In essence, the current approach taken only thirty two years after its last restoration was not that dissimilar, it was clear that the original image of the artist had been lost and in the words of Gerry Hedley we were put in a position to ‘construct a new relationship between the artist’s original intention, the present work and the passage of time’. In doing so an effort was made to ‘establish a coherent relationship with a changed work of art’ by taking into account the importance of the portrait within the Kröller-Müller Museum and accepting that the ageing of the materials used by the artist had ‘serious consequences for overall pictorial unity.’[24]

The Portrait of Eva Callimachi Cartagi is one that shall remain a damaged work, but it is hoped that it is now a portrait whose face is more in keeping in its reconstruction with that of the Eva Callimachi Catargi’s and can again be hung in the galleries seen in a new light and be appreciated by those who are fortunate to visit the Kröller-Müller Museum in future (fig 11).

ACKNOWLEDGEMENTS

Thank you to the Members of the Paintings Conservation Council of the J.P. Getty Museum for their financial support and to the Directors of the J.P. Getty Museum and the Kröller-Müller Museum, William Griswold and Evert van Straaten. Special thanks to Mark Leonard, Scott Schaefer and The Paintings Conservation Department at the Getty Museum. The staff of the Kröller-Müller Museum, especially Piet de Jonge and Luuk van der Loeff. We are also grateful to the Getty Conservation Institute for carrying out insightful analyses: Karen Trentelman, Joy Keeney, Herant Khanjian and Joy Mazurek. Thanks also to Julia Armstrong-Smith from Collecting and Provenance department, to Michael Smith and Jack Ross from Photography and Imaging services at the J.P. Getty Museum. Thank you also to Teio Meedendorp and to Brame & Laurenceau for sharing their knowledge and source material with us.

This article is dedicated to Ana who remains sorely missed.

ENDNOTES

1. On 15 May 1913, Anton gave Helen the portrait of Eva along with the Sorrowing Old Man by Van Gogh. The Fantin painting cost considerably more than the Van Gogh indicating something of the popular taste at the beginning of the 20th century (personal communication with Teio Meedendorp).

2. This image is from the archives of the Kröller-Müller Museum dated 1931-37 after Lange Voorhout residence closed and before the museum in Otterlo opened. Information on the location of the house was kindly provided by Teio Meedendorp.


5. An image of the reverse of the painting shows the original stretcher on which a label from the art dealers E.J. van Wisselingh & Co., 23 &27 Spui. It shows the title of the painting as being ‘Portrait of Mad de Basily’.

6. As quoted in the letter by M.N. van Loon and found in Kröller-Müller Museum archives.

7. Ibid. This letter was translated by Bertine Centen, administrator at the Kröller-Müller Museum.

8. Rijksmuseum Kröller Müller et al., Paintings of the Riksmuseum Kröller Müller. 1969. There is no evidence showing that the material used was bitumen resulting in the disfiguring cracks. This was one of the questions to be
answered in conjunction with the Conservation Scientists at the GCI.


10. IIC Nederlands symposium Aesthetic en technisch: Het Retoucheren in de Restauratie van Kunstwerken, 11th and 12th December 1990 held at the Jan van Eyck Academie. Vol 7(10)

11. This is Madame de Basily’s description of the paint layer on the sitter’s face as written in her letter of 1967.

12. Thanks to Brame & Laurenceau. This image was probably reproduced in the Adolphe Julien biography of Fantin Latour, published in 1909, four years after the death of Fantin.

13. XRF was performed with a Jordan Valley EX-3600/6600 XRF Spectrometer equipped with a Rhodium target x-ray tube at 50 kV, no filter and 200µA in air. Each spectrum was collected for 100 seconds. SEM/EDS was carried out on the Getty’s Philips XL30 ESEM-FEG with Oxford INCA EDS system and run in standard SEM (HiVac) mode.

14. That is to say the major elements present are Pb, Cu, Zn, Fe, Co and the trace elements present are Cr, Ca, Mn. See The Getty Conservation Institute, Museum Research Laboratory Analytical Report Accession # L2004.80 6th July 2005. pg 6

15. Samples were mounted in Technovit 2000 LC resin and cured in UV light. The samples were exposed and polished by dry polishing with various grades of Micromesh. Samples were examined without cover slips or solvent. The analysis of the layer structure was undertaken with dark field optical and ultra-violet (UV) microscopy. Analysis and photography was carried out on a Leica DN400M microscope equipped with a DFC 480 digital camera and a cube for fluorescence.

16. Thanks to Joy Mazurek from the GCI who carried out the media analyses.

17. To analyse the layers in cross-sections, Herant Khanjian carried out reflectance FTIR on the Getty’s Thermo Electron FTIR microscope.

18. The recipe for Roberson’s Medium was found in a letter dated 1868. The drying oil was made by ‘boiling copal again with extra Red Lead and Litharge’ as quoted in Carlyle, L., The Artist’s Assistant, pg 128.


21. Regalrez 1094 is a hydrogenated hydrocarbon low molecular weight resin.

22. Mowiol 4-88 is considered to be a stable material that remains easily soluble in water with ageing. Furthermore, the handling properties are conducive to this type of damage (shallow, wide cracks surrounded by a surface that exhibits minute textural changes). Mowiol 4-88 can be thinly applied and accurate textures can be achieved to allow for the successful re-integration of the cracks into the painted image. A binding medium of Mowiol 4-88(10% in distilled water w/v) was mixed with calcium sulphate and used as the filling material.

23. Gamblin Conservation Colours are made from a low molecular weight binder. Gamblin Conservation Colors are made from Laropal A-81, mineral spirits, and lightfast pigments. Alumina hydrate is added to the modern organic colors to adjust tinting strength.


REFERENCES


Ormond and Arslanoglu *The Changing Faces of Eva Callimachi Cartagi: A Portrait by Henri Fantin Latour*  


Riksmuseum Kröller Müller et al., *Paintings of the Riksmuseum Kröller Müller*. 1969  

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Devi graduated from Trinity College, Dublin in 1993 and began her training in the Masters programme in the Conservation of Easel Paintings at the University of Northumbria at Newcastle, UK. She then spent two years at the Hamilton Kerr Institute, Cambridge, UK before accepting a position at the Stichting Kollektief Restauratie Atelier in Amsterdam.  
In 2001, she began to work on primarily 19th century paintings at the Kröller-Müller Museum, Otterlo before taking a position on the renovation of the 19th century galleries at the Victoria & Albert Museum, London. She returned to the Kröller-Müller Museum to work on several projects during which time she was accepted as a guest conservator at the Getty Centre in 2005. She has been working as a paintings conservator at the Van Gogh Museum since 2005 and is involved in a large scale project carrying out in depth research into the materials and techniques of Vincent Van Gogh and those of both his Dutch and French contemporaries.  

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Julie Arslanoglu is an Associate Research Scientist in the Department of Scientific Research at the Metropolitan Museum of Art. She obtained degrees in organic chemistry at the University of Michigan, Ann Arbor and at The Pennsylvania State University. She then joined the National Cancer Institute at the National Institutes of Health, Bethesda, Maryland followed by the Biochemistry Department at The University of Texas, Health Science Center at San Antonio. After a pre-program Fellowship at the Smithsonian Museum Conservation Institute, Washington, D.C. she obtained a Post-graduate Diploma in the Conservation of Easel Paintings from the Courtauld Institute of Art, London where she also volunteered in the science departments of the Tate Gallery and the National Gallery of London. After graduation she joined the Victoria &Albert Museum, London, Science Department as a Project Scientist. She returned to the United States as a Mellon Fellow in Paintings Conservation at the Balboa Art Conservation Center, San Diego, CA where she completed research projects at the Los Angeles County Museum of Art and at the Getty Conservation Institute. She then joined the Museum Research Laboratory in the Getty Conservation Institute where she was Assistant Scientist before joining the Metropolitan Museum of Art in 2006  

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Thermal Mechanical Transitions in Artists’ Oil Paints and Selected Conservation Materials: a Study by Dynamic Mechanical Analysis (DMA)

ABSTRACT

Thermal softening transitions young artists’ oil paints were measured using the instrumental method of Dynamic Mechanical (Thermal) Analysis. Data on the glass transition, $T_g$, are reported for around thirty paint films, including proprietary artists’ colours and custom-made paints composed of single pigments, without driers. The paints vary markedly in their mechanical properties, from soft and flexible at room temperature to stiff and brittle: the range of glass transition temperatures observed for cured/dried films is -2 to 45ºC depending on composition. Changes in $T_g$ occurring during the early stages of paint drying/curing are reported, as are changes caused by mild accelerated light ageing. Many of the paints tested showed a distinct transition in mechanical properties in the ambient range, but most of the fully-cured lead-white-containing paints, and some other whites, showed only a weak transition in this range; the dominant thermal transition for these paints was above 75ºC.

A postscript includes a comparative summary of $T_g$ values obtained by DMA and by Differential Scanning Calorimetry on selected oil paints and selected acrylic and vinyl acetate polymer dispersion products.

INTRODUCTION

Easel paintings are complex structures which respond dynamically to external factors such as changes in relative humidity or temperature, or an applied force. It is now well understood that temperature and relative humidity changes, especially, subject the various layers of the painting composite to internal strains and to consequent stresses neither of which are usually uniformly distributed across or within the object (Mecklenburg and Tumosa 1991b). How the paint and ground materials respond to these various stresses is effectively governed by their intrinsic physical characteristics. As Hedley et al. 1990 observed “Oil paint films exhibit a wide range of mechanical properties...”, a fact which has been well demonstrated by the large body of research on this subject, including the studies of Mecklenburg and co-workers using the method of uniaxial tensile testing Mecklenburg and Tumosa 1991a). Michalski, 1991 provided an excellent distillation of the state of knowledge up to the early 1990s pertinent to understanding of the mechanical behaviour of paintings and of the paint with which they are made.

An important element of Michalski’s discussion was consideration of the visco-elastic nature of many of the organic components of the painting composite, including paints bound with drying oil. Without using the term ‘visco-elasticity’ per se, Michalski described some key features of this physical characteristic, perhaps the most important of which was the variation in effective stiffness of oil paint as a function of temperature. His interpretation indicated that, like many thermoplastic polymers, despite being a cross-linked and filled system, dried/cured oil paint shows a distinct change in physical condition from ‘glassy’ to ‘leathery’ and, eventually, ‘rubbery’ behaviour as temperature is increased. In other words, oil paints show a glass/rubber transition which is characterized by a glass transition temperature ($T_g$) (Schilling 1989). Essential features of this kind of physical behaviour are that, in the transition region, the modulus (stiffness) of the material changes quite markedly within a relatively narrow range of temperatures, and above the glass transition temperature the material may show a greater component of viscous, liquid-like character. Another important element of Michalski’s discussion of the visco-elastic behaviour of painting materials was what is known as ‘time-temperature equivalence and superposition’: namely, that a material will behave similarly – that is,
with a more glassy response - if subjected to either a decrease in temperature or a more rapid application of force, and vice versa (Ward and Hadley 1993). Essential points that must be borne in mind when considering the \( T_g \) are first that it must be regarded as a range of behavior rather than as a single point, and secondly the \( T_g \) value obtained for any given material is dependent on the method and conditions used to actually measure it.

Rather surprisingly, given the considerable body of research that has been carried out into the mechanical properties of artists’ oil paints, the issue of \( T_g \) has received relatively little explicit consideration in terms of experimental study. McGlinchey, 1991 is one of the few studies which has addressed this topic directly: in this case Differential Scanning Calorimetry (DSC) was the analytical method employed. In some respects, the scant collection of data that does exist presents a picture somewhat at odds with subjective understanding of this material. Michalski collated and interpreted data on stiffness/temperature relationships of oil paints reported in a variety of published sources. The “spotty collection of data” he obtained was sufficient “to piece together the glassy/rubbery transition of oil paint” (Michalski 1991: 229). The overall conclusion of this analysis was that “the fundamental glass/rubber transition for oil paint starts near \(-30^\circ\text{C} (-22^\circ\text{F})\) and ends before \(0^\circ\text{C} (32^\circ\text{F})\) for linseed, walnut and poppy oil, with or without pigments, with or without aging.” The \( T_g \) of oil paints - even aged paints - was understood, then, to be well below room temperature: that is, at room temperature they would be in the rubbery/leathery condition. More recently, it has been suggested by Mecklenburg and co-workers (Mecklenburg and Tumosa 2001; Erhardt, Tumosa, and Mecklenburg 2005) that a properly prepared, fully cured oil paint will be flexible and will remain so even after long periods of ageing [1]. Whether this observation suggests a \( T_g \) below room temperature is unclear: a resilient polymeric material may still be flexible as a thin film even if its \( T_g \) is well above ambient: poly(styrene) is a good example. Nevertheless, the view that oil paints, even those which have been appreciably aged, will have \( T_g \) well below room temperature remains difficult to rationalize with the usual subjective experience of old paint which, in many instances, appears to behave in a brittle, glassy manner.

Whether a paint is in its glassy or rubbery/leathery condition at room temperature has important implications for the way the material responds to stress and, crucially, to the conditions under which it fractures. In the glassy condition, the issue of stress cycles and fatigue will, for example, become far more significant.

**Dynamic Mechanical Analysis (DMA) of artists’ paints**

Theoretical and experimental treatments of visco-elasticity have derived vector-based descriptors of mechanical properties in terms of complex modulus \( (E^*) \), storage or elastic modulus \( (E') \), and viscous or loss modulus \( (E'') \), where \( E^* = E' + iE'' \) (Sepe 1998). More usually, this relationship is expressed as \( G^* = G' + iG'' \) where the \( G \) terms represent the corresponding shear moduli of the material. A further useful parameter, \( \tan \delta \), is the ratio \( G''/G' \) (Gearing 1999). The most common DMA test is a thermal scan during which changes in the parameters of \( G', G'' \) and \( \tan \delta \) are measured as the temperature is increased at a set rate. The temperature at which any thermal transition occurs will depend on the frequency of the applied periodic stress. Conventionally, the temperature at the peak in the \( \tan \delta \) trace at 1Hz is taken as the \( T_g \) of polymers (Duncan 2008; Gearing 1999: 509). Typically, the \( T_g \) value determined by the 1 Hz \( \tan \delta \) peak using DMA will be higher than the \( T_g \) obtained for the same material by Differential Scanning Calorimetry (DSC) (see ‘Postscript’ below). The difference will usually be in the order of 15–20°C. A comprehensive critical overview of the determination of \( T_g \) using DMA is provided by Chartoff, Weissman, and Sircar 1994.

The typical output of a DMA thermal scan is shown in fig.1 which shows the glassy/rubbery transition of a typical thermoplastic polymer, here Plextol™ B500. Note that, for

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**Figure 1.** DMA thermal scans showing storage modulus and \( \tan \delta \) traces for Plextol™ B500 as free film, Plextol™ B500 supported on polyester film, and polyester film alone. The overall pattern of the glass transition of Plextol™ B500 is very similar whether supported on polyester or unsupported. The polyester film itself is thermally stable across this temperature range: it shows very little change in modulus, and the \( \tan \delta \) values are near zero.
Phenix Thermal Mechanical Transitions in Artists' Oil Paints and Selected Conservation Materials: a Study by Dynamic Mechanical Analysis (DMA)

this material, the modulus diminishes by almost two orders of magnitude across the glass transition region and the value of tan δ (1Hz) measured at the glass transition is high (> 1.0); the T_g is around 21-24ºC.

The glassy-rubbery transition in oil paints might be expected to be somewhat different in character and magnitude than for a conventional thermoplastic polymer. Depending on the formulation, artists’ oil paints will contain a cross-linked oil network. Cross-linking is known to influence the thermal mechanical behaviour of materials according the schema shown in fig. 2. The effect of cross-linking has been demonstrated, for example, in acrylic artists’ paints by Ormsby et al 2006 using DMA (see their figs. 3 and 4). The T_g shifts to higher temperature as a consequence of thermal ageing/cross-linking. For a tightly cross-linked system, the change in modulus (stiffness) across the glass-rubber transition will be relatively small in magnitude compared to system with low cross-link density. Oil paints are also a filled system in the sense that the organic binder phase is filled with pigments and other inerts. The influence of fillers and pigments on the mechanical properties of polymers is known to be complex and dependent on any physical and chemical interactions between the pigments and the binder (Toussaint 1973/4; Sato 1976). Paints composed of different pigments will be expected to show somewhat different thermal mechanical behaviours and a range of glass transition temperatures.

Further to the initial study by Hedley et al 1990, who used DMA to demonstrate the effects of some conservation treatments (exposure to solvents and water) on the physical properties of oil paints, Odlyha 1998 used the same technique to examine a range of samples (mostly primed or painted canvases) bearing oil-based paints, again to evaluate the effects of some conservation treatments. While not directed primarily to the issue of the T_g of oil paints, Odlyha does report some relevant data for unaged, naturally aged and artificially aged paints which point strongly to possible changes in the near-ambient softening transition as a consequence of ageing. A fresh, dried paint film (canvas priming) composed of Winsor & Newton ‘Cremnitz White’ tube paint showed a main 1Hz tan δ peak (i.e. the T_g) at around 1ºC with a broad shoulder peak extending up to 40-50ºC; after 22 months of natural (dark) ageing this paint showed a shift in the positions of the main peak and shoulder peaks to slightly higher temperatures (ca. 6ºC and > 50ºC respectively). Quite vigorous accelerated ageing by combinations of light exposure and elevated temperature caused significant changes to the softening behaviour: the main transition (1Hz tan δ peak) of the light/heat aged samples occurs now at temperatures well above ambient (ca. 50-62ºC, depending on the duration of ageing), with a small shoulder peak appearing at low temperature, ca. -5 to -6ºC. DMA scans presented by Odlyha for 19th century canvas primings, presumably oil grounds containing lead white and chalk, generally show an absence of peaks in the 1 Hz tan δ trace in the ambient range of temperatures, ca. 0-50ºC. Where they do occur, the principal softening transitions for this type of sample material, as reflected by the 1Hz tan δ peaks, occur at temperatures above 75ºC and mostly in the region of 100ºC.

In the context of a larger project aimed at the development of paint-based dosimeters for monitoring museum environments, Odlyha, Cohen and Foster 2000, reported results of DMA studies of smalt-pigmented egg tempera paints that were tested still supported on the polyester film substrate on which they were cast.

Recent work using DMA within the field of paintings conservation has addressed modern artists’ paints and grounds. As part of wider research Ormsby et al 2007 have reported on the mechanical properties of various acrylic grounds and paints composed of titanium white, and Young and Hagan 2007 compared the mechanical properties of a range of commercial artists’ primers including several acrylics and alkyds containing titanium white pigment, and one drying oil-based product Winsor & Newton ‘Foundation White’. This study reports values of T_g for the various products determined by

Figure 2. Generalized plot of the effects of polymer structure on storage (i.e. elastic) modulus properties. After Sepe, 1998.
the 1Hz tan δ peak using DMA. The acrylic primers had Tg within the range 21-30°C, the alkyls between 26-44°C, and the oil-based ‘Foundation White’ 40°C. These findings of Tg mostly above normal room temperature present a rather different picture to the earlier data, summarized by Michalski, which suggested a sub-zero °C values for the Tg of aged and unaged oil paints.

The present study sought to examine the issue of the glassy/rubbery transition of oil paints in more detail and to evaluate the potential of the instrumental technique of Dynamic Mechanical Analysis (DMA) for elucidating this important physical property.

EXPERIMENTAL

Samples and sample considerations
The sample materials tested in this study came from three main sets. (See Table 1 on following page for details)

Sample set #1: Four series of paint samples prepared by the author in 2005 from proprietary artists’ oil paints. These samples were made from paints, direct from the tube, of Michael Harding ‘Artists’ Oil Colours’, as follows:

- Flake White, pure;
- Yellow Ochre, pure;
- a mixture of Flake White and Yellow Ochre 1:1 (w/w);
- a mixture of Flake White and Yellow Ochre 1:3 (w/w).

The paints were prepared as uniform coatings onto 100μm polyester film using a doctor blade-type paint applicator fitted with spacer shims of 200μm thickness. The dry films were generally between 160 and 200μm thick. Unless specifically mentioned in the following discussion, samples from these sets of paints were tested by DMA 9-11 months after their initial preparation. The Harding Flake White paint sample used in the test to monitor curing/drying was prepared separately, by a doctor blade method: that sample was 140-180μm thick. The paint samples above could, if needed, be removed from the polyester film support by careful peeling, after chilling if necessary. The majority of tests, however, were performed on paint samples still supported on the polyester film.

Selected pieces of the four Michael Harding paints from sample set #1 were subjected to forms of accelerated ageing by exposure to relatively high dosage of light. One subset of the four Harding oil paints was irradiated in a xenon arc light exposure cabinet fitted with filters to simulate daylight through window glass.[2] A second subset of the four Harding paints was subjected to accelerated light ageing by exposure, for various periods, to strong natural California daylight, indoors behind window glass.

Also tested in this study were several series of paint samples prepared and supplied by Marion Mecklenburg, Smithsonian Institution, which included:

Sample set #2: Six Winsor & Newton Artists Oil Colours, prepared as uniform coatings on polyester film, made in March 1999 (i.e. 7 years old at the time of testing);

Sample set #3: Two sets of paints containing specific single pigments bound in cold-pressed linseed oil with no driers added, made in late 1998–early 1999 and in 1990–92 (i.e. respectively 7 and 14-16 years old at the time of testing.

Equipment and method
Dynamic Mechanical Thermal Analysis was performed using a Triton Technology DMA 2000 instrument. The majority of tests were performed in single cantilever bending mode, with a free sample length of 2 – 2.5mm. In single cantilever bending tests the samples were tested still mounted on their polyester supports.[3] For stiff, more brittle paints, the tensile mode was used, on unsupported samples (that is, removed from the polyester film), using a free length of 5mm.

The DMA tests reported here are time/temperature scans in air: the sample is subjected to a sinusoidal oscillating stress whilst the temperature is progressively increased from cold to warm. The heating rate was 2°C per minute. The amplitude/displacement of the vibration was generally 25μm, though this was reduced to 10μm for stiffer samples in order to avoid problems of sample fracture, especially at low temperature. The thermal scans were routinely carried out using vibration frequencies of 1Hz and 10Hz, though the 1Hz data only are reported here. In all tests, whether in bending or tension mode, the sample would be first fitted in the instrument clamps, with the clamp nuts tightened finger-tight; the measuring head was then cooled to the experiment starting temperature at which point the clamp nuts would be fully tightened. Clamping of the sample, accordingly, was done with the sample in the glassy condition. Cooling was effected by circulating liquid nitrogen through the body of the DMA measuring head. The starting temperature for each experiment varied depending on the nature of the sample, but in general the aim of most tests
Table 1. Summary description of paint samples tested.

### Sample set #1: Michael Harding ‘Artists’ Oil Colours’, 9-11 months old at the time of testing.

<table>
<thead>
<tr>
<th>Paint</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flake White, pure;</td>
<td>150-200</td>
</tr>
<tr>
<td>Yellow Ochre, pure;</td>
<td>150-190</td>
</tr>
<tr>
<td>Mixture of Flake White and Yellow Ochre 1:1 (w/w);</td>
<td>150-180</td>
</tr>
<tr>
<td>Mixture of Flake White and Yellow Ochre 1:3 (w/w)</td>
<td>160-180</td>
</tr>
</tbody>
</table>

### Sample set #2: Winsor & Newton Artists Oil Colours, 7 years old at the time of testing (Smithsonian Inst.).

| Paint                              | Medium*          | Thickness (µm) |
|------------------------------------|------------------|
| Flake White No. 2, 247, Series 1   | Safflower oil    | 250-300        |
| Titanium White, 644, Series 1      | Safflower Oil.   | 240             |
| (Titanium Dioxide and Zinc Oxide)  |                  |                 |
| Yellow Ochre, 744, Series 1        | Linseed /Safflower oils | 230             |
| Raw Sienna, 552, Series 1          | Linseed /Safflower oils | 220-255        |
| Burnt Umber, 076, Series 1         | Linseed /Safflower oils | 230-260        |
| Ivory Black, 331, Series 1         | Linseed oil      | 220-250        |

### Sample set #3: single pigments in cold-pressed linseed oil with no driers added; (Smithsonian Inst.)

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Pigment Weight (%)*</th>
<th>Oil Weight (%)*</th>
<th>7 year old paints, prepared 1998-99 Thickness (µm)</th>
<th>14-16 year old paints, prepared 1990-92 Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow Ochre</td>
<td>57</td>
<td>43</td>
<td>230</td>
<td>150</td>
</tr>
<tr>
<td>Lead White</td>
<td>84</td>
<td>16</td>
<td>190-220</td>
<td>120</td>
</tr>
<tr>
<td>Titanium White</td>
<td>77</td>
<td>23</td>
<td>190</td>
<td>180</td>
</tr>
<tr>
<td>Zinc White</td>
<td>75</td>
<td>25</td>
<td>400</td>
<td>120-160</td>
</tr>
<tr>
<td>Raw Sienna</td>
<td>58</td>
<td>42</td>
<td>220</td>
<td>140</td>
</tr>
<tr>
<td>Lamp Black</td>
<td>36</td>
<td>64</td>
<td>240-270</td>
<td>-</td>
</tr>
<tr>
<td>Smalt</td>
<td>61</td>
<td>39</td>
<td>280</td>
<td>160</td>
</tr>
<tr>
<td>Malachite</td>
<td>78</td>
<td>22</td>
<td>290</td>
<td>150</td>
</tr>
<tr>
<td>Raw Umber</td>
<td>45</td>
<td>55</td>
<td>140-150</td>
<td>140-150</td>
</tr>
<tr>
<td>Lead Tin Yellow</td>
<td>90</td>
<td>10</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>Red Iron Oxide</td>
<td>41</td>
<td>59</td>
<td>240</td>
<td>120-150</td>
</tr>
<tr>
<td>Alizarin</td>
<td>37</td>
<td>63</td>
<td>200-210</td>
<td>220-240</td>
</tr>
<tr>
<td>Ivory Black</td>
<td>40</td>
<td>60</td>
<td>270-300</td>
<td>140-160</td>
</tr>
</tbody>
</table>

*data supplied by Marion Mecklenburg
was to start at a temperature at least about 20°C below the principal softening transition, as indicated by the 1Hz tan δ peak. In general, two or three repeat tests were done for each sample tested.

The samples were conditioned to the prevailing room environment (approximately 50%RH, 20°C) prior to testing, but relative humidity was not actively controlled during the test. Although the Triton DMA instrument has a humidity control unit which comes as an attachment, this unit was not operated in the tests reported here.

RESULTS

Reproducibility of $T_g$ by 1Hz tan δ max. Michael Harding Oil Paints: Sample set #1

In order to assess the reliability and reproducibility of determinations of $T_g$ by 1Hz tan δ max, a series of extended repeat tests were run for each of the four principal test paints prepared from Michael Harding tube colours (Sample set #1). The results, with mean values and standard deviations for each of the test paint films, are reported in Table 2. Variability in the measured $T_g$ values is relatively small and the four paints are quite reliably distinguished. The two mixed paints of flake white and yellow ochre differ only slightly in mechanical properties despite the difference in their proportions, and they are close in $T_g$ to the pure flake white paint, which reflects the strong influence of the white pigment in determining physical behaviour. Typical thermal scans for the four paints from sample set #1, 9-11 months old, are shown in fig. 3(a,b).

<table>
<thead>
<tr>
<th>Paint Description</th>
<th>Temperature of tan δ max, mean (ºC)</th>
<th>No of samples tested</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Michael Harding Flake White, pure;</td>
<td>17.8</td>
<td>11</td>
<td>0.6</td>
</tr>
<tr>
<td>Mixture of Flake White and Yellow Ochre 1:1 (w/w);</td>
<td>16.2</td>
<td>11</td>
<td>0.78</td>
</tr>
<tr>
<td>Mixture of Flake White and Yellow Ochre 1:3 (w/w);</td>
<td>15.5</td>
<td>13</td>
<td>0.56</td>
</tr>
<tr>
<td>Michael Harding Yellow Ochre, pure;</td>
<td>-2.3</td>
<td>10</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 2. Reproducibility of $T_g$ determinations by DMA, tan δ max (1Hz) for paints from sample set #1: Michael Harding 'Artists' Oil Colours', 9-10 months old.

and yellow ochre differ only slightly in mechanical properties despite the difference in their proportions, and they are close in $T_g$ to the pure flake white paint, which reflects the strong influence of the white pigment in determining physical behaviour. Typical thermal scans for the four paints from sample set #1, 9-11 months old, are shown in fig. 3(a,b).

Curing/hardening of lead white (Harding Flake White) paint

Clearly, the physical properties of an oil paint change most dramatically during the early stages of curing (drying) when the paint effectively converts from a (pasty) liquid to a (soft) solid. It seemed a good starting point for investigating the visco-elastic properties of oil paint to examine the changes which occur during the curing, hardening process. The example of Michael Harding Flake White, 100% was chosen, since the curing process was expected to occur relatively rapidly. figs. 4a and 4b present the overlaid traces (storage modulus and tan δ) of DMA temperature scans of this paint made at intervals after its initial application onto polyester film up to 810 days afterwards. The paint was allowed to cure under moderate diffuse indoor daylight. It can be seen in fig. 4a that, for any value of temperature, the modulus increases as the curing period continues: the paint becomes appreciably stiffer as it cures. The effect is most marked at temperature range around, say, 0-5°C: at 21days old the Harding Flake White oil paint is...
still very much in the rubbery/leathery condition, but by 300 days it shows predominantly glassy behaviour at 0°C. In fig. 4b can be seen the associated change in glass transition temperature ($T_g$) as evidenced by the shift to higher values over time of the peak of the 1Hz $\tan \delta$ trace. At 7 days after application, when the paint film is just touch dry, it shows a very strong $\tan \delta$ peak with a maximum below -20°C. Although dry to the touch, the film retains a high proportion of viscous behaviour even at temperatures well below ambient ($\tan \delta_{\text{max}} > 0.35$). In the course of the first two months of curing/hardening the $T_g$ increases quite rapidly and the magnitude of the softening transition diminishes. After about 300 days the peak in the $\tan \delta$ trace approaches room temperature, and its magnitude is much reduced ($\tan \delta_{\text{max}} < 0.2$) indicating diminished viscous behaviour. In fact the near-ambient softening transition diminishes quite markedly during the early months of the life of the Flake White paint, to the point where this peak in the $\tan \delta$ trace becomes barely distinguishable after about a year. fig. 4c shows results of a broader temperature scan (5 – 80°C) for a different sample of the Harding Flake White paint cured for 810 days. After this time the material shows little in the way of a distinct change in properties in the near-ambient region; rather, it undergoes only a moderate progressive thermal softening over this temperature range. However, an additional broad softening transition develops at temperatures beyond 80°C, which peaks around 100°C. This pattern has been observed for several different lead white paint films and is similar to that observed by Odlyha for 19th century primed canvases (see Odlyha 1998: 148. Figure 5.9c). The 810 day old Harding Flake White paint appears to demonstrate the typical thermal-mechanical behaviour of a stable, fully-cured lead white paint. At this degree of curing, the paint is stiff and inflexible: it fractures easily under slight deformation. The changes in modulus at room temperature (ca. 20°C) for the Harding Flake White oil paint, going from touch dry to 16 months old, are not much less than an order of magnitude.

Figure 4a. Curing of Harding Flake White oil paint (on polyester film): modulus traces from DMA thermal scans recorded at intervals after initial application.

Figure 4b. Curing of Harding Flake White oil paint: $\tan \delta$ traces from DMA thermal scans recorded at intervals after initial application.

Figure 4c. Harding Flake White oil paint: modulus and $\tan \delta$ traces from DMA thermal scans, in tensile mode, unsupported paint film after 810 days curing; extended temperature scale, 0 – 80°C.
The mechanical changes (in modulus and loss tangent) that occur during curing of the Harding Flake White paint (figs. 4a and 4b) are similar to those typically associated with increased crosslink density (see, for example, fig. 12, in Chartoff, Weisman, and Sircar 1994: 100), but other factors may also be involved here, including diminution of the fraction of organic binder.

Glass transitions of Winsor & Newton Artists’ Oil Colours, 7 years old (Sample set #2)

Fig. 5 shows the tan δ traces obtained from thermal scans of the six Winsor & Newton paints comprising sample set #2:

![DMA tan δ traces for selected Winsor & Newton Artists’ Oil Colours, 7 years old (Sample set #2).](image)

Flake White, Titanium White, Yellow Ochre, Raw Sienna, Burnt Umber and Ivory Black. Immediately apparent is the somewhat different behaviour demonstrated by Flake White and Titanium White. In similar fashion to the Harding Flake White discussed in the preceding section, Winsor & Newton Flake White shows only a very slight peak in ambient range (0–30°C) and a steady broad increase in tan δ above this range, with a maximum tan δ above 75–80°C. Winsor & Newton Titanium White is a stiff, brittle paint; it shows a pattern similar to that of the Flake White, but the small peak at lower temperature is higher, around 45 °C. By contrast, the four other paints have principal softening transitions in the ambient range, increasing in the order Ivory Black (1°C), Yellow Ochre (17°C), Raw Sienna (21°C), Burnt Umber (23°C). The $T_g$ values observed for Winsor & Newton Yellow Ochre and Raw Sienna paints are relatively high compared to paints composed of these pigments in cold-pressed linseed oil (sample set #3: Raw Sienna ca. 4–5°C at 7 and 16 years old; Yellow Ochre ca. 2–5°C at 7 and 14 years old) and to the Harding Yellow Ochre, 10 months old (sample set #1: ca. –2°C). This difference may be due to driers in the Winsor & Newton paints.

Glass transitions of paints composed of single pigments cold-pressed linseed oil (Sample set #3)

A summary of the essential data (temperature and value of tan δ max) from DMA thermal scans of paints composed of single pigments in cold-pressed linseed oil is given in Table 3. The principal softening transitions cover a broad range of temperatures from -4 – 40°C. At 7 years old the paints might be grouped into three broad, relative categories:

- $T_g$ below 10°C: Yellow Ochre, Titanium White, Raw Sienna, Lamp Black, Raw Umber, Red Iron Oxide, Alizarin, Ivory Black;
- $T_g$ 10 – 20°C: Smalt;
- $T_g$ above 20°C: Lead White, Malachite, Lead Tin Yellow.

A similar pattern, generally, is observed for 14–16 year old paints, though several of the older paints have lower $T_g$s than the 7 year old equivalents; this applies for Yellow Ochre, Lead White, Smalt, Malachite, Raw Umber, Red Iron Oxide and Ivory Black. The $T_g$ values measured for the smalt/cold-pressed linseed oil paints indicate quite a marked reduction between 7 and 14 years old.

The Zinc White paints, both 7 and 16 years old, showed no distinct measurable tan δ peak, only a progressive general thermal softening in the ambient range which continues beyond 60°C. The reason for this behavior remains uncertain, but may result from chemical interaction between pigment and medium.

Effect of accelerated light ageing

The four paints of sample set #1 were subjected to accelerated light ageing by exposure in a xenon-arc light exposure cabinet and, together with two Raw Sienna paints (Winsor & Newton, 7 years old; Mecklenburg/Smithsonian cold-pressed linseed oil, 16 years old), also to exposure to strong daylight behind window glass. The data are summarized in Table 4. Traces of tan δ against temperature for selected aged and unaged paint films (Harding Yellow Ochre; Harding Flake White: Yellow Ochre 1:3 and Raw Sienna/cold-pressed linseed oil, 16 years old) are shown in fig. 6a–c.
Phenix  

**Thermal Mechanical Transitions in Artists’ Oil Paints and Selected Conservation Materials: a Study by Dynamic Mechanical Analysis (DMA)**

<table>
<thead>
<tr>
<th>Paint Sample</th>
<th>Age at testing (Years)</th>
<th>1 Hz tan δ&lt;sub&gt;max&lt;/sub&gt; (°C) [mean]</th>
<th>Tan δ (1Hz) Max. value [mean]</th>
<th>No of samples tested</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cold-Pressed Linseed Oil Paints. Ca. 7 years old</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow Ochre</td>
<td>7</td>
<td>4</td>
<td>0.62</td>
<td>2</td>
</tr>
<tr>
<td>Lead White</td>
<td>7</td>
<td>28.2</td>
<td>0.25</td>
<td>4</td>
</tr>
<tr>
<td>Titanium White</td>
<td>7</td>
<td>7.6</td>
<td>0.34</td>
<td>2</td>
</tr>
<tr>
<td>Zinc White</td>
<td>7</td>
<td>No measurable tan δ peak.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw Sienna</td>
<td>7</td>
<td>4.1</td>
<td>0.46</td>
<td>2</td>
</tr>
<tr>
<td>Lamp Black</td>
<td>7</td>
<td>1.7</td>
<td>0.43</td>
<td>2</td>
</tr>
<tr>
<td>Smalt</td>
<td>7</td>
<td>16.6</td>
<td>0.38</td>
<td>1</td>
</tr>
<tr>
<td>Malachite</td>
<td>7</td>
<td>27.4</td>
<td>0.28</td>
<td>1</td>
</tr>
<tr>
<td>Raw Umber</td>
<td>7</td>
<td>8.9</td>
<td>0.29</td>
<td>1</td>
</tr>
<tr>
<td>Lead Tin Yellow</td>
<td>7</td>
<td>38.1</td>
<td>0.23</td>
<td>1</td>
</tr>
<tr>
<td>Red Iron Oxide</td>
<td>7</td>
<td>0.2</td>
<td>0.54</td>
<td>1</td>
</tr>
<tr>
<td>Alizarin</td>
<td>7</td>
<td>-3.9</td>
<td>0.49</td>
<td>2</td>
</tr>
<tr>
<td>Ivory Black</td>
<td>7</td>
<td>2.1</td>
<td>0.41</td>
<td>2</td>
</tr>
<tr>
<td><strong>Cold-Pressed Linseed Oil Paints. 14-16 years old.</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow Ochre</td>
<td>14</td>
<td>1.9</td>
<td>0.43</td>
<td>2</td>
</tr>
<tr>
<td>Lead White</td>
<td>16</td>
<td>27.0</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>Titanium White</td>
<td>16</td>
<td>11.2</td>
<td>0.28</td>
<td>2</td>
</tr>
<tr>
<td>Zinc White</td>
<td>16</td>
<td>No measurable Tan δ peak.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw Sienna</td>
<td>16</td>
<td>5.0</td>
<td>0.29</td>
<td>2</td>
</tr>
<tr>
<td>Smalt</td>
<td>14</td>
<td>8.2</td>
<td>0.49</td>
<td>1</td>
</tr>
<tr>
<td>Malachite</td>
<td>14</td>
<td>23.4</td>
<td>0.30</td>
<td>1</td>
</tr>
<tr>
<td>Raw Umber</td>
<td>14</td>
<td>8.2</td>
<td>0.31</td>
<td>2</td>
</tr>
<tr>
<td>Red Iron Oxide</td>
<td>14</td>
<td>-1.3</td>
<td>0.35</td>
<td>3</td>
</tr>
<tr>
<td>Alizarin</td>
<td>14</td>
<td>-3.7</td>
<td>0.42</td>
<td>2</td>
</tr>
<tr>
<td>Ivory Black</td>
<td>14</td>
<td>-0.6</td>
<td>0.38</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3. Summary of T<sub>G</sub> data from DMA thermal scans for paints composed of single pigments in cold-pressed linseed oil with no driers added. (Sample set #3: Smithsonian Inst.)
<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unaged</td>
<td>76 days strong daylight, behind window glass</td>
<td>486 days strong daylight, behind window glass</td>
<td>375 hours; xenon arc, uv/window glass filters.</td>
</tr>
<tr>
<td><strong>Sample Set #1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Michael Harding Flake White, pure; 10 months old</td>
<td>17.8</td>
<td>*</td>
<td>**</td>
<td>*</td>
</tr>
<tr>
<td>Mixture of Flake White and Yellow Ochre 1:1 (w/w); 10 months old</td>
<td>16.2</td>
<td>21</td>
<td>27</td>
<td>19.6</td>
</tr>
<tr>
<td>Mixture of Flake White and Yellow Ochre 1:3 (w/w); 10 months old</td>
<td>15.5</td>
<td>17.9</td>
<td>27</td>
<td>19.9</td>
</tr>
<tr>
<td>Michael Harding Yellow Ochre, pure; 10 months</td>
<td>−2.3</td>
<td>0.9</td>
<td>2.3</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Sample Set #2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winsor &amp; Newton Raw Sienna; 7 years old</td>
<td>20.7</td>
<td>23.8</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td><strong>Sample Set #3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw Sienna in cold-pressed linseed oil, 16 years old</td>
<td>4.7</td>
<td>12.5</td>
<td>19.8</td>
<td></td>
</tr>
</tbody>
</table>

* $T_g$ was so indistinct as to prevent ascription of a specific temperature value.

** Sample too brittle to test.

Table 4. Summary of $T_g$ data from DMA thermal scans for selected un-aged and light-aged paint films.
The $T_g$ of all paint films were shifted to higher values as a consequence of exposure to accelerated light ageing. Under the milder exposure conditions used here the changes in $T_g$ were relatively slight, generally in the order of 3–5°C, although an increase in $T_g$ of almost 8°C, was observed for the 7-year old Raw Sienna/cold-pressed linseed oil paint aged just 76 days by exposure to strong daylight behind window glass. For the longer period of daylight ageing behind window glass (469–486 days = ca. 16 months), the changes in $T_g$ compared to the unaged samples were greater, ranging from about 5°C for Harding Yellow Ochre (see fig. 6a), to 15°C for Raw Sienna in cold-pressed linseed oil, 16 years old. (see fig. 6b).

Although the increases in $T_g$ due to light ageing may be just a matter of a few degrees, changes of even this small magnitude can have a marked effect on the normal mechanical behaviour of the paint if the $T_g$ is close to room temperature. Taking the example of mixture of Flake White and Yellow Ochre 1:3 (w/w) from sample set #1 (see fig. 6c), the cured, unaged paint film had a measured $T_g$ of 15.5°C which increased on mild daylight ageing behind window glass to 17.9°C. After more prolonged (16 month) daylight ageing behind window glass, the $T_g$ increased further to 27°C. The shift in $T_g$ to higher temperature is accompanied by a marked reduction in the magnitude of this softening transition. In its cured, unaged condition, the Flake White and Yellow Ochre 1:3 (w/w) paint is leathery, resilient and flexible enough to withstand bending to a high degree of curvature; but at the more severely aged condition (16 months, daylight) it is stiff and tolerates only a slight bending before fracturing in brittle fashion. In fact, after this period of light ageing, the Flake White and Yellow Ochre 1:3 (w/w) paint has similar mechanical properties to the pure Harding Flake White paint cured 300 days. (See figs. 4a, 4b) A progressive upwards temperature shift combined with diminution in magnitude, to the point of disappearance, of the glassy-rubbery softening transition seems to be a general pattern of response of oil paints to accelerated light ageing, though the rate at which these changes occur appears to depend strongly on pigmentation.

Figure 6. Influence of various forms of mild accelerated light ageing on thermal-mechanical properties: tan δ traces from DMA thermal scans for selected paints.
(a) Harding Yellow Ochre (Sample set #1);
(b) Smithsonian Raw Sienna/cold-pressed linseed oil, 16 years old (Sample set #3);
(c) Mixture of Harding Flake White/Yellow Ochre 1:3 (w/w) (Sample set #1).
CONCLUSION

Dynamic Mechanical analysis has been shown to be an effective method for measuring glass transitions in young oil paints. Some practical difficulties remain with the method for the investigation of very stiff, weak samples. Peaks in the 1Hz tan δ traces were observed for the majority of paints tested, corresponding to the transition from glassy to rubbery/leathery condition. Glass transition temperatures (Tg) determined by the temperature of the 1Hz tan δmax show good correlation with subjective observations of the change in physical properties with temperature. For the young-mature paints tested here the Tg varied within the range of about -5 - 40°C depending on composition.

Some fully-cured paints, particularly those containing mostly lead or zinc white pigments, showed no distinct glass transition in the near-ambient range: their thermal-mechanical behaviour was characterized more by progressive thermal softening. Significant changes were detected in the Tg and visco-elastic behaviour of lead white paint during its curing/drying process under moderate diffuse daylight. When the paint was just dry to the touch, it showed a strong component of viscous behaviour and a Tg of below -20°C; but the Tg increased quite rapidly during the first few months of curing and the viscous component of mechanical behaviour diminished correspondingly. Within two years of initial application the near-ambient softening (glass) transition had effectively disappeared at ambient temperatures, the paint behaved predominantly elastically.

Accelerated ageing of selected paints by exposure to high intensity light caused increases in Tg. Although the changes in Tg measured were relatively small (15°C max.), in some instances - where the initial Tg was close to room temperature - they were accompanied by marked changes in the mechanical properties of the paint at ambient conditions. The results presented here help demonstrate the importance of considerations of visco-elastic state (i.e., glassy or rubbery/leathery) in studies of the mechanical properties of artists’ oil paint films.

Postscript: Comparative DMA and DSC Analysis

In order to explore the different thermal responses measured respectively by DMA and DSC, a limited series of comparative tests were conducted using each of these instrumental techniques, both on selected oil paints samples from sample set #1 and on a selection of acrylic and vinyl acetate polymer dispersion products that find use in conservation.

The polymer dispersion products were cast as uniform solid films on polyester (Mylar) sheet using a simplified form of the method described by Hansen and Taketomo, 1989. DSC analyses were performed on a Mettler Toledo DSC 822e instrument, and the data analyzed using the manufacturer’s StaRe software. The DSC tests were performed in nitrogen following a standard two-cycle heating and cooling protocol:

- Heating: -60 - 150°C @ 10°C/min.
- Cooling: 25 - -60°C @ 10°C/min.
- Heating: -60°C, 4 mins.
- Cooling: 100 - -60°C @ 10°C/min.
- Heating: -60°C, 4 mins.
- Heating: -60 - 150°C @ 10°C/min.

Michael Harding Oil Paints: sample set #1

The four different paint types from sample set #1 [Flake White, pure; Yellow Ochre, pure; mixture of Flake White and Yellow Ochre 1:1 (w/w); and mixture of Flake White and Yellow Ochre 1:3 (w/w)] were tested by DSC after four years of natural ageing. The DSC traces obtained for these paints for the first heating cycle (-60 - 100°C @ 10°C/min.) are shown in Figure 7a. The most significant observation on this set of data is the difference in thermal response of the lead (Flake) white-containing paints and the pure yellow ochre paint: the lead-containing paints show no distinct thermal transitions in the temperature range -60 - 100°C. However, the yellow ochre oil paint shows a sharp low-temperature endotherm in the range 40 - 60°C, which is interpreted as being caused by melting of free fatty acids. (A similar, but weaker, low-temperature endotherm was observed also in the yellow ochre in cold-pressed linseed oil paint from sample set #3.) The endotherm associated with free fatty acid melting remained also in the DSC trace for the Harding yellow ochre oil paint aged 486 days by exposure to strong daylight behind window glass.

The DSC traces for these same paints under the second heating cycle (-60 - 150°C @ 10°C/min.) are shown in Figure 7b. Again the yellow ochre oil paint behaves differently to the lead white-containing paints: the yellow ochre paint retains the low-temperature endotherm, albeit now over a broader range (ca. 25 - 55°C); but over the broader temperature range...
Phenix  *Thermal Mechanical Transitions in Artists’ Oil Paints and Selected Conservation Materials: a Study by Dynamic Mechanical Analysis (DMA)*

Figure 7a. (top) DSC traces, first heating cycle (-60 - 100°C @ 10°C/min), for Harding oil paints from sample set #1 after four years of natural ageing.

Figure 7b. DSC traces, second heating cycle (-60 - 150°C @ 10°C/min), for Harding oil paints from sample set #1 after four years of natural ageing.
Phenix Thermal Mechanical Transitions in Artists’ Oil Paints and Selected Conservation Materials: a Study by Dynamic Mechanical Analysis (DMA)

of the second heating cycle (−60 − 150°C @ 10°C/min.), the lead white-containing paints all show a strong high temperature endotherm that peaks at about 110°C. This transition is interpreted as melting of lead soaps.

Acrylic and vinyl acetate polymer dispersion products
A selection of acrylic and vinyl acetate polymer dispersion products commonly used in conservation were analyzed by DMA one month after initial film preparation and again three years later. The values of $T_g$ obtained, as indicated by the temperature of the peak in the 1Hz tan $\delta$ trace, are summarized in Table 5. It can be seen that the various materials differ appreciably in their $T_g$s, ranging from well below ambient for soft materials to above 40 °C for harder, stiffer materials like Elmer’s Carpenter’s glue. Furthermore, it can be seen also that measurable changes in $T_g$ occur for most of the products over the course of three years’ natural ageing. The precise cause of these changes remains unclear; gradual loss of absorbed water, coalescing solvent and/or surfactant may play a part, but other chemical processes, such as crosslinking, may also contribute to the phenomenon in some cases.

Some of the cast polymer films were analyzed also by DSC after three years. $T_g$ values obtained by this technique are also summarized in Table 5, for comparison with values obtained by DMA. Where data for $T_g$ exists from both DMA and DSC after three years’ ageing, it can be seen that the DSC values are all lower than those obtained by DMA by anything from about 6 to 20 °C.

The typical output from the two heating cycles of the test protocol is illustrated in Figure 8, which relates to the acrylic dispersion Rhoplex AC33. As is usually the case, the first and second heating cycles give slightly different values of $T_g$, but a stronger difference between the two traces is the occurrence in that for the first heating a large endotherm at ca. 46 °C, which is attributed to melting of ‘original’ surfactant retained in the dry polymer film. The absence of this endotherm in the trace for the second heating suggests the substance responsible

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Figure 8. Typical DSC output, first and second heating cycles: Rhoplex AC33.
Phenix Thermal Mechanical Transitions in Artists’ Oil Paints and Selected Conservation Materials: a Study by Dynamic Mechanical Analysis (DMA)

for this transition is no longer present, presumably lost by evaporation or thermal decomposition.

ACKNOWLEDGEMENTS

The work presented here was mostly undertaken whilst the author was a visiting research scholar at the Getty Conservation Institute, 2005-6, taking leave from his regular post at Northumbria University, Newcastle-upon-Tyne, UK. The assistance of the J. Paul Getty Trust in supporting the research scholarship is gratefully acknowledged. Thanks also go to many staff at Northumbria University, especially Anne Bacon, for accommodating my temporary absence from Newcastle and for allowing use at the Getty of the University’s DMA instrument.

Thanks are due also to Cameron Trowbridge, Valerie Greathouse and Andras Ambrus of the GCI Information Center for their help with references and research support. Special thanks go also to Michael Schilling at GCI for assistance with the DSC work. Marion Mecklenburg kindly donated paint samples to test and offered interesting insights into paint mechanics. Dr. Christina Young, Courtauld Institute of Art, London, also kindly donated samples for testing.

MATERIALS AND EQUIPMENT

Tritec DMA 2000 and humidity controller:

<table>
<thead>
<tr>
<th>Product</th>
<th>$T_g$ (°C) by DMA 1 Hz tan$\delta$ (sample age = 1 month)</th>
<th>$T_g$ (°C) by DMA 1 Hz tan$\delta$ (sample age = 3 years)</th>
<th>$T_g$ (°C) by DSC (midpoint, 2nd heating) (sample age = 3 years)</th>
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</thead>
<tbody>
<tr>
<td>BEVA D8</td>
<td>6.1</td>
<td>13.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Elmer’s Carpenter’s glue</td>
<td>41</td>
<td>46.5</td>
<td>38.5</td>
</tr>
<tr>
<td>Elmer’s glue, all-purpose</td>
<td>31.0</td>
<td>*</td>
<td>29.8</td>
</tr>
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<td>EvoStik Resin W</td>
<td>28</td>
<td>34.0</td>
<td>25.1</td>
</tr>
<tr>
<td>Jade 403N</td>
<td>10.9</td>
<td>Double tan$\delta$ peak 15 and ~35</td>
<td>6.4</td>
</tr>
<tr>
<td>Lascaux Medium for Consolidation</td>
<td>3.2</td>
<td>*</td>
<td>No obvious $T_g$</td>
</tr>
<tr>
<td>Mowilith DM427</td>
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<td>Plextol B500</td>
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<td>*</td>
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</tr>
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<td>Rhoplex AC234</td>
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<tr>
<td>Vinamul 3252</td>
<td>8.8</td>
<td>*</td>
<td>3.8</td>
</tr>
</tbody>
</table>

* = not tested

Table 5. Summary of $T_g$ data from DMA thermal scans (sample ages one month and 3 years), and from DSC for...

Michael Harding Artists’ Oil Colours
See www.michaelharding.co.uk (accessed 25 September 2008)

Q-Sun Xe-1 xenon arc light exposure cabinet
Q-Lab Europe, Ltd.
Express Trading Estate,
Farnworth
Bolton BL4 9TP
UK

ENDNOTES

1. Erhardt, Tumosa and Mecklenburg, 2005 suggest, somewhat controversially, that stiffness and brittleness in oil paints is caused not so much by natural ageing processes but by exposure to elevated temperatures or to treatment with solvents, as occurs in conservation treatments, such as lining and varnish removal. This conclusion is reached from linear extrapolations of data on the tensile mechanical properties of young reference oil paint films tested at different strains. However, close scrutiny of the mathematics used to reach this conclusion (published earlier in Mecklenburg and Tumosa, 2001) reveals that the method involves linear extrapolations from just two data points. In view of this methodological flaw, it is the opinion of the present author that the conclusion reached by Erhardt, Tumosa and Mecklenburg, 2005 – that “....even a 250-year-old paint film will not be substantially stiffer or more brittle than a film only decades old.” – cannot supported by the evidence they present.

2. Equipment: Q-Sun Xe-1 xenon arc light exposure cabinet. Exposure duration: 375 hours. Irradiance was set to 0.6 W/m² at 420nm; internal chamber temperature was controlled at 25 °C. Overall exposure was monitored by means of ISO Blue Wool Standards (BWS). Fading of the Blue Wool Standards was measured using reflectance spectrophotometry. By comparison with data presented by Bullock & Saunders, 1999, it was estimated that the cumulative light exposure received by the samples during accelerated ageing in the Q-Sun light exposure cabinet was very approximately equivalent to 40-50 years under normal museum conditions of 200lux.

3. The first tests of this project were performed on unsupported paint samples, in tensile mode. It was felt that this approach, which followed common practice in DMA studies, would give the optimum results. However, many problems were encountered early on which derived from fracture of the samples, especially the stiffer ones, during tightening of the DMA instrument clamps at the start of a run, or else during the course of a run, usually towards the start when the sample was still cold and glassy. Minor defects in the test samples, which had been cut from larger stock, appeared to be a significant factor contributing to the problem. The difficulties of performing mechanical tests on free, unsupported paint samples, because of the influence of defects, have been noted by other workers in this field, for example, Ormsby et al, 2008. During the course of the early experiments, however, it was observed that the polyester film support on which the test paints had been applied showed surprisingly little change in its mechanical properties in the temperature range of interest, -20 - 80°C: its principal softening transition occurred above 80°C. (See fig. 1). It was found, then, that the softening transitions of the paint coating could be accurately and reproducibly measured by DMA, in bending mode, while the paint was still mounted on the polyester film. Whilst the absolute values of storage modulus (E’) appeared to be somewhat variably recorded for polyester-supported samples, the temperature of the softening transition (Tδ), as indicated by the temperature of the peak in the 1Hz tan δ trace, was found to be accurate, quite reproducible and consistent with results obtained for unsupported samples. Accordingly, the majority of tests in this study were conducted in bending mode on polyester film-supported samples. One disadvantage to this approach is that, although modulus values obtained for paint films supported on polyester film appear to be generally internally comparable within a set of tests performed under similar conditions, the absolute values measured by the instrument are unlikely to properly reflect the true value of the paint modulus. The calculations of moduli within the instrument software assume the sample is homogeneous, not a laminate composed of two materials, as is the case here. For the stiffer paint samples, the tensile testing mode using unsupported films was found to be more effective: in bending mode the stiff paints often delaminated from the polyester film during the course of a thermal scan, so producing errors in the data. Clamping of the sample in the cold, glassy state remains a difficult practical problem for
Phenix Thermal Mechanical Transitions in Artists’ Oil Paints and Selected Conservation Materials: a Study by Dynamic Mechanical Analysis (DMA)

the study of weak, stiff material using the Triton DMA 2000 instrument.

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A Delightful Restoration: The Turkish Smoking Room, Victoria Mansion

ABSTRACT

Victoria Mansion, in Portland, Maine, built circa 1860 by Ruggles Morse, was designed by architect Henry Austin, decorated by interior designer Gustave Herter, and decorative-painted by Giuseppe Guidicini. The Mansion contains the first known smoking room in a private American residence, the Turkish Smoking Room, which is painted with Islamic-inspired motifs. The room is executed in distemper paints and gilt accents, which were flaking and covered in soot. The wall and ceiling surfaces were consolidated, surface cleaned, and missing design elements were in-painted and re-gilded. Cross-sectional analysis characterized the materials and painting techniques and informed treatment procedures.

INTRODUCTION

The Victoria Mansion was built between 1858-1860 in Portland, Maine, as a summer residence for Ruggles and Olive Morse. Ruggles Morse had earned a fortune as a luxury hotelier in New Orleans, and his experience in hotels influenced his vision for the lavish new construction. It was designed by Connecticut architect Henry Austin in the Italian villa style (fig. 1). Gustave Herter, in his earliest known commission, designed the interiors, and presumably oversaw the completion of the elaborate interior decorative painting by Giuseppe Guidicini and his assistants. A prime example of this work is the Turkish Smoking Room, a small room located in the tower structure (fig. 2). While smoking rooms were common in hotels of the period, this room is the first known smoking room in a private residence in America as well as the earliest surviving room decorated with Islamic-style motifs such as arabesques, trefoils, and banding.

Besides those superlatives, the room is remarkable for its use of strong patterns and bold color combinations. The designs are painted predominantly in red, blue, green, and ochre with accents of green, teal blue, and black. There is also an extensive use of gold leaf for stripes, highlights, and special motifs. The artisans achieved the masterful results with simple layering of paint and using underdrawing, stencils, and guided and free-hand paint application.

After about 150 years the decorative painting of the room was suffering from condition problems including: heavy surface grime overall, flaking and friable paint, lost gilt accents, abrasions, water stains, and overpainted moldings. Gianfranco Pocobene Studio, Inc., was contracted to work on the conservation of the room by Victoria Mansion Director, Robert Wolterstorff, and Curator, Arlene Palmer Schwind. The initial...
The goal was to work to preserve the decorative finishes, and as work proceeded, decisions were made in dialogue with the Director and Curator as to the extent of restoration that would be appropriately conducted.

Ultimately, the conservation/restoration work included an initial phase of documentation of the condition problems and a technical study of cross-section samples; a second phase of conservation work to consolidate the actively flaking and friable paint and remove surface grime; and a third phase of restoration that included compensation for paint and gilding losses and reinstatement of the original color scheme for the moldings. The progression to a high level of restoration of the painted surfaces was pushed forward by the simultaneous restoration or reproduction of other decorative elements in the room (ormolu gasolier, curtains, pasmenterie, upholstery), and conducted with supporting technical information from cross-section samples. Special challenges included consolidating and color-matching water-sensitive, matte distemper paints and addressing extensive loss of gilding.

**TECHNICAL DESCRIPTION AND CONDITION**

The Turkish Smoking Room, which measures 113” wide by 107” deep and 130” in height, is located in the second floor of the tower and contains some of the most elaborate and opulent painted decorations in the Victoria Mansion. The room is entered through sliding pocket doors in the north wall. A window pierces each of the exterior south and west walls. The east wall, an interior wall, does not have a window but is decorated with the focal point of the room: an elaborately designed trompe l’oeil gold metal grille over a red damask background. All of the walls and ceiling are decoratively painted. A green faux marble dado surrounds the lower portion of the whole room, and a rope and dentate molding cornice surrounds the top.

**Decorative Paint on Walls and Ceiling, Technical Description**

The ceiling and walls above the faux marble dado are elaborately and completely painted with Islamic-inspired motifs and patterns, as previously mentioned. The paint is matte and luminous, and cross-section staining indicated that it is water-based distemper paint (pigments bound in protein glue). Solubility tests, which indicated that the paint is extremely water-soluble, substantiated that finding. Close visual examination and extensive cross-section analysis yielded abundant evidence of the painting technique.

The wall and ceiling substrate is smoothly finished plaster. The porous plaster was sealed with a thin layer of proteinaceous glue and then primed with a consistent layer of white distemper paint, which acted as a smooth reflective surface for the subsequent design layers. The design layers were applied efficiently with large areas of background color blocked in and foreground details painted on top. The red, blue, and white trefoil-pattern panels in the corners of the room are an example of this economy of paint layers. Each trefoil panel was blocked in with white paint, and areas for the white trefoils were left in reserve when the red and blue trefoils were painted on top. These repeated shapes were painted using two-part stencils, which is evident especially in the more thinly painted blue trefoils where the bridge between the two parts is darker, because the connection was reinforced freehand after the stencils were lifted.

Cross sections showed that the ochre bands that define different sections of the walls and ceiling were painted with a single layer of ochre-colored paint, with stripes of darker brown and cream added to outline the edges. This banding and line work in the room was most likely laid in with the aid of edge guides, both straight and curved.

The most elaborate buildup of paint was found in a cross section from the blue and gray arabesque design on the ceiling—it revealed six layers of paint (figs. 3–4). At the bottom is the white priming layer, followed by the red background color. Next a pinkish gray layer was applied for the whole arabesque. A neutral gray layer was applied on the outer edges of the arabesque, followed by a light blue layer for the larger outline, and the darker blue outline on top. While six layers may seem complex, this cross section shows that the painters simply built the design from the broad elements (background colors) to the finer details (dark blue outlines). Close visual examination of this motif revealed some underdrawing, indicating that the design was probably

Figure 3. (top) Cross-section 23, showing six paint layers
Figure 4. Sample site of cross section 23
transferred from a pattern book onto the ceiling with graphite (or other dark drawing medium) and painted freehand.

Many of the cross sections showed that the bold colors were achieved by using pure pigment or simple mixtures of two to four pigments. While pigment analysis was not conducted as part of the study, a remarkable identification was made during the cross-section analysis. Emerald green (copper (II)-acetatoarsenite) was unmistakably visible as distinct radial green particles in samples taken from brilliant green decorative bands in the ceiling and in lighter green panels on the east wall (figs 5-6). The pigment was first available in 1814 and was prized for its unique intensity until it was banned in the 1960s for being highly poisonous.

Decorative Paint on Walls and Ceiling, Condition
While most of the distemper paint was well adhered to the plaster substrate, there were areas of active flaking and paint losses, and this was the main conservation issue. Examination of flaking areas revealed that the distemper paint was brittle and friable. Small areas of flaking and loss were scattered across the walls and ceiling, and were usually associated with designs built up with multiple layers of thicker paint and along the edges of small stable cracks in the plaster substrate. Other losses were associated with water infiltration, such as a large area of flaking and loss on the north edge of the ceiling (fig. 7). Almost all of the paint losses extended down to the white plaster substrate, and were therefore extremely visually disruptive. Besides causing flaking and losses, water infiltration also caused staining and tide lines, especially visible on the east side of the ceiling (fig. 8). (Recent restoration and repairs to the exterior of the building should protect the decorative surfaces in the room from further water damage.)

The painted rope molding cornice was declared a complete loss. What little original paint remained had been overpainted in the past with a water-based paint, which was also actively flaking with large areas of loss down to the white priming. Only an eighteen-inch length area in the left corner of the south wall remained, that was not overpainted, with intact original distemper paint finish.

The mansion’s original coal heating system and 150 years without cleaning left the distemper paint surfaces covered in soot and grime that grayed and obscured the original colors.
foils were discovered to be white beneath all the grime, which was corroborated by cross sections.

**Gilding**

Cross-section analysis was necessary to identify the intended finish of several components of the room that were in extremely poor condition, including thin double stripes accenting the ocher bands, stripes along the rope molding cornice, outlines of the faux grille on the east wall, special medallions on the walls and ceiling, and the central ceiling motif surrounding the gasolier mount. Samples from each of these sites indicated that they were originally finished with gold leaf using a natural resin as a mordant (figs. 9-10). The fact that gold leaf had been used extensively was difficult to imagine, as close to 100% of this gilding was lost, leaving behind loss down to the white plaster or loss down to an underlying distemper paint layer. So much gilding loss probably occurred as a result of the natural resin mordant expanding and contracting and degrading with changing environmental conditions.

**Faux Marble Dado**

Along the lower portion of the walls a dado is painted in a faux green marble design. Cross-section analysis indicated that the finish is original and staining indicated that it is an oil-based paint. The convincing faux finish was created by a buildup of paint as follows: plaster substrate (or wood substrate on baseboard), white priming layer, several layers of translucent and variegated greens, and white highlights to mimic marble veins. While the paint layers were well preserved with only minor abrasions and loss along the baseboard, the whole of the dado was obscured under a heavy layer of soot and grime.

**Interior Paint Surfaces of Pocket Doors**

The interior of the wooden pocket doors is finished in two shades of pale, low luster green paint. The inner inset moldings are a slightly darker tone than the surrounding outer rails and stiles. Gilt beads accent the inner portion of the trim work. Cross sections showed that the wooden door was first coated with an extremely thin layer of a clear resin, then a white priming layer, followed by a green paint film composed of an oil-emulsion paint. The resin coating initially caused concern that a clear coat was the original finish of the doors, but the thinness of the coating, its penetration into the wood, and its presence on all of the wood sampled in the room indicated that it was applied as a sealant, probably in the woodshop before installation, and that the green finish was the original intent. The finish paint was found to be stable and well adhered to the wood support although heavily soiled with a greasy layer of grime and fingerprints present on the inside door edges.

**Door and Window Moldings**

Cross-sectional analysis indicated that the door and window moldings were over-painted with an off-white oil paint. A mechanical exposure with a scalpel blade revealed a consistent layer of light green oil paint below the overpaint (fig. 11). In tone and hue, this green layer resembles the lighter outer rails and stiles of the pocket doors, though slightly lighter in value.

**CONSERVATION AND RESTORATION TREATMENT**

**Distemper Paint Surfaces**

Several materials were considered and tested for consolidating the flaking distemper paint, which was of primary importance and had to be conducted before the unstable paint could be cleaned. Proteinaceous glues were ruled out, as the distemper...
paints are extremely water sensitive and prone to developing tide lines, as evidenced by old water stains. Aquazol, poly(2-ethyl-2-oxazoline), was seriously considered since it is stable, reversible, and soluble in low-toxicity solvents, such as ethanol and water. Aquazol 50 and Aquazol 200 (different molecular weights) were each tested in a variety of concentrations and solvents: 5g/100mL and 10g/100mL in pure ethanol, and 5g/100mL and 10g/100mL in a mixture of ethanol and water (3:1). Water was added to the ethanol in hopes of plasticizing the brittle distemper paints. The Aquazol formulations were rejected because, while they reattached the paint well, they left staining and darkening around the treated paint as well as a sparkly surface. Attempts to remove the excess Aquazol damaged the paint layers.

A series of tests with BEVA-371 (ethylene vinyl acetate) were conducted, and ultimately warmed BEVA-371 in odorless mineral spirits (1:4) was found to effectively flow under the distemper paint flakes and provide enough strength to re-attach the unstable paint. The adhesive was flowed under paint flakes in one or two applications with small sable brushes and allowed to evaporate overnight. The paint flakes were then set down with a heated tacking iron applied with gentle pressure through silicone release Mylar. Excess BEVA-371 on the surface, which saturated and darkened the surrounding paint, was removed with xylenes applied with cotton swabs. Sooty grime, feared consolidated to the paint surface by the BEVA-371, was also easily lifted from the surface during this step. This consolidation method left the flaking areas stabilized, clean, and matte, and was used on all of the flaking distemper paint on the walls and ceiling.

Cleaning of the surfaces could be tackled after consolidation, but this also presented special challenges. The deposits of soot and grime were heavy and uneven, and it was not initially clear that cleaning would have even results. Since aqueous cleaning methods were not usable, a series of dry cleaning methods were tested and a three-step process was developed for consistent cleaning with latex sponges (Wonder Sponge, Gonzo Products) and kneaded erasers (Design Kneaded Rubber, Sanford, Corp.) (fig. 12). First, the surfaces were cleaned with two to three passes of the latex sponges, cut to size and dragged over the paint surface, which was effective for cleaning the less soiled areas (ceiling and interior north and east walls). The kneaded eraser was used in the second step of cleaning for the more heavily soiled areas (higher portions of the walls, and exterior south and west walls). The third cleaning step was a final pass overall with the latex sponges to even out the cleaning.

The results of the cleaning were more even and complete than thought possible in the beginning, and most of the soot and grime was removed revealing the boldness of the original color palette. A thin layer of deeply ingrained grime remains on the upper portions of the south and west walls, near the ceiling. A 4-by-5-inch section of the trefoil pattern on the upper right corner of the west wall was intentionally left uncleansed as evidence of the pre-cleaning condition.

After cleaning, several thin coats of Paraloid B-72 (ethylmethacrylate methylacrylate) solution, 8% in xylenes, were applied with an automotive spray gun to all of the distemper paints. This reduced the friability of the paint and subtly re-saturated the matte surface. It also served as an isolating layer for re-touching layers that would follow.

All of the paint losses on the walls and ceiling, through which glaring white plaster was visible, were in-painted to closely match the surrounding original distemper paint and re-unify the designs. Several different conservation palettes were tested, as well as pigments bound lightly in PVA, but none of the palettes were matte enough to match the distemper paint. Therefore, artists’ gouache colors (Opaque Watercolor Gouache, Da...
Vinci Paint Co., Inc.) were used to inpaint losses on the walls, which worked well. When inpainting began on the ceiling, the issue became even more challenging, because the light that raked across the ceiling from the windows made the gouache paint, which is slightly glossier than the distemper, more apparent. Matte synthetic paints (Atelier Absolute Matte Artists’ Paint, Chroma Australia Pty Ltd.) were required for inpainting the ceiling.

Larger areas of paint loss along the north edge of the ceiling, the water-stained portions of the east ceiling edge, and the rope molding cornice (almost entirely repainted in the past) required a more workable paint with good covering power. Acrylic artists’ colors (Galeria Acrylic Colour, Winsor & Newton) were chosen for repainting the large losses. The acrylics were mixed in large quantities and applied in a tone slightly lighter than the surrounding original surfaces. Dilute acrylic colors were glazed on top of the base layer to achieve a close color match and aged appearance. The rope molding was re-painted in this manner, as it was declared irretrievable by conservation methods since it had been over-painted in the past with water-based paint and little original paint remained beneath the over-paint. The eighteen-inch length of the rope molding in the left corner of the south wall that retained original finish was left intact for future study.

Gilding
The original gilding was declared a complete loss, as the very little that remained was crumbled, unrecognizable as gilding, and deemed unsalvageable. The decision to re-instate the gilding was made after much deliberation on the basis of the following arguments: 1) the Turkish Smoking Room was intended to be opulent and extravagant, and not compensating for gold loss undermined that intent; 2) other elements in the room, such as the ormolu gasolier, curtains, passmenterie, and upholstery, were being restored or reproduced at a high level, and the decorative paint finishes should be restored to a similar level.

Shell gold was initially considered and tested as a substitute for gold leaf, since it would be less expensive and easier to apply, but it was deemed a poor substitute—it cannot mimic gold leaf’s ability to brightly reflect direct illumination or darken dramatically when unlit. This indicated that real gold leaf would need to be applied, and a series of materials were considered and tested for use as a mordant. Rabbit skin glue, commonly used for water gilding, was ruled out since the surrounding distemper paints are extremely water-sensitive. Natural resins were ruled out since the original natural resin mordant was short-lived. An oil size (Luco Quick Dry Gold Size, Leo Uhlfelder Co.) was tested, but the oil bled into and darkened surrounding distemper paints.

Luco Aquasize (Leo Uhlfelder Co.), a synthetic-resin-and-water dispersion, was tested and proved satisfactory—it was easy to apply, it stayed in place, and did not bleed into surrounding distemper paints. A sample of the material was sent to the Scientific Research and Analysis Laboratory, Winterthur, for analysis by Dr. Joseph Weber to ensure that the resin is stable and appropriate for use. FTIR analysis revealed that the main resin component is poly(ethyl acrylate), which Dr. Joseph Weber considers a stable resin, more so than poly(vinyl acetate).

The Luco Aquasize was therefore chosen as the mordant for re-gilding. It was applied undiluted with a thin, flat, hog hair brush over areas of gilding loss (fig. 13). Tiny crumbled remnants of original gilding were gilded over, not removed. Straight and curved wooden guides were used for applying the size to stripes; it was applied freehand to other motifs. The size was allowed to dry for about thirty minutes, and when the tack was correct, gold leaf was pressed over it and excess leaf brushed away (fig. 14). Twenty-three carat patent gold leaf (Giusto Manetti) was cut with a scalpel and straight edge to the approximate size and used for this purpose. The paper backing on the leaf made cutting and handling it much easier.

An area of vertical stripes to the right of the door on the north wall was not re-gilded. The original gold leaf that remains there can be used for future study, and the area can be displayed as an example of extremely poor condition of the original gilding.

Figure 13. Applying the Luco Aquasize with a brush and curved guide
Heavy deposits of soot and grime were removed from the dado and doors using an aqueous cleaning solution, as these surfaces were painted in oils and not water-sensitive. They were cleaned with cotton swabs dampened in a 2% citrate solution in water at pH 7.5. Several passes were needed to completely remove the dirt layer. After cleaning, the surface was rinsed with water and cotton swabs. To revive the somewhat weathered and dry paint surfaces, a thin brush coating of Paraloid B-72 (8% in Shell Sol 100) was applied, and also protects the surfaces from future accumulations of dust. Minor paint losses in the dado that exposed white plaster were inpainted with Golden MSA Conservation Paints. Scuffs that exposed the wood substrate of the baseboard were not retouched, because they were not visually distracting.

The most feasible treatment option for the overpainted door and window moldings was to repaint them to match the original pale green paint revealed in the exposure. Victoria Mansion contracted a local painter to complete the task. The restoration of the door and window moldings to the original pale green color re-unified these elements with the rest of the room.

At the request of the Victoria Mansion, samples of the soot and surface grime were analyzed to determine the possible presence of tobacco and opiates residues. Analysis of a small distemper paint sample was performed by gas chromatography-mass spectrometry (GC-MS) at the Scientific Research and Analysis Laboratory at Winterthur Museum by Dr. W. Christian Petersen. In brief, the analysis found no traces of nicotine or opiates but stresses the fact that the sample was too small to detect either. While these compounds were not found, it does not preclude the possibility that they are there in a level below the detection of the present analysis.

The treatment of the Turkish Smoking Room was challenging in multiple ways, but the first challenge was in determining the original intent of the finishes. An initial technical study of cross-section samples proved crucial in that regard. Cross sections showed that many decorative elements had been gilded, although they were so deteriorated that it was not immediately apparent. The cross sections also revealed that the door and window moldings were overpainted.

Treating the extremely matte and friable flaking distemper wall paints was also challenging. After testing several different adhesives, the distemper paint was satisfactorily consolidated with BEVA-371. The water-soluble paint had to be cleaned with dry techniques, so Wonder Sponges and Design Kneaded Erasers were used. Finding a paint matte enough to retouch losses in the distemper paints was difficult, but Atelier Absolute Matte Artists’ Paint was found to work well.

Determining the appropriate extent of the restoration of the Turkish Smoking Room required consultation with the curator and director of Victoria Mansion. They decided that reinstating the lost gilding was necessary to restore the room.
to its originally intended opulence. The re-gilding was done with Luco Aquasize and 23 carat patent gold leaf.

The outcome of several months of work and collaboration was a delightful restoration of the Turkish Smoking Room, as evidenced by the contrasting before- and after-treatment photographs (figs. 16-25).

Figure 16. The Turkish Smoking Room, before treatment

Figure 17. The Turkish Smoking Room, after treatment, with reproduction textiles

Figure 18. Ceiling, before treatment

Figure 19. Ceiling, after treatment
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Figure 20. Northwest corner, before treatment

Figure 21. Northwest corner, after treatment

Figure 22. Trompe l’oeil gold metal grille, before treatment

Figure 23. Trompe l’oeil gold metal grille, after treatment
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ABSTRACT

In 1947 Saul Steinberg was asked to paint a large mural for the main restaurant of the Terrace Plaza Hotel in Cincinnati. The Mural of Cincinnati is one of Steinberg’s masterpieces, a spatially complex and witty view of the city. When the hotel was sold in 1965, the mural was donated to the Cincinnati Art Museum. This paper discusses the design of the Terrace Plaza, the mural commission, and Steinberg’s working methods. It details the mural’s conservation treatment in 2006-2007 by the Intermuseum Conservation Association, focusing especially on the complex varnish removal. The project represents a second major collaboration between the Cincinnati Art Museum and the ICA.

THE TERRACE PLAZA HOTEL

Shortly after the Second World War in 1946, real estate developer Thomas Emery’s Sons began an ambitious project to construct a new hotel in downtown Cincinnati. Having completed the magnificent art deco hotel, the Netherland Plaza, during the depths of the depression, John J. Emery (president of Thomas Emery’s Sons) saw this new project as an opportunity to help jump start the war ravaged economy of the mid-1940s. Emery looked to the architectural firm of Skidmore, Owings & Merrill (SOM) not only to design something “new and forward-looking” but also to develop an architectural program that would maximize his profit.

SOM was selected in 1946 largely because their analysis showed that placing a modern hotel over a base devoted to retail would return a greater profit. Their design of the Terrace Plaza Hotel envisioned a modern, sleek hotel whose lobby would be located on the eighth floor over retailers JC Penney and Bond Clothiers (fig. 1). This was the first hotel built in the United States in the International Style and SOM had complete control over the entire design. They had a hand in everything from the architecture to staff uniforms and match book covers. Ground was broken in 1947.

SOM focused on selecting the newest materials for construction finishes including Formica and stainless steel. Devoid of architectural ornamentation, the hotel would feature art work specifically commissioned for the public spaces. Emery, then president of the Cincinnati Art Museum’s Board of Trustees, consulted with the museum director Philip Adams on the selection of contemporary artists for these important commissions. Adams recommended Joan Miró for the mural to be featured in the intimate roof top Gourmet Room restaurant, while SOM recommended Alexander Calder for a large mobile to be suspended from the lobby ceiling directly across from the bank of passenger elevators, and Saul Steinberg for...
what was originally a 120 foot long mural of Cincinnati in the main dining area on the lobby level – the Skyline Room.

Thomas Emery’s Sons vice-president, Ellsworth “Dutch” Ireland, who oversaw the Terrace Plaza construction, entered into a contract with Steinberg in 1947, to paint the mural depicting Cincinnati landmarks for $5,000 plus the cost of materials. [1] Steinberg visited Cincinnati in late May 1947, to gain a sense of the city and to sketch major landmarks. He wrote to his friend Aldo Buzzi in Milan,

*I’ve been to Cincinnati, which is a pretty lousy city, to see the place where I’m supposed to do the ‘mural,’ a large painting on a wall (120 feet long, 10-12 high). I’ll start work in October and do it in New York in sections, oil on canvas (and if it interests you, you can be my assistant with excellent pay). It’s sure awful, but I’m starting to like it… [2]

This mural was not Steinberg’s first. Bonwit Teller commissioned Steinberg to design a mural for their New York store; however, he was not pleased with the outcome since he laments that it was executed by “a bunch of hooligans.”[3] For the Cincinnati project, Steinberg realized that it was an important commission and wanted to maintain greater control so he decided to execute it largely by himself.

Steinberg produced an initial sketch or maquette that he submitted to SOM and Emery for approval (fig. 2). Even in this preliminary drawing, Steinberg obviously had communication with the architects in order to specifically locate the air diffusing grills and kitchen doors as indicated in this sketch. To begin painting, Steinberg rented studio space from the photographer Gjon Milli.

Steinberg painted the mural on approximately ten foot long sections of stretched canvas. A photograph reproduced in ‘48 the Magazine of the Year shows Steinberg on scaffolding working on one section of the mural and demonstrates the scale of the project (fig. 3). [4]

To transfer his design to canvas, Steinberg used 2 ¼ x 2 ¼ inch glass slides, each of which projected a corresponding section of the mural design.[5] In comparing the initial sketch (fig. 4) with the images on the glass slide (fig. 5), Steinberg has both refined and simplified his design. While there is a greater difference between the initial sketch and corresponding glass slide, the final mural is largely rendered from the projected image with only minor changes to the composition. Steinberg left the vertical edges of the composition unfinished and would complete the design once the mural sections were mounted on the wall in Cincinnati. The authors were fortunate to learn of the existence of well preserved 8 x 10 inch color transparencies of almost every mural section as they left his studio in Steinberg’s papers at Yale University’s Beinecke Rare Book and Manuscript Library.[6] These images proved to be very useful during the course of the mural’s treatment.

Steinberg completed the mural by early December and the sections were rolled and taken away in preparation for their shipment to Cincinnati. Two months after completing this phase of the mural, Steinberg writes,

*I’ve been a little tired and depressed and I still haven’t recovered. Maybe the Cincinnati mural was too big (those nuts who construct cathedrals out of toothpicks must feel like this when they’ve finished. For a while you stop eating so as not to use toothpicks)… [7]

Figure 3. Steinberg at work on mural

Figure 2. Steinberg discussing maquette with Ellsworth Ireland
The mural sections arrived in Cincinnati in March 1948, at which time Steinberg came to oversee its installation in the Skyline Room and to complete the painting so that the design would flow uninterrupted across the length of the mural. The Terrace Plaza opened in June 1948 to great acclaim. It received not only local attention but also national publicity in the New York Times, Chicago Tribune, and Harper’s Weekly. Over 10,000 people passed through the building on its opening day (fig. 6).

EXHIBITION OF THE MURAL AT THE CINCINNATI ART MUSEUM

In 1964, Thomas Emery’s Sons sold the Terrace Plaza to Conrad Hilton. Emery offered Hilton two prices, one with the Miró, Calder, and Steinberg, and one without. Hilton chose the latter. As a result, Emery donated these three works to the Cincinnati Art Museum (CAM) in 1965. The Steinberg mural was on display from the year of the gift up until 1981, when it was covered over with a false wall to create additional hanging space. Later in 1991, the mural was deinstalled in preparation for a major renovation. At that time, the mural sections were rolled on large diameter tubes and placed in storage. They were not reinstalled after the renovation because of space limitations in the galleries and the mural's compromised aesthetic condition.

THE SAUL STEINBERG RETROSPECTIVE AND THE IMPETUS FOR CONSERVATION TREATMENT

The opportunity to conserve and exhibit the mural arrived in 2002 when the museum began to investigate whether the mural could be included in a major Steinberg retrospective being organized by Joel Smith, then curator at the Frances Lehman Loeb Art Center at Vassar College. The museum decided this could be an appropriate opportunity to display the mural again – a long standing favorite of many visitors. The mural, however, was covered by an extremely uneven, discolored varnish (fig. 7), and it had no safe or efficient hanging system for installation in a temporary exhibition.
With the generous support of the Save America’s Treasures grant program administered by the National Park Service in partnership with the National Endowment for the Arts, the National Endowment for the Humanities, the Institute of Museum and Library Services, and the President’s Committee on the Arts and the Humanities, the museum engaged the Intermuseum Conservation Association (ICA) to undertake its treatment.

The project represented a second major collaboration between the ICA and the CAM. The first was the examination, treatment, and reinstallation of the Joan Miró mural, also from the Terrace Plaza. A discussion of the Miró project can be found in an article by Frederick Wallace, Per Knutås, and Stephen Bonadies in the 2009 AIC Paintings Specialty Group Postprints (2008 meeting, Denver, Colorado).

Several months before the murals arrived at the ICA, a three day meeting was scheduled in Cincinnati. Participating in the meeting were Joel Smith; Julie Aronson, CAM’s curator of American paintings; Stephen Bonadies, deputy director at CAM; Albert Albano, executive director of the ICA; Per Knutås, associate paintings conservator at the ICA; and conservation scientist James Martin of Orion Analytical, LLC. One of the main concerns was the aesthetic impact of the mural. From visual examination it appeared that the varnish had been applied selectively, in multiple coats. The irregular layering of the coatings resulted in dark forms that appeared intentional (fig. 8). Gone were the images, seen in the 1948 photo of the Skyline Room, created using black lines with crisp colored accents on a white ground (fig. 6). On-site cleaning tests indicated a difficult varnish removal, and a number of varnish samples were taken. The hope was to determine the varnish
composition and layering structure in order to help devise a safe, effective cleaning protocol.

ANALYSIS OF THE COATINGS

Orion Analytical collected twenty-one samples of varnish, paint, and primer layers from the mural for examination of structure and composition. Visual examination of cross-sections of five samples using fluorescence microscopy and scanning electron microscopy with backscattered electron imaging showed at least three varnish layers.

Elemental analysis of the varnish layers using scanning electron microscopy with x-ray energy-dispersive spectrometry (SEM-XEDS) revealed significant amounts of silicon in the bottom varnish layer and magnesium in the middle varnish layer. Molecular analysis of the layers using Fourier transform infrared (FTIR) microscopy identified the silicon as silicate (probably silica) and the magnesium as basic magnesium carbonate. These inorganic compounds, contamination from adjacent paint layers, and metal soap complicated FTIR characterization of varnish media: a probable oil or alkyd in the bottom and intermediate varnish layers and a natural resin in the top varnish layer. A simplified schematic of the coatings’ composition and layered structure is as follows:

- Natural resin coating – upper coating
- Oil or alkyd coating, containing magnesium – intermediate coating
- Oil or alkyd coating, containing silicon – coating closest to paint layer.

Silicate and basic magnesium carbonate could have been used as matting agents, and the basic magnesium carbonate might also have been a fire retardant. Coatings on three other public murals in Ohio were analyzed in 1999 by Janice Carlson of the Winterthur Museum Analytical Laboratory and found to contain basic magnesium carbonate. Carlson noted in her report that while magnesium carbonate is not commonly used in artists’ materials, it is used for fire resistant coatings.[8] The occurrence of this type of coating on the Steinberg mural has caused ICA staff to wonder if a commercially available product was recommended at one time on murals in public places in Ohio.

One cross-section taken at the edge of the mural showed the upper and intermediate coating layers on top of architectural overpaint from a painted molding (fig. 9). This strongly suggests that these layers were not original to the painting. The lowest coating layer was not found in all the samples, and it is possible that this lowest, discontinuous layer had been applied by Steinberg. Steinberg might have applied a local varnish when he was on-site in Cincinnati to address passages that had “sunken in.” However, it is conceivable that this coating too had been applied at a later date, possibly by restaurant maintenance staff.

ESTABLISHING A CLEANING PROTOCOL

The Steinberg mural, in eight sections, arrived in Cleveland in September 2006. To meet the exhibition deadline the project had to be completed by the end of June 2007, all eighty feet of mural in ten months.[9]

With the mural at the lab, the ICA conservators read the analytical reports, performed cleaning tests, and looked at the few extant images of the mural installed in the restaurant. On some of the murals the darkened varnish so closely followed forms, discussions arose as to whether or not Steinberg had deliberately been trying to create matte and gloss distinctions with local varnish applications. And although the analytical
Bonadies and Partridge *Modernism on the Ohio River: History, Analysis, and Conservation of Saul Steinberg’s Mural of Cincinnati*

The report did not indicate pigment particles in the varnish, could Steinberg even have been using very subtle toning layers?

The concerns about intentional gloss variations lessened when a letter in the curatorial file showed that Steinberg had planned for the mural to be varnished overall. The letter, dated May 10, 1948, was to Steinberg from Ellsworth Ireland, vice president of the Terrace Plaza Hotel and stated:

*While we have not applied the coat of plastic over your mural, in all other respects the mural has been completed. We are, therefore, making the final payment of $1,500 which pays in full your contract price of $5000.*[10]

The 1948 photo of the mural installed in the Skyline Room, images of a mural Steinberg produced a year later in Detroit (fig. 10), Steinberg’s work as an illustrator, and the scientific analysis all argued against toned varnish layers. Then the conservators received a CD that contained photographs from the collection of Steinberg’s papers at the Beinecke Library of the individual mural sections still on their stretchers, before they had left Steinberg’s studio (fig. 11). These images had been found by Joel Smith in the course of his research. This is the sort of information that conservators long for and so seldom find. So the path was clear, and the plan was to restore the original color balance and pristine white background to the mural (fig. 12).

This proved to be considerably easier said than done. Even the surface dirt, accumulated from years in the restaurant, was

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Figure 10. Saul Steinberg, detail of the mural commissioned for *An Exhibition for Modern Living*, a show of modernist interior design at the Detroit Art Institute in 1949. Photo from 1949 exhibit catalogue, republished in Smith 2006

Figure 11. Saul Steinberg, *Mural of Cincinnati* (section 2), in Steinberg’s studio. Note that the lines at the right and left edges connecting the imagery to sections 1 and 3 have not yet been painted.

Figure 12. Saul Steinberg, *Mural of Cincinnati* (section 2), after treatment
tenacious. It did yield to a 2% triammonium citrate solution, which also seemed to swell the varnish slightly. Cleaning tests executed in Cincinnati had indicated some success with acetone for varnish removal, but in larger tests the results were very uneven. To increase contact time an acetone gel was tried. This cleaned further than the free solvent, but the results were still uneven. Next an acetone/benzyl alcohol gel was tested. Although this gel did remove the surface coatings, it worked too quickly and began to dissolve the paint and ground layers as well.

Since the aqueous tri-ammomium citrate solution had affected the varnish, resin soaps were taken into consideration. Tests indicated that deoxycholic soap could begin to gel and fracture the varnish. During clearance with dry swabs, water, and benzine, sometimes the varnish layer could be almost completely removed. Usually, however, there remained a thin yellow coating that could now be dissolved with acetone.

**CONSERVATION TREATMENT: CLEANING**

Even with a cleaning strategy in place, the coating removal presented challenges. The black lines, while generally not affected by the resin soap, were sensitive to acetone. After the first application and clearing of the soap, the black lines had to be avoided, and cleaning between the lines was carried out with tiny brushes or swabs (fig. 13). The conservators were chagrined to discover how many of the ladies in the mural were wearing fancy feathered hats consisting of very closely spaced black lines (fig. 14). In especially thick or oxidized passages all the steps might have to be repeated several times. Subtle cleaning lines could be created at cleaning boundaries, especially in large expanses of white where it was impossible to use forms to guide the application of gel. There were also passages where the varnish residues could not be safely removed, and these had to be left in place. Finally, although the conservators tried very hard to clean to the same level, this was not always possible, especially from one panel to the next. It was clear that the mural would require visual integration with thin glazes during the retouching campaign.

**CONSERVATION TREATMENT: STRUCTURAL WORK AND INPAINTING**

Even before all eight of the sections had been cleaned, structural work had to be started to keep the project on schedule. As noted in the article on the Terrace Plaza Miró, the ICA’s solution for mounting large-scale murals involved lining to flexible fabric supports. This system allows the murals to be rolled on wide diameter tubes for transport or storage. The outer perimeter of the lining fabric can be grommeted and screwed into the wall for installation, creating the appearance of a mural completely flush to the wall. Since the process was discussed in depth in the earlier article, it will not be revisited here. \[11\]

Two issues did come up that were not often encountered in typical mural treatments. Because the mural consisted of multiple panels forming a continuous image, putting grommets along all four edges of the lining fabric was not an option (fig. 15). Although the upper and lower edges could be grommeted as usual, another solution was required for the side edges. Velcro was considered, but industrial strength Velcro is not easy to release once the hook and loop sides have locked. There was concern that an installation crew would
find it nerve-wracking or impossible to make the small shifts required to align the painted lines from one section to the next. Instead, magnetic stripping was attached along the side edges of each section. On site at the museum metal plates were aligned to the seams in the mural and attached to the gallery walls. The system held the murals flush to the wall, ensuring that the painted lines read clearly across sections.

Steinberg’s use of the restaurant’s air diffusing grills as design elements created another installation issue. In one panel, for example, a grill created the span of a bridge (fig. 16), and the museum wanted the option of showing the mural both with and without grills. To this end, Per Knutås drew up a design for a stylized grill that was laser die cut from Sintra board, a lightweight PVC material that could be attached to the face of the mural with rare earth magnets.

The final phase of the treatment included varnishing and glazing. The sections were installed in groups of three on a wall and evaluated. A rotation system (which taxed the brains of tired conservators) was set up whereby the last section would become the first of the next set of three (fig. 17). Each panel was given several brush coats of Regalrez 1094. After varnishing, the surfaces were minimally glazed with very dilute Golden acrylic paints to integrate visually any areas of residual varnish with the rest of the mural and to give the panels a unified appearance (fig. 18). The paint layer itself was in very good condition, and minor scratches and losses were retouched with Gamblin Conservation Colors.

The mural was installed on two walls at the Cincinnati Art Museum. It opened in July 2007 several weeks ahead of the traveling Steinberg exhibit, putting the spotlight on a major work commissioned for and about the city of Cincinnati (fig. 19).
ACKNOWLEDGEMENTS

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ENDNOTES

1. Contract dated August 4, 1947 for Cincinnati mural, made out for Thomas Emery’s Sons Inc. and Steinberg, Beinecke Rare Book and Manuscript Library at Yale University, personal communication from Joel Smith.


4. ’48 the Magazine of the Year. 1948. 2(6) June: 115.

5. The Steinberg Foundation, personal communication from Sheila Shwartz.

6. Personal communication from Joel Smith.


8. Carlson, J. 1999. Analytical Report from the Winterthur Museum Analytical Laboratory prepared for the ICA. Analysis of coating material found on three paintings commissioned for the Cleveland Public Library in the 1930s. The three paintings are Ambrozi Paliwoda, Out of the Past the Present, Out of the Material the Spiritual, 1933-34; Ora Coltman, Dominance of the City, 1933-34; and Donald Bayard, Transportation, 1934.

9. While originally the mural was approximately 120 feet, two sections near the kitchen doors were not transferred to the museum in 1965.

11. A difference between the Miró and Steinberg linings was the fabric used. The lining fabric for the Steinberg mural was Reemay 2470, a spun bonded polyester fabric that had the advantage of coming in a 148” width.

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The use of the microtome for preparing cross-section paint samples was first shown to me by John Hook, who was at the time senior paintings conservator at the Queensland Art Gallery in Brisbane Australia. Previous to this introduction from John, whenever I thought of microtoming, I thought only of making thin sections. However, the purpose of his technique is aimed not at thin section preparation but rather at preparing the flat planed surface of the mounted sample for cross-section analysis. The thin section slices produced in the process, are seen as rubbish to be discarded, mainly because they fall apart though on occasion it has been possible to randomly salvage a thin section for further analysis.

The primary advantage in microtoming is that sanding and polishing are replaced by slicing. This saves a tremendous amount of time. An embedded sample can be easily prepared for the microscope in as little as 5 minutes. Currently the restorers at the Rijksmuseum are writing technical examinations of paintings for the systematic catalog. Two samples are taken from each painting, and microtoming is saving considerable time.

The key to the ease of this technique is the use of tungsten carbide microtome blades. Traditionally glass blades have been used by some laboratories and I am sure that the operators achieve satisfactory results. However, glass blades must be individually prepared and need to be frequently changed, whereas, a single tungsten carbide blade can give hundreds of slices in one position, thus each blade is capable of thousands of slices. Further, the hardness of the carbide tungsten is superior to glass for slicing through the minerals found in pigments. Disposable diamond blades offer some possibilities; however, we have found them to be too flexible for cutting pigment samples. Carbide tungsten blades are thick (2mm thick) and rigid.

The following outlines John Hook’s initial description of the technique, stream-lined to accommodate preparation of batches of samples by various conservators.

**PROCEDURE:**
1. Samples are prepared in a mold using a typical two-cast mount system. Our molds are approximately 1x2x1 cm. divided in two to give sample blocks 1x1x1 cm. The media used can be either a 2-part polyester, a light cured resin or any other suitable mounting material. At the Rijksmuseum we are currently using Technovit 200LC, which cures after 20 minutes of exposure to blue light in a blue light “oven.”

2. When imbedding the paint sample it is best to situate it close to one edge of the cube to keep the size manageable for mounting in the microtome.

Once cured the sample is shaped into a half-pyramid shape with the sample near the top (fig. 1). This reduces wear on the microtome blade by reducing the area being sliced. A simple stationary disc sander (fig. 2) with a fine grit paper (240, 320 or finer) expedites this step. 10–20 samples can be easily shaped in as little as 10 minutes. Grinding down the top to get close to the sample also reduces slicing.

3. The shaped sample is fitted into the microtome’s sample holder and slowly sliced to reach the sample. (fig. 3) Depending on the microtome it is best not to exceed 10-15µm per cut. Thicker slices can result in chatter, that is, irregular cutting that vibrates through the sample resulting in chips popping out of the mount material (one of which might contain the paint sample!). When near or in the sample, slices can be reduced to 3-4µm with final slices at 1µm.
4. As the sample is being sliced it can be closely watched using a stereo microscope mounted on a table stand. This allows optimal viewing of the sample during slicing (fig. 4), which is useful in evaluating how far to slice before removing the sample from the microtome for further analysis.

If, after having removed the sample from the microtome, it is necessary to continue cutting or re-cut the sample, it can simply be remounted in the holder. It is not necessary to perfectly reposition the sample. Though slicing may start slightly out of plane, after a few cuts, the whole surface will again be fully sliced and flat.

Once removed from the microtome further polishing is usually not necessary but if desired a few passes over 6-8000 grit micro-cloth would be enough to reduce any distraction. Or, depending on the microscope lens and magnification being used, a cover slip with a drop of aromatic-free mineral spirits over the sample can also add clarity.

CAUTION: Mineral spirits should not be used on tungsten carbide blades as it can have the effect of loosening carbide and tungsten particles.

EQUIPMENT
Microtome: The microtome used at the Rijksmuseum is an older, manually operated rotary microtome from Jung. It was purchased 2nd hand from a microscope collector and is nicknamed “Morton Bay Bug” in memory of Brisbane. Older microtomes are often available from second-hand scientific equipment dealers, as well as from schools and laboratories as they upgrade equipment. Because it had no sample holder, the one pictured here was custom made by the seller. A sample holder is often attached but can also be simply fabricated as...
Sozzani  Studio Tips: Using the Microtome for General Surface Preparation of Paint Samples for Cross-Section Examination

was the one pictured here. It is designed to hold square or round samples (fig. 5). The total cost for both was less than US$ 500.

Blade holder and disposable tungsten carbide blades. The blade is the key to the ease of this technique. Our original blade and holder is from Ausetome and were originally purchased from ProSciTech, Australia. The holder is designed for disposable tungsten carbide blades and blades (80 x 2 mm, 35°) (fig. 6).

Other possible distributors include the following: Delaware Diamond Knives, Inc. (DDK) also carrying the Ausetome blade holder and is a maker of custom tungsten carbide blades, made to specification for the holder. DDK is our current source for the blades. The Canadian company Canemco and Marivac also advertise the Ausetome holder and blades. (See EE366-RT-1 Starter kit includes Holder and 2 blades; EE366-RT-2 2 extra blades).

An option to the holder and the blades mentioned above might be to use a larger (+/-18 cm) or other large heavy custom made tungsten carbide blade that fits the blade holder of a given microtome. Both ProSciTech and DDK can supply custom made blades sized for a specific microtome blade holder. The disadvantage compared to the Ausetome holder is that the larger blades are expensive.

A small disk sander is useful for quickly shaping the sample. A low priced simple disc sander can also be found either second hand or from a discount tool distributor. One can also be easily made by attaching a disc to any stationary mounted small motor.

Figure 5. Sample holder - Note the small piece of wood in the holder, this facilitates positioning the sample by preventing it from being pushed too far into the holder.

Figure 6. Left, Ausetome blade holder and blades; right, DDK custom made blades.

Figure 7. Three microtomed paint samples – sliced, not stirred, sanded or polished: Note – the small moon shaped indentations in surface of sample on the right, this is chatter caused by taking too thick a slice. (SK-A-4837, G. Honthorst, Crowning with Thorns, Rijksmuseum Amsterdam).
Technovit 2000LC mounting resin:  http://www.kulzer-technik.de
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Studio Tips: Canvas Stretching Pliers

Having used many different types of pliers for stretching very large paintings, both lined and unlined, I finally found a pair that are really worth knowing about (D and E in the photo). The pliers in A, B, and C are there for comparison. Others, such as, the “Texas Bear Claw” are no longer available to be illustrated. The canvas puller illustrated in (D and E) are available from the company FOME in Italy. It is located just north of Treviso. I have not purchased directly from them but they can be found:

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info@fome.it www.fome.it

To find the pullers on their website:
Click on – Divisione belle arti; Cornici; Acessori per I cornici; and there is No. 2183. “Tenaglia tendi tela professionale in acciaio forgiato e saldato. Indistruttibile.” Indestructible canvas pliers!!

Figure 1
A. The ones on the left are very small and just very cute. B. A couple of old atelier pliers. Left a commonly available small one and right a large heavy duty one. The large ones were custom made with 20 and 30 cm long handles for extra leverage. Both are very hard on the hands, needing a lot of grip resulting in blisters. C. A style commonly sold as ‘Holbein Heavy Duty’ or ‘Professional.’ They work relatively well and the plastic covered handles are easier on the hands but the canvas tends to slip and thus it takes a lot of pressure to hold the grip. The rubber pads are generally not well-glued and need re-gluing with epoxy before any real use. D. This one is the one I recommend. It takes little pressure to securely hold the fabric, so is very easy on the hand. The length of the handle makes stretching seem effortless with these pliers. They are custom made by FOME Italy from long handled snips. Mine were bought in an art supply store that no longer carries them. So they must be ordered from the maker. E. The markings on the side are from the snip handles onto which the tips were added.
Studio Tips: A Long-Distance Microscope (aka Binoculars)

The Pentax Papilio Binoculars are a compact, reverse-Porro-prism binocular that doubles as a long-distance microscope. As you turn the focus wheel to focus on something at short distance, the two objective lenses automatically move closer together. As the focus distance changes, each eye’s line of sight converges with the other eye, so that both eyes are always looking at the same thing. The result is that you get a true binocular view of the object.

I have found this pair of binoculars useful for examining murals. Because they focus at 18 inches (minimum), you can examine dark corners at 8.5x magnification while either standing on the floor or on a ladder. Even at low light levels these have high resolution and clarity. For a non-conservation but clear example, I can be sitting in my living room at night with a table or floor light on and use the binoculars to see the hairs and whiskers of my cat across the room (10-15 feet away)—even inspect his ears! Hopefully the museum going public won’t catch on and start inspecting works of art in the galleries at close range.

Pentax Papilio Binoculars
8.5x magnification
21 mm objective lens
Focus from infinity to 18 inches
10 oz
Description from www.birdwatching.com
$149 + free shipping
Also available through Amazon

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Studio Tips: A Pocket High-Magnification Microscope

I purchased the Micro Brite MM-24 microscope during the 2008 holiday season at The Container Store, fully expecting that I would return it. I found it extremely useful in the studio, when working on site, and when doing condition reports in situ (i.e. for courier trips!)

The 4-inch high microscope has an internal LED light, a dial that switches from 20x to 40x, and a lever that focuses the image. Essentially you hold it with two hands (as you would binoculars). If you are right handed, use your right thumb to hold the light button on, your left pointer finger to switch from 20x to 40x, and your left thumb to focus. The microscope can be turned 180 for lefties, but the button/lever will be on the outside face of the unit, but still fully functional (for those of us who are a bit ambidextrous!)

I attached felt-tape to the foot of the scope so that I could put it in direct contact with the object, otherwise it is hard to get a clear image (the kid on the packaging is not really seeing anything).

Available at [www.carsonoptical.com](http://www.carsonoptical.com) or through various retailers including the children’s section of the Huntington Book Shop. Retail cost: $11.99 to $15.00
A dental assistant chair may be useful for inpainting, as it has a curved, padded “arm” which can be moved and locked in place in front of the user, and could provide an area of arm support while inpainting at the easel. Having a padded support in front of the conservator as s/he leans forward could also relieve back stress.


A great source for high quality surgical cotton rolls: http://www.wheelchairmedical.com/p-67135-cotton-rolls-sterile-1-pound-case-of-25.aspx The price currently is $7.02/per roll when a case of 25 is purchased, with free shipping.

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