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THE EVALUATION OF LAROPAL A81: PARALOID B-72 POLYMER BLEND VARNISHES FOR PAINTED AND DECORATIVE SURFACES: PHYSICAL PROPERTIES AND STABILITY.

Julie Arslanoglu* and Tom Learner*

Abstract

Although much of the recent research into stable varnishes has successfully focussed on low molecular weight (LMW) synthetic resins, many conservators still make wide use of the high molecular weight (HMW) polymer, Paraloid B-72, for its known stability, despite its low saturating power. Here, the potential of using varnish blends composed of ratios from 2% to 98%, of Laropal A81 (a highly stable and commercially available LMW urea-aldehyde resin) in Paraloid B-72 is explored, in order to capitalise on the positive properties of the individual resins and allow tailoring for specific surface problems in a single application. The results relevant to the investigation of the physical properties of the blends as well as their chemical stability under artificial ageing conditions are summarised here. Optical effects on painted surfaces, including gloss and saturation studies, and their working properties are reported elsewhere (Arslanoglu and Learner 2001). Blends of these two resins in all proportions were found to exhibit high thermal and chemical stability under artificial ageing conditions, with stability evaluated by measurements on glass transition temperature (Tg), hardness/stiffness, yellowing, removability and loss of gloss. In addition, film morphology was determined using transmitted light microscopy, refractive index (RI) and differential interference light microscopy (DIM). The blends were typically observed to form two phase systems, characterised as spherulites of Paraloid B-72 in a matrix of Paraloid B-72 : Laropal A81.

Introduction

The search for stable and aesthetically pleasing picture varnishes has recently focussed on the modification of stable LMW synthetic resins, in an attempt to mimic the desirable optical and working properties of mastic and dammar (de la Rie 1993; Whitten 1995). These two natural resins are still widely used in conservation for these properties, which enable the production of a variety of surface finishes, despite their known and inherent instability, resulting in a rapid increase in brittleness, yellowing and insolubility in non-polar solvents (de la Rie 1988). This focus on LMW resins is justified due to their tendency to exhibit high saturation and surface gloss and to remain readily re-dissolved, compared to many polymeric materials (de la Rie 1990). Although some of these LMW resins, such as ketone resins (e.g. Laropal K-80) and reduced ketone resins (for example, MS2A), are now also known to be unstable, hydrogenated hydrocarbon (HHC) resins (for example, Arkon P-90 and Regalrez 1094) and certain aldehyde resins (for example, an experimental BASF resin and Laropal A-81) have been shown to exhibit superior stability (de la Rie 1993; de la Rie 2000).

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However, many conservators still make extensive use of Paraloid B-72, a highly stable, but HMW acrylic copolymer. For many, varnishing with Paraloid B-72 provides an entirely appropriate finish for many situations, although it is widely accepted that it can exhibit poor saturating power in dark colours and areas of blanched or abraded paint. One approach to increasing the saturating power (if needed) of a varnish system that incorporates Paraloid B-72 is to consider a layered system with a LMW varnish applied over an ‘isolating layer’ of Paraloid B-72, since it is the last layer of varnish that affects the overall appearance most strongly. If designed appropriately, such a system also holds the advantage that the final varnish will not disturb the isolating varnish layer or areas of inpainting.

Another largely unexplored possibility of modifying the properties of individual varnishes is to use a blended system, that is, two (or more) resins mixed together in a single layer. Blends are already used as artists’ and conservation materials; for example, dammar and mastic are blends of LMW and HMW components. Recently, Winsor & Newton developed Conserv-Art Picture Varnish, which is a blend of Paraloid B-67 with a small proportion of Laropal K-80. The varnish is reported to provide good gloss and saturation, albeit a slightly lower gloss to dammar (Blakney and Roth-Wells 1998), but unfortunately neither of its components is of particularly high stability.

The main advantage of a blended system over a layered structure is that the possibility of interlayer delamination or optical disturbance (that is, refraction at the interface) is eliminated, as long as the individual components are truly miscible in the dried state. If two resins are not completely miscible they form a ‘two phase system’ (see Figure 1), and the resulting dried films usually contains areas of microscopic inclusions or spherulites of one component within the other (Arridge 1993; Ougizawa and Inoue 1999). Wax added to resins as a matting agent, for example with MS2A, Laropal K80 or Paraloid B-72 (Buckley and Houp 1998; Cox 1998; Fischer 1998), is known to produce two-phase blends. Such phase separation may affect the physical and optical properties of a varnish film through the manifestation of perceptible cloudiness or texture, although in thin films, such as the typical thickness of varnish, these effects are often minimal.

![Figure 1. Phase Diagram. This diagram illustrates how at a single concentration of one component within another, with increasing temperature, a mixture can move from a two-phase system to a one-phase system.](image-url)
A possible candidate for a stable LMW resin to be evaluated in a blended system with Paraloid B-72 is the aldehyde resin Laropal A81, since both resins are soluble in similar organic solvents, in particular the aromatic mineral spirits such as Shellsol A (Shell Chemical 2000) or Solvesso 100 (Exxon Mobil 2000). Although the precise structure of Laropal A-81 is still not known, all aldehyde resins are condensation product of formaldehyde and urea, and their general structure is shown in Figure 2 (Stoye and Freitag 1996). The resin has been shown to exhibit the highest degree of stability of any commercially available aldehyde resin and has recently been developed as a medium for inpainting (de la Rie, et al. 2000; Leonard, et al.2000).

In order to broaden the range of varnishes available to the conservator, research was carried out to investigate blended systems between these two stable resins. If these blends did indeed prove stable, the consideration of a whole series of stable varnishes with a wide range of surface finishes and working properties would be a possibility. The results are reported in two parts. Investigation into the appearance of the varnishes particularly when applied to painted surfaces, as well as some observations on their working properties and inpainting is reported elsewhere (Arslanoglu 2000; Arslanoglu and Learner, 2001). In summary, a small addition of Laropal A81 to Paraloid B-72 produced a varnish with increased saturating power, while still retaining its known working properties. Conversely, a small addition of Paraloid B-72 to Laropal A81 was seen to improve the coating’s resistance to disruption through inpainting or overvarnishing, without adversely affecting its more desirable optical properties, especially on surfaces that were difficult to saturate or contained, for example, degraded glue deposits.

In this article, the physical properties of fresh varnish films of Paraloid B-72, Laropal A81 and varnish blends of the two resins are described including film morphology, RI, Tg, hardness/ stiffness, yellowing, solvent retention and removability. Stability of the pure resins and their blends was also investigated through the evaluation of artificially aged films. The evaluation techniques included film morphology, RI, Tg, hardness/ stiffness, yellowing, solvent retention, removability and gloss. Further details of the methodology and results can be found in Arslanoglu 2000. Hardness and stiffness are discussed in more detail in Arslanoglu, et al.
Experimental


Shellsol A was selected as the solvent because both Laropal A81 and Paraloid B-72 are soluble in it and because it is a solvent commonly used by conservators (Shellsol A is now known as Shellsol A 100.) Two batches of Laropal A81, two years apart in manufacture, were prepared in 20% w/v solutions for batch variance investigations. Paraloid B-72 was prepared as 20% w/v solution. The more current batch of Laropal A81 was selected for the testing of blends. Blends of constant resin concentration (20% w/v) were prepared by mixing volumes of stock solutions of Laropal A81 (50% w/v) and Paraloid B-72 (20% w/v) in Shellsol A. Blends were prepared with the following percentages of Laropal A81 in Paraloid B-72: 2, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 85, 90, 95, 98%. All solutions were filtered through Whatman filter paper before use.

2. Sample preparation.

2.1 Preparation of thin films on glass slides.

Thin films were prepared by spreading 1ml of each varnish solution on a standard microscope slide. Four identical sets of the two batches of Laropal A81, Paraloid B-72 and all of the blends were prepared. Three complete sets of sample films were artificially aged, one kept in the dark as a control, and their gloss assessed. Films with increasing concentration of Laropal A81 were slightly thinner than those containing higher concentrations of Paraloid B-72. The variance in film thickness occurred because a constant volume of resin solution was placed on each slide and HMW resins tend to have thicker films.

An additional complete set of resins and blends were prepared in Solvesso 100 in order to investigate the effect of solvent on morphology and solvent retention. Solvesso 100 is another solvent currently used for Paraloid B-72 varnishes, however more so in the United States. Solvesso 100 has been described as a preferred solvent for Paraloid B-72 as it forms a less viscous solution (for a given concentration) and exhibits better working properties (Gritt 1999). Solvesso 100 and Shellsol A have similar boiling points, RI, aromatic content and K-B values (Exxon Mobil 2000; Shell Chemical 2000), although Shellsol A evaporates slightly faster and is slightly more toxic. This set of films was kept as a control. Due to lack of space, no artificial ageing studies were done.

Solutions of dammar (20% w/v in 1:1 white spirit: Shellsol A) and MS2A (20% w/v in white spirit) were also prepared. These varnishes would be used for comparison during hardness and stiffness evaluation as well as gloss.

2.2 Preparation of thin films on linoleum tiles.

Varnish was applied by brush to light yellow linoleum (melamine laminate) tiles (40x 20mm²). The tiles provide a uniformly rough, non-absorbent surface so any changes in gloss due to artificial ageing can be clearly observed. Four sets of fifteen tiles were prepared: Laropal A81, Paraloid B-72, dammar, MS2A and 11 blends (2, 5, 10, 20, 30, 50, 60, 70, 80, 90, 95% Laropal A81). One tile was not coated as a control. Three complete sets of sample films were artificially aged, one kept in the dark as a control, and their optical and physical properties assessed.
3. Artificial Aging
The methods and interpretation of artificial ageing are a continued source of discussion. In these experiments, the resins and their blends were exposed to three modes of artificial ageing.

3.1 Light artificial ageing
Light ageing was performed at the National Gallery in London at 18,000 lux/hour, 30°C and 45% relative humidity. A sheet of Makrolon (Lexan) polycarbonate was suspended above the samples in order to block ultraviolet wavelengths below ~400nm. There is evidence that the range of ultraviolet wavelengths selected can influence the ageing products produced. However, for the purposes of this study it was decided to simulate museum conditions where most ultraviolet illumination would be blocked. All samples were light aged for ~60 days except for the second batch of Laropal A81 (the new batch) which was light aged for ~50 days. This corresponds to 50.6 and 46 years of gallery exposure at 200 lux, respectively.

3.2 Thermal artificial ageing
Thermal ageing semi-crystalline materials above their Tg may not be acceptable because the materials can then flow and secondary structure can be lost. Amorphous polymers, such as Paraloid B-72 and Laropal A81, are not as dramatically affected by thermal ageing above their Tg because they have no secondary structure to be lost. Thermal ageing was performed at the Tate Gallery in a Fisons Environmental Equipment ageing chamber 60°C, 55% relative humidity. Samples were aged for ten days.

3.3 Light followed by thermal artificial ageing.
After light ageing, one set of samples was also thermally aged for ten days. This method is thought to present a combination of the reactions manifested in light and thermal ageing alone.

4. Physical Properties.
4.1 Refractive Index.
The RI of the stock resins and varnish films of Paraloid B-72 and Laropal A81 and their blends was measured by immersion (Tennant and Townsend 1984). Because of the nature of the samples' axial illumination was used to determine the RI. Index of Refraction Liquids, Series EH from Cargille were used to determine RI. The microscope used was a Leica DMRX, magnification was 10x and 40x and an Olympus SC35 type 12 camera mounted on the microscope was used for photography. Observation of the movement of the Becke line allowed the determination of the RI of the matrix and, where appropriate, the RI of the spherulites and the vacuoles.

4.2 Glass transition temperature.
The Tg was measured by using differential scanning calorimetry (DSC). By plotting heat flow (mW) versus temperature (°C) this transition can be seen. The instrument used for analysis was a Perkin Elmer DSC Pyris 1 with Pyris software. Between 5 and 10mg of material was scraped from the control and artificially aged slides and sealed into closed aluminium sample pans. These closed pans are not completely sealed so vaporised material can escape during the heating cycle. The pans were placed inside the DSC and the cycle begun: 1) Heat from 30° C to 120° C at
20/ min., 2) Cool from 120° C to -50° C at 20° / min., 3) Hold for 2 min at -50° C, 4) Heat from -50° C to 120° C at 10° / min. The initial heating run is to remove thermal history from the sample and drive off any volatile components such as solvent. Trial runs had shown that heating even to 180° C did not change the Tg of the samples.

4.3 Examination of morphology.

In polymer science the term morphology generally refers to form and organisation on a size scale above the atomic arrangement but smaller than the size and shape of the whole sample. The term 'structure' refers to the more local atomic and molecular details, however, the two terms are often used interchangeably. Examples of polymer morphology include the size and shape of fillers and additives, and the size, distribution and association of the structural units within the macrostructure.

Amorphous polymers include polymers which are glassy or rubbery at room temperature. Many amorphous thermoplastics are brittle, limiting their range of application. Toughening a brittle polymer with the addition of another, more flexible polymer is well known to enhance fracture resistance and toughness. Small additions of a HMW polymer, such as a synthetic rubber, to Regalrez 1094 (de la Rie 1993) is one example of such modification in conservation. The blending of Laropal A81 and Paraloid B-72 will also presumably take advantage of Paraloid B-72's flexibility.

Important issues in the design of polymer mixtures are compatibility, deformation and characterisation. When two polymers are mixed together and they form an arrangement of spherulites of one polymer within a matrix of the other polymer (i.e. they are not miscible), the spherulite size distribution and adhesion to the matrix must be determined by microscopy to develop structure-property relationships. There is a wide range of microscopy instruments available which can resolve details ranging from the millimetre to the subnanometer size scale. The size and distribution of spherulites can be observed by optical techniques and interference microscopy enhances contrast between polymers which are transparent but which have different optical properties, such as RI and thickness.

4.3.1 Transmitted light microscopy.

Transmitted light microscopy allowed the visualisation of spherulites and vacuoles in the polymer blends. With the aid of a calibrated graticule in the eye-piece the particle size could be determined. Spherulites were observed and measured at a magnification of 10x and 40x using a Leica DMRX microscope, equipped with an Olympus SC35 type 12 camera, and a Leitz Aristomet microscope equipped with a 35mm camera.

4.3.2 Differential interference contrast microscopy (DIC)

Both Paraloid B-72 and Laropal A81 are anisotropic in polarised light. This would be expected as both polymers are amorphous. Only their RI make them distinguishable under a microscope. DIC takes advantage of this feature. The illumination of DIC is split into two beams. One beam is displaced at the specimen plane and the beams are recombined to give contrast by interference. The important difference between this and other interference methods is that in DIC, the beams are displaced a very small distance, much smaller than the beam diameter. Thus a region of constant properties shows no contrast because both beams see the same material, but a sudden change in thickness or
RI gives strong contrast. DIC is most often used in reflected light, where surface topography is highlighted and a pseudo three-dimensional image produced (Sawyer 1996).

The microscope used was a Leica DMRX equipped with a DIC module, magnification was 10x and 40x. An Olympus SC35 type 12 camera mounted on the microscope was used for photography.

4.4 Hardness and stiffness.

Hardness is generally defined as the resistance of a material to localised surface deformation, and mostly deals with the permanent displacement of the material. Such resistance may be measured in several ways; for example, resistance to scratching, rebound efficiency and resistance to normal indentation. The latter method is currently the most widely utilised technique for polymers (Parsonage 1999).

All the normal indentation experiments were performed using a commercially available apparatus, Nano Indenter® II (Nano Instruments, Oak Ridge, USA). The machine uses a compliance indentation system, capable of operating at loads in the microgram range. The theoretical depth resolution is in the sub-nanometer range. The continuous stiffness method was applied in this project. It is a method for continuously measuring the stiffness of contact between the indenter tip and sample, comprising the steps of: applying an oscillatory mechanical force of known magnitude to the mechanical contact junction of the tip and sample; and simultaneously measuring the phase and amplitude of the resulting oscillatory displacement between the tip and sample relative to the applied oscillatory force as an indication of stiffness of contact between the tip and sample.

Samples coated on slides were loaded at a set force at a set rate. The probe is programmed to only penetrate until a preset stiffness is reached. At that point the probe will be retracted. Control samples of Laropal A81, Paraloid B-72, 2, 5, 10, 15, 20, 50, 60, 70, 80, 90, 95, and 98% Laropal A81 were tested. Light, thermal and light-thermal aged samples for Laropal A81 and Paraloid B-72 were also tested. Fresh dammar and MS2A films were also tested for comparison. Details of the experimental method can be found in Arslanoglu, et al.

4.5 Colour.

In the accelerated ageing of polymers, yellowing is an indication of the formation of unsaturated bonds during chemical reactions induced by heat or light. When monitoring the colour of transparent objects, it is important to remember that they have diffuse transmission, resulting from cloudiness, and regular transmission, responsible for perceived colour (HunterLab 1996). For these experiments, only regular transmitted light was measured.

A Minolta CR-22 chroma-meter was used to measure colour in the CIELAB 1976 system, with CIE light source C and a 2° standard observer. In these measurements, a control reading was taken for an identical glass slide on a white ceramic tile. This control reading was subtracted from each sample reading to obtain the change in each of the coordinates. Sample readings were taken by placing a varnished glass slide face down on the white tile, then placing the chromameter on the slide. Eight separate measurements were averaged for each value. The multi-sample feature of the chromameter was also used: three reading were taken per measurement.
4.6 Gloss.
Gloss is an indicator of the quality of the surface finish. Diminished gloss in the sample coatings arises from imperfection or roughness of the coating. This causes light to be reflected at angles slightly offset from the specular. Changes in surface gloss may indicate crazing and loss of adhesion due to cross-linking reactions induced by heat or light during accelerated ageing.

Specular gloss of the varnished linoleum tiles (control and 3 sets of artificially aged samples) was measured with a Tri-Microgloss M #206085 glossmeter at 20°, 60° and 85° observation angles, calibrated on a standard glossy surface. Eight gloss measurements were taken at each viewing angle for each tile, and the mean and standard deviation (typically below 5%) were calculated.

4.7 Removability.
Removability of the unaged pure resins and the blends was evaluated in order to characterise the solvent sensitivity of the blends. It was also assessed for the artificially aged films in order to determine if artificial ageing caused any cross-linking reactions or changes in polarity which would affect the ability to remove the varnish blends in solvents similar to those of their application. Pure resins Laropal A81 and Paraloid B-72 were evaluated as controls. The solvents tested were white spirit, xylene, toluene, propan-2-ol, ethanol, acetone, methyl-ethylketone, and water. Dry swabs were rolled for one minute with minimal mechanical action and pressure. The effectiveness of the solvent was rated on how readily the film was dissolved or removed under 20x magnification.

4.8 Solvent retention.
Solvent retention can be monitored by measurement of weight change and the change in film thickness over time. In order to determine if solvent type affected the rate of solvent evaporation films made from varnishes containing Shellsol A and Solvesso 100 were both determined. Weight change was monitored by weighing the slides before the varnish solutions were applied and then weighing the slides and drying films after one day over a period of time. The film thickness was monitored after one day and over a period of time with a micro-calliper.

Results and Discussion

1. Physical Properties of pure resins.
The physical properties of the pure resins was investigated in order to ensure that the experimental methods were correct, by comparison of the experimental values with the literature ones, and in order to have comparable data for the evaluation of the physical properties of the blends. Overall, the physical properties of Paraloid B-72 and Laropal A81 coincided with the literature values. The reported batch variance of Laropal A81 was not apparent in these experiments: both batches tested exhibited the same properties. However, molecular weight investigation, which was not done here, has demonstrated batch variance of Laropal A81 (de la Rie 2000).
1.1 Refractive Index.

The experimental RI for Paraloid B-72 was found to be the same as the literature (RI=1.53) (Horie 1995). The RI for the two stock resins of Laropal A81 was 1.503, with the same results obtained for the dried films. This is lower than the RI reported by the manufacturer, 1.531 (BASF 1999), but has been confirmed by reproducible experiments.

1.2 Glass transition temperature.

Tg measurements were made from stock pellets of the two batches of Laropal A81 and from Paraloid B-72. The literature value of Tg for Paraloid B-72 is 41°C (Horie 1995) and the experimental value obtained was 36°C. The literature value of Tg for Laropal A81 is 57°C (BASF 1999) and the experimental values obtained for the two year old batch of resin was 48°C and the value obtained for the new batch of resin was 47°C. The difference between the literature and experimental values can be explained by the dependence of these values on the protocol used for Tg measurement. The rate of heating or cooling during a Tg measurement cycle is critical to the magnitude of the Tg value obtained. The method for determination of the literature Tg value for Paraloid B-72 used a heating rate of 5°C/min (Schilling 1989). A rate of 10°C/min was used in these experiments. This variation in heating rate may account for the differences in the Tg of the stock solutions. The similarity in the experimental Tg of the two batches of Laropal A81 indicates that any molecular weight variance between the batches does not affect Tg, although batch variance can not be excluded by this result alone.

The Tg were also determined for the dried films of Paraloid B-72 and of the two batches of Laropal A81 that were control and artificially aged. All of the control and light aged samples had a depressed Tg. The thermal and light-thermal aged samples, however, had Tg that were similar to the Tg determined for the stock resin. The depression of the Tg in the control and light aged samples indicated the retention of solvent. There have been several reports of solvent retention by Paraloid B-72 and other synthetic resins (Dauchot-Dahon and de Witte 1978; Khandakar 1992). The Tg data showed that both Paraloid B-72 and both batches of Laropal A81 retain Shellsol A after almost five months. In addition light aged samples also retained solvent in films of Paraloid B-72 and Laropal A81. It is only in films that had been thermally or light-thermally aged that there was no solvent retention which indicated that thermal ageing below the boiling point of the solvent, but above the Tg of the resins (thermal ageing was at 80°C while the boiling point of Shellsol A is 167°C), could drive off residual solvent.

1.3 Hardness and stiffness.

The nano-indentation results are summarised here and can be found in more detail elsewhere (Arslanoglu, et al.). The results showed that Laropal A81 is five to ten times harder than Paraloid B-72 and its modulus, or stiffness, was twice as much. All of the films, control and artificially aged, appeared harder at the surface and softer beneath. The hardness remained the same until the end of the experiment (except for light-thermal aged). This observation was a true result because it was reproducible. There is a phenomenon called the 'indentation size effect' which can cause such a pattern. As the pointed probe pushes into the material, the surface area of the tip in contact with the sample surface increases and thus the resistance increases. The radius of the tip is 50nm so if indentation size effect was a
concern, data collected before a depth of 50nm would be disregarded. The Nano-Indentor II has a computer algorithm which compensates for the indentation size effect so any information before 50nm is reliable.

Dividing the hardness by the modulus gave an indication of the material's ability to withstand deformation. Both Laropal A81 and Paraloid B-72 had a value of ~3% which was very similar to silicon elastomers (2%). For comparison, the value for polymethylmethacrylate (Perspex), a relatively hard polymer, is 12%.

Both resins were very soft which means that these results were very dependant upon the rate at which the force was applied during the experiment. At a higher velocity of loading, the values would increase.

Hardness and moduli were also calculated for MS2A and dammar for comparison. The order of hardness from softest to hardest was dammar, Paraloid B-72, Laropal A81 and MS2A. The order of stiffness from flexible to stiff was dammar, Paraloid B-72, Laropal A81 and MS2A.

<table>
<thead>
<tr>
<th>Resin</th>
<th>E (Young's Modulus) (GPa)</th>
<th>H (hardness) (GPa)</th>
<th>H/E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraloid B72</td>
<td>1.37 ± 0.14</td>
<td>0.025 ± 0.0055</td>
<td>1.82</td>
</tr>
<tr>
<td>Laropal A81</td>
<td>2.20 ± 0.14</td>
<td>0.076 ± 0.0076</td>
<td>3.46</td>
</tr>
<tr>
<td>Dammar</td>
<td>0.64 ± 0.03</td>
<td>0.00478 ± 0.0007</td>
<td>0.75</td>
</tr>
<tr>
<td>MS2A</td>
<td>2.83 ± 0.12</td>
<td>0.247 ± 0.03</td>
<td>8.73</td>
</tr>
</tbody>
</table>

Table 1. Hardness and Stiffness Data for Pure Unaged Control Resins.

1.4 Colour
The films of both the pure resins and the blends were all slightly red (positive Δa*) and slightly yellow (positive Δb*). This very slight colour did not perceptibly influence the colour of varnished surfaces.

1.5 Removability.
Removability was very similar for Laropal A81 and Paraloid B-72. Both resins were not affected by water but were readily soluble in xylene, toluene, acetone and methyl-ethylketone. Laropal A 81 was more soluble than Paraloid B-72 in the propan-2-ol and ethanol. The most significant difference was that Laropal A81 was swollen by white spirit, turned cloudy and could be removed by mechanical action whereas white spirit had no effect on Paraloid B-72.

1.6 Solvent retention.
There was a slow but steady loss of weight over the time the drying films were monitored for films made from Shellsol A and from Solvesso 100. The film thickness remained about the same from the first measurement onward also for both solvents. After one day the Solvesso 100 films were slightly more tacky than the Shell Sol A films which may have indicated a slight difference in solvent evaporation. There was a slow but steady loss of weight over 10 weeks for both films of single resins and blends made with Shellsol A and Solvesso 100, which suggested some solvent retention.
2. Physical properties of the blends.

Once the blended films in Shellsol A and in Solvesso 100 were dried, several blends appeared cloudy, especially in the thicker edges. All of the blends proved to be phase separated resulting of inclusions of Paraloid B-72 in a matrix of Laropal A81 and Paraloid B-72. They were thermally and chemically stable under artificial ageing conditions.

2.1 Refractive index.

In the blends, the inclusions always had a RI similar to Paraloid B-72 while, with increasing concentration of Laropal A81, experimental measurement of RI of the matrix became closer to that of Laropal A81 than that of Paraloid B-72.

2.2 Glass transition temperature.

The Tg were determined for the dried films of 50:50 and 80:20 Laropal A81:Paraloid B-72 in Shellsol A that were control and artificially aged. Again, in both blends the control and light aged samples had depressed Tg while the thermal and light-thermal aged samples had higher Tg. The depression of the Tg in the control and light aged samples compared to the thermal and light-thermal aged samples indicated the retention of solvent.

Because solvent retention was known to depress Tg, only the thermal and light-thermal aged films gave a true Tg result. The 50:50 blend had only a single Tg for thermal aged (36°C) and light-thermal aged (37°C) samples. The Tg is in between the Tg for pure Paraloid B-72 and Laropal A81. This indicated that at a 50:50 concentration of Paraloid B-72 and Laropal A81, the resins form a phase separated blend which did not give distinct Tg for each phase. Because the transitions (i.e. the increase in heat flow) for each phase were very small, they were difficult to separate and calculate discrete Tg for each phase. Two phases were known to exist because of other physical characterisation (morphology and RI). The blends were also known not to be cross-linked because cross-linking would have increased the overall Tg of the material.

The thermal and light-thermal aged samples of 80:20 Paraloid B-72 and Laropal A81, however, showed two distinct Tg of 36°C and 50°C (thermal) and 38°C and 52°C (light-thermal). These Tg were also in between the Tg for pure Paraloid B-72 and Laropal A81. This indicated that at a blend 80:20 Paraloid B-72 and Laropal A81 had two distinct phases which were not miscible. It was also noted that thermal ageing (80°C for 10 days) above the Tg of the resins did not eliminate phase separation from the film.

2.3 Examination of blend morphology.

2.3.1 Transmitted light microscopy.

Microscopical examination with incident light showed white spherulites, and transmitted light illumination revealed a complex film morphology of spherulites and vacuoles (Figure 3) in blends of 30 to 98% Laropal A81 in both Shellsol A and Solvesso 100. The spherulites were identified as concentrations of Paraloid B-72 within a matrix of Laropal A81 and Paraloid B-72, from examination with differential interference microscopy (DIC) and RI measurements. There was a distribution in inclusion size from 0.48-17μm with a maximum at 80% Laropal A81 (Figure 4), markedly larger than the size of the phase separated material measured for MS2A: Cosmoloid 80H.
blends exhibit phase separated domains of 50 to 100Å (XRD performed by Dr. Gordon Crassey, National Museum of Natural History, London).

Figure 3. Inclusions in 80: 20 Laropal A81: Paraloid B72 varnish blends. Transmitted light. Magnification 40 x 6.3.

There was a shift in the spherulite size distribution between the two solvents (Figure 4). This indicated that the solvent did have some effect on the film formation of the blends. Both Laropal A81 and Paraloid B-72 are amorphous polymers and in order for the polymers to dissolve in a solvent, the intermolecular forces between the molecules must be disrupted by the solvent. The state of the polymer in solution will affect the character of the dried film (Reichardt 1988; McGlinchey 1993; Paul 1996). The more stretched out the molecule is, the higher the viscosity of the solution. In addition, solvent choice is known to affect the final appearance, working properties and ease of re-solvation of polymer varnishes (Hansen, 1989; Lawrence 1990; Whitten 1995). The distinct shift in inclusion size distribution may have indicated the effect of the solvent on the blend morphology.

The inclusions could be expected to have some effect on the gloss and overall finish of the blended coatings however they did not impart cloudiness to the thin varnish films of typical thickness (<30μm).

Figure 4. Inclusion distribution in Laropal A81: Paraloid B-72 blends. Note that the maximum inclusion size shifts with solvent selection. Error was ± 0.3mm.
2.3.2 Differential Interference Contrast Microscopy

A pseudo-cratered surface was clearly seen for control and artificially aged samples containing 30, 50, 70, 80, 85, 90 and 95% Laropal A81. (Figure 5) The pseudo-cratered surface was caused by the variation in RI of the particles which gave strong contrast. The image showed that the particles were of a different molecular weight than the surrounding matrix. Phase separation most likely occurred in the lower and higher percentage blends, but the spherulite size was not measurable at the magnifications available.

![Figure 5. DIC of 50:50 Laropal A81: Paraloid B72 varnish blend showing a pseudo three-dimensional image due to phase separation. Magnification 50 x 1.0.](image)

2.4 Hardness and stiffness.

Nano-indentation results showed that all of the blends had very similar hardness and moduli. The blends all had moduli between 1 and 2 GPa and very small hardness values. All of the experimental graphs had the same pattern as the pure resins.

2.5 Removability.

As the concentration of Laropal A81 increased in the blends, the removability profile began to resemble that of Laropal A81. The turning point appeared to be at the 50:50 blend.

2.6 Solvent retention.

There was a slow but steady loss of weight over 10 weeks for films of blends made with Shellsol A and Solvesso 100, which indicated some solvent retention.


Paraloid B-72’s stability was confirmed. In this preliminary investigation, Laropal A81 was found to be photochemically and thermally stable under artificial ageing conditions, in concurrence with results from de la Rie and colleagues (de la Rie, Quillen Lomax et al.; de la Rie, Quillen Lomax et al. 2000).

Blends of Paraloid B-72 and Laropal A81 also proved to be stable to artificial ageing. There were no changes in RI, colour or removability profiles observed between the control and artificially aged samples of Paraloid B-72, both batches of Laropal A81 and the blends. The artificially aged blends also retained the same morphology as seen in the control films.
The Tg of the thermal and light-thermal aged Paraloid B-72 and Laropal A81 were similar to that of the stock resin. These results indicated that there were no significant chemical changes which would alter the cross-linking or polarity of the resins. The evaluation of the blends’ Tg clearly showed phase separation, as discussed above, and also did not exhibit cross-linking.

Colour was also unaffected by artificial aging although, there was a slight increase in ΔL* in the light-thermally aged samples of Paraloid B-72, Laropal A81 and the blends. This may have indicated a slight increase in surface roughness although no crazing, cracking or other surface disruption was observed microscopically.

There was also no significant weight loss from any of the samples after heating for Tg. This indicated that there were no volatile components in the resins or blends, possible products of chain scission, which were driven off during the heating cycle.

The moduli of the control and thermally aged samples both Laropal A81 and Paraloid B-72 were not that different (Table 2). Thermal ageing caused both the hardness and modulus to increase by a factor of approximately two for both Paraloid B-72 and Laropal A81. Light ageing caused both the hardness and modulus to decrease for both resins. Light-thermal ageing was more complicated for both resins. It showed a mixture of effects and without more complex analysis, they were not interpretable. In terms of light-thermal ageing, light ageing had a greater effect on the hardness and modulus than thermal ageing. However, once the probe had penetrated some depth into the film, thermal ageing appeared to predominate (The depth the probe penetrates the material is determined by the hardness of the material.) There was a synergy between the artificial ageing components. Thermal ageing increased toughness (the ratio is >3%) while light ageing decreased toughness (the ratio is <3%). Light-thermal ageing for Laropal A81 increased toughness while it decreased toughness for Paraloid B-72. The most durable surface was thermal aged Laropal A81. Overall, there was no evidence that the aged materials were significantly harder. Thus solvent retention did not significantly effect the moduli or hardness and there were apparently no cross-linking reactions taking place during artificial ageing.

No hardness and stiffness data from artificially aged samples was available at the time of this publication. It may be presumed that there would be no significant changes seen since both of the hardness and stiffness of the pure resins were unaffected under these artificial ageing conditions.

Gloss of the control and artificially aged varnishes on the linoleum tiles was measured in order to determine if the varnishes would crack, craze or undergo some other type of surface deformation during artificial ageing. There was no change in the gloss measurements of Paraloid B71, Laropal A81 and the blends after light ageing. This indicated that no crazing or cracking occurred during light ageing. Thermal ageing of Paraloid B-72 increased the gloss readings at all three angles indicating that the film became more 'mirror-like', increasing the amount of spectral reflectance overall. Thermal ageing of the blends and Laropal A81 caused an increase in 20 and 60 degree gloss and a decrease in 85 degree gloss. This would appear to indicate that thermal ageing caused the vanish blends and Laropal A81 to become smoother, more glossy. The gloss readings of the varnished tiles after light-thermal ageing...
gave results similar to thermal ageing except that there was much more variance in the results. The overall trend was the same but there were some samples where readings at all three of the angles increased (Laropal A81, Paraloid B-72, 15%, 40%, 50%, 60%, 85%, 90% and 98%).

Conclusions

In summary, Paraloid B-72 and Laropal A81 (irrespective of batch) were found to be photochemically and thermally stable under artificial ageing conditions, in concurrence with previous investigations (Feller and Curran 1975, de la Rie, Quillen Lomax et al. 2000). These studies showed that Laropal A81 is stable to artificial ageing, harder and stiffer than Paraloid B-72, has RI of 1.503, and is not miscible with Paraloid B-72 in dried films although it has a similar solvent solubility (although not soluble in alcohols and swollen in white spirit). No batch variance in the physical, chemical and optical properties was found when two batches of Laropal A81, two years apart in age, were examined. Both resins also appear to retain some solvent.

All blends of Paraloid B-72 and Laropal A81 are also photochemically and thermally stable under artificial ageing conditions. They remain removable in toluene and xylene, as well as other solvents, after all regimes of artificial ageing, indicating that significant changes in polarity or cross-linking reactions had not occurred. They form phase separated dried films which have been characterised as spherulites of Paraloid B-72 in a matrix of Paraloid-B-72 and Laropal A81. The phase separation has been shown to exhibit a range of optical properties, expanding the repertoire of varnishes available to the conservator (Arslanoglu and Learner 2001). Different blends of Laropal A81 and Paraloid B-72 displayed unique saturation and gloss properties as well as surface finishes. In addition, the blends appeared to vary in their ability to cope with different types of surfaces (medium lean, glue coated, pigment type, etc.). It is these variances which illustrate the promise of the blends as varnishes in conservation. With further investigation, blends may be selected for specific surface requirements.

The results of the investigations reported here indicate that Laropal A81, Paraloid B-72 and blends of the two resins are photochemically and thermally stable. Blends containing a small addition of Laropal A81 in Paraloid B-72 have been shown to expand the possible finishes and appearance of a Paraloid B-72 varnish, which would lead to more control over saturation, retain stability, employ common working processes so as to avoid the use of less stable materials such as dammar or ketone resin. Conversely, a small addition of Paraloid B-72 to Laropal A81 can lead to similar results in situations which would require more of the LMW component (i.e. on surfaces that are difficult to saturate or contain degraded glue deposits) (Arslanoglu and Learner 2001). In addition it can improve the resistance of a LMW varnish to disruption through inpainting or overvarnishing. Further exploration and refinement of Laropal A81 and Paraloid B-72 blends would provide a broader range of options to conservators for treating materially complex and optically difficult surfaces.

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References


Materials.

Laropal A81: BASF Coatings AG, Glasuritstraße 1, 48165 Münster, Germany.

Paraloid B-72: Rohm and Haas, Lenning House 2, Masons Avenue, Croydon, CR9 3NB, United Kingdom.

Ketone N: Picreator. 44 Park View Gardens. London, NW4 2PN, United Kingdom.

MS2A: Laporte Industries Limited, P.O. Box 51, Moorfield Road, Widens, Cheshire W1H 9AB, United Kingdom.

Dammar: L. Cornelissen & Son, 105 Great Russell Street, London, WC15 3RY, United Kingdom.

Shellsol A: Shell Chemicals Ltd., Shell Centre, London, SE1 7NA, United Kingdom.

Solvesso 100: Exxon Chemical Ltd., 4600 Parkway Whitely, Fareham PO15 7AP, United Kingdom.

Other solvents obtained from BDH Laboratory Supplies, Poole, Dorset BH15 1TD, United Kingdom.

Minolta Chromameter CR-221: Minolta (UK) Ltd., Rooksley Park, President Drive, Pooksley, Milton Keyens, MK13 3HF, United Kingdom.
In May 1937, Howard Cook was awarded the largest mural commission ever given to a Taos artist, to create one of the largest fresco murals in the United States. Through the United States Treasury Department’s Section of Painting and Sculpture, Cook was appointed to develop 16 panels to decorate the lobby of the main post office in San Antonio, Texas. In November, 1937, Cook began work on the full-scale cartoons needed for the mural and tore out and replaced the original plaster walls in the post office lobby, which were too uneven to serve as a ground for the fresco. During the summer and fall of 1938, Cook lived and worked in rented spaces on the Joseph Foster ranch in Ranchos de Taos, New Mexico where he completed the cartoons for the mural panels, as well as larger revised color sketches and much experimenting in fresco on a large wall built in the studio. The fresco wall study was nearly 10 feet by 10 feet; he worked out most of his design and color in pastel studies with the result that the completed paintings are very close in all respects to the preliminary drawings. He returned to San Antonio in November 1938 to begin work on the actual frescoes, which were completed in May, 1939.

In 1997, I was contacted by the Snite Museum of Art, University of Notre Dame, who wanted me to remove the fresco study from the studio wall in Ranchos de Taos and stabilize it so it could travel with the Taos Artists and Their Patrons 1898-1950 exhibition. Over the years, the rented studio at the Foster ranch was used as a storage shed for garden tools, and as time took its toll on the structure, the roof began to leak. In 1997, the Leona Foster contacted the Snite Museum and offered the fresco wall study as a gift, provided the museum could remove it from the studio wall.

The video presented at AIC 2000 documents the process of removing the mural, transporting it to Roswell, and stabilizing the study for inclusion in a traveling exhibition. Following is the detailed report the video was based on.

Removal of Fresco from Wall – Ranchos de Taos, NM, August 11 – 14, 1997

The surface of the fresco was first brushed and vacuumed, then washed with clear water and soft sponges. Since multiple protective layers needed to be applied to the painted surface, the fresco surface itself needed to be as clean as possible for good adhesion of the layers of facing. Two paper conservators were brought in to make paste and contribute their expertise for the application of the layers of wet-strength paper and fabrics.

The good attachment of the first layers was pivotal in the attachment of the subsequent layers of protection. Wheat paste was rolled onto the fresco surface to be certain of even and thorough application. Two layers of wet strength tissue was coated with cooked wheat starch paste, attached and brushed onto the surface. A door had been plastered over during the crafting of the original fresco, causing an undulation of the relatively flat surface. This area became a section of concern and possibly a weak link in the whole of the structure. Added paper was attached in this area.
A third layer of cotton/polyester cheese cloth was attached on top of the paper layers, using more of the diluted cooked wheat paste. A fourth layer of cotton/polyester muslin was attached on top of the first fabric layer using the wheat paste. All four layers were allowed to thoroughly dry. Any small bubbles that appeared during the drying were set down by hand with wheat paste, massaging pressure, and quickly dried with hair dryers.

A final layer of cotton/polyester, tightly closed, basket weave fabric was attached on top of the pasted layer with an ethylene vinyl acetate copolymer film (Beva 371, Conservation Products Co.). The film was first attached to the wall with controlled heat, the fabric placed on top of the film, and heat and pressure applied to both to attain a solid attachment to the wall. A 10" wide strip of a woven acrylic fabric (Sunbrella, Ameritex) was attached to the length of the left vertical edge of the fresco with Beva 371 film and heat. This acted as an auxiliary edge for attachment to the temporary moving frame.

Lengths of an extruded aluminum framing material were cut to fit around the perimeter of the fresco, but only the top and bottom horizontal members were initially attached. The painting was attached to the horizontal bars using nylon cable ties tied through the chicken wire and around the aluminum frame. Two large screw-eye bolts were attached to the top horizontal bar. These, in turn, were threaded with metal chain and anchored to supports in the roof above the mural. A similar system was connected to the lower horizontal bar but attached to a ratchet pulley system.

The adobe wall behind the fresco was removed/dug away by hand. As the fresco began to detach from the wall, the lower pulley system was also given a slight pull, bringing the mural away from the wall for better access for detachment. The door behind the fresco was unhinged and moved to another area. This door opening gave better working access to the reverse of the painting. The process of carving away the adobe wall and pulling the whole painting away from the wall with the help of the ratchet pulley continued until there was complete detachment of the mural from the wall and the fresco was hanging free.

The two vertical members of the aluminum frame were attached to the horizontal members with L-brackets. The sides of the fresco were attached to the metal frame with more nylon cable ties. Horizontal boards in the roof, above the mural, were sawed near the cross-beam Vega and removed to give access to a vertical removal of the mural. The top chains were attached to a crane and the fresco was slowly brought up and out of the interior room. As the mural was slowly ascending, all the U-shaped nails, or staples, were cut and removed from the reverse of the painting. In this position, and with the staples removed, a moderately dilute solution of the wheat paste, with the addition of about 16 oz. (by volume) of “Fibermesh” fiber, was brushed onto the reverse of the mural. This was to begin a consolidation process on the reverse of the fresco. Giving some added strength to the mural before transporting to Roswell was a consideration.

The mural was slowly hoisted out of the building and lowered to a crate which had been assembled in situ. The next day the crate was hoisted onto the flatbed of the crane and secured. The flatbed was outfitted with a secondary plywood floor and supported by inflated inner tubes to allow a better “air ride” of the crate to Roswell.

**Consolidation and Treatment of Fresco – Roswell Museum and Art Center, Roswell, New Mexico, January 13 – 27, 1998**

The front of the crate was removed, exposing the face of the fresco. Only minor crumbs were on the floor of the crate. The facing and careful handling had kept the fresco intact. The crate was removed from around the fresco. The entire fresco unit (including the aluminum framework) was rotated 180 degrees to an adjacent wall, attaching and stabilizing the unit in an upright position. The fresco was positioned for front and back access and kept in place by using medium lengths of the extruded aluminum which were attached to the top corners of the existing aluminum frame and secured to the wall behind the fresco.

The fresco was positioned with the reverse out for best access to accomplish the needed structural conservation work. The reverse was thoroughly vacuumed. Special care was taken to remove as much of the “Fibermesh” particles as possible. The earlier application, in Taos, of dilute wheat paste and the “Fibermesh” fiber resulted in the paste being absorbed into the plaster (a desired effect) but the fibers not being secure to the reverse surface of the fresco. Their insecure state warranted removal. Also, loose particles of the original adobe or plaster from the fresco were removed with the help of the vacuum and a somewhat stiff brush.
The reverse of the fresco was infused with two brush-coatings of an 8%, followed by a 12% solution of Acryloid B-72 (ethyl methacrylate-methyl acrylate copolymer, Rohm & Haas). The consolidant was used in varying strengths to encourage migration and penetration of this material into the reverse of the fresco. These also served as barrier layers for the next layers of reinforcement.

The chicken wire on the reverse was trimmed and secured. Any holes leading to the front (primarily around the perimeter) were covered. The reverse of the fresco was ready to receive the initial layer of stabilization, which consisted of fiberglass resin and fiberglass fabric. The reverse was sprayed with Stypol 040-9981, an unsaturated polyester in monomer (Cook Composites and Polymers Co., North Kansas City, MO), with a resin activator/hardener/polymerization initiator of Cadox M-3, a methyl ethyl ketone peroxide in solution (Akzo Chemicals, Inc., Chicago, IL). Lengths of resin-saturated fiberglass mat fabric were placed on the reverse, adhering to a still somewhat tacky polyester resin layer. This fiberglass layer was the minimum thickness possible to accomplish maximum strength. Once the fabric was placed on the reverse, a second this coat of polyester resin was sprayed onto the back.

Anchors had been fabricated of a 3/16" thick steel plate, 5" square with a threaded 3/8" diameter rod welded to the center of the steel square. Nine of these anchors were secured to the reverse of the fresco with lengths of resined fiberglass fabric applied in overlapping patterns, encasing and reinforcing each anchor. The positioning of the anchors on the back of the fresco was 3 over 3. The reverse of the fresco was highly irregular. Some of these irregularities, including the planar distortion at the center, could not be entirely rectified due to the substantial amount of fabric and resin required to bring them into plane, which would also add considerable weight without lending proportional structural stability. However, it was desirable to fill less pronounced irregularities, primarily around the perimeter, to increase structural stability. This was accomplished with the polyester resin, combined with Cabosil, an inert material (a silicon dioxide hydrophilic silica, Dequessa Corporation, Ohio), after the fiberglass and resin were set.

An aluminum honeycomb, aluminum faced panel was fabricated by Museum Services Corporation, Burnsville, MN, and shipped to Roswell. The panel measured 109" X 125", somewhat larger than the actual size of the fresco (107" X 122"). The aluminum panel was placed upright, on edge and parallel to the reverse of the fresco. The ends of the anchor bolts were tipped with a colored grease marker and the panel was placed against the bolts to mark their positions on the panel. 1-1/2” holes were drilled through the panel at each mark where the threaded rods hit. Nuts with washers were attached to the four corner anchors. The panel was slipped onto all 9 anchors through the drilled holes, and adjusted for a parallel and level juxtaposition. The 4 corner nuts and washers were then tightened flush against the back side of the panel. Nuts and multiple washers were attached to all 9 anchor rods on the front of the panel and tightened. This system secured the panel to the fresco.

The multiple layers of facings on the front of the fresco were removed. The top polyester fabric was removed using moderate heat supplied by hand ironing. The remaining four layers were removed using varying amounts of water. Additional dirt came out of the fresco’s “pores” when the last layer of wet strength paper was gently removed from the face of the fresco. Paste residue was reduced on the face.

The panel was parallel to the reverse of the fresco. The plane of the back of the fresco was extremely irregular, resulting in a variation of space between the two surfaces. This was to be filled with an expanding inert material as a bridge between the panel and the fresco. Before this process could take place, dams had to be put in place to prevent any of this material from escaping to the front and onto the face of the fresco. Tape, silicon release paper, and Fome-cor were the main materials used for these very temporary dams. The material used as a structural and unifying bridge between the panel and the fresco was a 2 part, small cell, urethane expanding foam: Part A: a polymethylene polyphenyl isocyanate and methylene bisphenyl isocyanate (MDI); Part B: a polyether polyol, polymeric alcohol, hydroxyl terminated poly (oxyalkylene) polyether (Dow Chemical Co., Michigan) The foam was applied in thin, controlled layers allowing time to elapse during each application for the foam to expand into the desired areas of irregularity. This slow and calculated “foaming” continued until the entire space between fresco and panel had been filled. The foam not only filled the irregular space but also served as a substantial structural bridge between fresco and panel without adding significant weight. It could also be shaped, carved, fitted and inpainted for the final effect on exhibition.
The panel/fresco was turned 180 degrees so the face was easily accessible for the continuing conservation. The fresco was reattached to the back wall with the same aluminum bars that had already been used. The two vertical aluminum side bars were removed from the overall framework. Areas on the perimeter were shaved and sanded to bring about a relatively homogenous visual effect. Any remaining paste residue, as well as any paper fibers from the facing material, were removed from the face of the fresco. Areas of loss and abrasion, as well as obvious water runs and stains, were toned to give a pleasing aesthetic appearance. Inpainting/toning was accomplished using pigments in acrylic resin (LeFranc & Bourgeois/Charbonnel Restoration Colors).

The perimeter format of the fresco was irregular. When the fresco was attached to the rectangular panel and the foam applied, the foam filled the areas lacking fresco. This fill was once again shaved and sanded to obtain an acceptable level with the fresco. The bottom horizontal aluminum rail was removed from the fresco panel. The top horizontal remaining on the painting and the whole unit reattached to the wall behind the fresco. The removal of the last rail would take place just before the fresco would be installed into a specially constructed traveling frame and crated.

Consistent visual unity was achieved with additional fill material which covered the foam and served to fill some small losses and the obvious crack where the painting went structurally over a door in the original structural wall. Depending on the hardness or strength needed, a patching plaster or spackling powder was mixed with dry pigments and water to attain an acceptable tone, consistency, and hardness. The material was applied with putty knives and brushes. These products appeared to be a whiting or calcium carbonate bound with a protenaceous adhesive (The Synkoloid Company, New Jersey). Fine-tuning and toning of the actual fresco surface continued with the LeFranc & Bourgeois paints.

The remaining top horizontal aluminum rail was removed and the fresco/panel placed horizontally on sawhorses. The top exposed edge was sanded, filled, and toned to be consistent with the existent surfaces. All plaster fills were adjusted with a final toning material. The last unifying procedure was to sponge the new plaster surfaces with thinned acrylic paint glazes (Galeria Acrylic Paint, Windsor & Newton, England).

The fresco was attached to a specially designed/constructed frame. The fresco appears to visually float in the frame – all attachment was accomplished on the underside of the frame and anchoring to the panel. The frame construction was devised in this “float” manner so that any handling would be only with the frame itself. The framed/fresco/panel unit was slide into a custom made crate and secured.

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McCrone Associates is a consulting laboratory in microscopy and microanalysis. It was founded over 45 years ago by Dr. Walter McCrone, the scientist most famous for his studies of the Shroud of Turin, which he discovered to be a fine medieval painting, and the Vinland Map, which he found to be a 20th century forgery (Figure 1). Over the years, he has taught several generations of conservators the powerful capabilities of the polarizing light microscope as an analytical tool, and the company he founded continues to study works of artist, archeological and historical significance, frequently with the goal of determining the object's authenticity.

Works of art or objects of historical interest can command enormous prices, well worth the efforts of forgers to create modern imitations. It also happens that honest, well-intentioned people are convinced that the portrait of grandpa in the attic is a long lost Rembrandt. Our analytical approach is to arrive at a reasonable conclusion by the most economical means in the shortest amount of time possible. To this end, we utilize a vast array of analytical tools and techniques. This paper will introduce some of Raman's unique capabilities, in particular when integrated into the entire analytical strategy. We will discuss what it is, how it works on a practical level, some of its unique advantages, and finally several projects (and kinds of projects) in which it has made significant contributions. Our goal at this time was to explore Raman's potential, not to produce a systematic library of spectra.

The Authentication Process
An item might be deemed authentic if it is what it seems to be, or if a group of learned scholars agree to its authenticity. McCrone Associate's role is to help determine if it is scientifically possible for a piece to be authentic, that is to say, if the characteristics of the piece determined in our laboratory are consistent with its purported age and origin. The most basic algorithm is the following: does the piece only contain materials available at the time of its supposed creation? If the answer is yes, we conclude that the piece may be authentic; we can go no further than the possible, (very occasionally the probable), but the final answer must reside with the art historians acquainted with the artist or period in question; they then use the data generated by our laboratory to help determine ultimate authenticity. If the answer is no, that is, if it is seen to contain materials not available when it was created, then it cannot be authentic. (Figure 2).

Analytical Techniques: A Brief Survey
Isolated particles can be examined by several techniques in order to identify the types and phases of pigments present. The analyses used include polarized light microscopy (PLM) for identification of pigments and other materials based on optical characteristics including color, refractive index, birefringence, morphology, and size. Scanning electron microscopy (SEM) with energy dispersive x-ray spectrometry (EDS) is used to gain elemental information about particles to aid in their identification. In certain situations, SEM with wavelength dispersive x-ray spectrometry (WDS) can be called upon to resolve ambiguities from EDS studies. For organic pigments, IR spectroscopy (IR) is usually our first choice. And we also employ Raman spectroscopy (Raman) to collect molecular information about both organic and inorganic pigments (Figure 3). The data collected from each technique is combined and compared to references and historical data regarding identified pigments to make a determination of how well the chemical information agrees with the date and artist of presumed attribution. This by no means exhausts the list of useful techniques and instrumentation used to identify materials in works of art, but these are the most common.

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**Analytical Process Example: Painting**

A more detailed flow chart for the analytical process for, say, a painting, goes something like this (Figure 4):

1. Inspect the painting; document findings
2. Sample all significant colors and parts of the painting
3. Extract medium from paint; mount paint medium for IR
4. Mount all samples for PLM (glass microscope slide) and EDS (beryllium or carbon planchette)
5. Analyze all particles by PLM (color, size, refractive index, crystal habit, birefringence, optical sign, etc.
6. Analyze all particles by EDS for elemental constituents
7. Analyze medium (and organic pigments) by IR (mounted on salt plate)
8. Are all significant constituents identified?
   a. Yes
      i. Go to date question (9)
   b. No
      i. Modify methods or instrumentation
      ii. Perform new analyses
      iii. Go to 8
9. Date question: Were all materials available during the purported period?
   a. Yes: Work is consistent with artist or time period
   b. No: Work is not consistent with artist or time period

The first seven steps are completely routine and occasionally sufficient to answer all the important questions about a piece, but frequently are not. The choice of the next analytical method depends upon the information collected thus far. As noted above, PLM and EDS are the basic techniques used in every pigment analysis, supplying essential data. Other analytical techniques (such as Raman) help to complete the picture.

This is just one, relatively simple protocol. There are others; their application depends upon the nature of the object and the specific analytical goals.

**Raman Spectroscopy**

Raman spectroscopy is a powerful analytical technique capable of solving numerous problems in materials identification with great efficiency. The method is fast and reliable and needs little or no specimen preparation. In this capacity, it has enormous potential for utility to the conservation community, especially when attempting to determine an object’s authenticity. In many cases, it provides the most elegant solution; occasionally, it provides the only practical solution. On the other hand, it is not without its own limitations and pitfalls of which the analyst must be aware. Also, although it can be used as the only analytical method, it is at its best when integrated with other analytical methods.

**Raman Spectroscopy: a Brief History**

In 1923, Smekal predicted that monochromatic light scattered by a transparent medium could contain frequencies that were different from the incident radiation. In 1928, Chandrasekhara Venkata Raman demonstrated the phenomenon and, in 1930, he received the Nobel Prize for his subsequent development and elucidation of the effect. Today, the phenomenon and the spectrographic method developed from his studies bear his name (Figure 5).

This spectroscopic method was only rarely used until the development of powerful lasers in the 1960s provided a practical method for producing the exciting radiation. More recently, fully integrated “off the shelf” systems have become available, and spectral libraries are becoming more widely available.

**Raman Spectroscopy: Basic Theory**

When monochromatic light strikes a material, besides the expected reflection and refraction of the beam, a small amount of light is scattered in all directions by the electron field of the subject. The specific characteristics of the electron field of the material are related to the atoms present and molecular bonding. The greatest portion of the scattered radiation has the same frequency as the incident light; this is called Rayleigh scattering. A very small fraction of the incident light (about 10^-6) has a higher – or lower – frequency than the exciting radiation; this is the
Raman scattering. The Raman scattering contains information about the molecular vibrations present. The lower frequency radiation is called Stokes radiation, and the higher frequency, anti-Stokes. This is illustrated in Figures 6 and 7. Interestingly, the mathematical equations describing the Raman effect predict both the Stokes and the anti-Stokes Raman emissions (Figures 8 and 9).

It is frequently and correctly said that IR and Raman are complementary techniques. While both depend on the molecular vibrations of the substance under investigation, IR active bands depend on the molecules dipole moment, whereas Raman depends on the molecule's polarizability. Thus, one frequently finds that molecules that are inactive in one technique are active in the other (Figures 10 - 13).

**Raman and Pigment Identification: Advantages**

In 1995, Clark *et al* published Raman spectra of the most important pigments in use before 1850(1). This publication was one of the first attempts to promote Raman as a comprehensive tool for the identification of artists' pigments. By restricting the library to pigments invented prior to 1834, they laid a firm foundation for future studies.

Clark suggested that Raman is the “ideal analytical method for pigment analysis because the method is

1. Highly reliable
2. Sufficiently sensitive to positively identify the most minute samples
3. It is generally non-destructive
4. Relatively immune from interferences
5. Well adapted to *in situ* applications (Figure 14).

Our experience at McCrone Associates confirms those judgments. From our point of view, the practical advantages of Raman also include the following (Figure 15):

1. Provides information about the molecule not easily obtained by other methods
2. Very high spatial resolution
3. Great specificity
4. Little to no extra specimen preparation
5. *In situ* pigment analysis for sensitive media such as watercolor and pastel.
6. Economical and efficient.

Additionally, it is a truly microscopical method that fits in well with our overall analytical approach; frequently, we have only minute amounts of sample available for analysis. Its high spatial resolution allows us to analyze very small particles with confidence. Because the specimen can be on virtually any substrate, including those used for PLM (glass microscope slide, with a glass cover slip, embedded in a mounting medium), for SEM/EDS (beryllium or carbon planchette) or for IR (a salt plate), and because it provides information not provided by other analytical methods, it integrates well with other analytical techniques and is even well suited for *in situ* analysis. This has been exploited for studies of watercolor paintings and pastel drawing, which are particularly sensitive to sampling damage; see below for further discussion of these applications.

Considering the large number of pigment innovations since that date (pigments that frequently show up in forgeries), we felt it important to collect spectra of the more recently available pigments, as they can and do appear in contemporary forgeries.

**Molecular Structure Information**

Because Raman spectroscopy responds to the specific molecular bonds present in the material, it has the ability to distinguish between closely related polymorphs of the same material, some of which are of great importance in the conservation and authentication fields. Note below our discussion of the titanium dioxide white pigments.

**High Spatial Resolution**
The Raman scattering is excited by one of several possible lasers. The optics of the microscope permit a very narrow beam, about 1 μm in diameter. The smallest possible particle for which a reliable spectrum can be obtained is approximately 0.75 μm. This permits the analyst to characterize a mixture of pigments in a sample one particle at a time. This means that each pigment can be individually analyzed and identified without interference from other pigments. The microscope used to choose the particles for spectroscopy is also capable of providing polarizing light microscopical information as well; correlating the two techniques provides crosschecking information.

**Specimen Preparation**

A distinct advantage of Raman microscopy is the minimal or nonexistent sample preparation required to analyze a sample. As long as the particle is accessible to the laser, a Raman spectrum can be collected. Spectra can be collected through optically transparent materials such as glass, water, slide mountants, and colorless refractive index oils. The ability to work with the PLM preparation is of great importance since the pigment particles are already well dispersed and the particles in question can be easily found. Microscope slides are especially convenient. Both the glass of the cover slip and the mounting medium are relatively Raman inactive, so the particles of interest can be analyzed without further preparation. The same specificity can obtain using EDS or IR substrates, but frequently the paint was placed on the mount as a sample that includes a mixture of pigments. By choosing areas to analyze based on color or other qualities, or individual particles mounted for EDS, the same specificity can be achieved.

**Instrumentation**

The instrument used for this work was a Renishaw Raman 1000 microscope, consisting of an Olympus BH-2 polarized light microscope coupled to a Renishaw Raman spectrometer (Figure 16). The system is equipped with two lasers for sample excitation, a 30 mW argon ion laser for excitation at 514 nm and a 50 mW diode laser for excitation at 782 nm. The 514 nm argon ion laser was used for the majority this work. The Renishaw Raman spectrometer uses holographic notch filters to remove the laser light reflected and scattered from the sample (Rayleigh scattering), and a 1200 groove/line diffraction grating to disperse the Raman scattered photons onto the Peltier cooled CCD detector. Spectra are collected with a 50X, 0.75 NA Olympus objective, providing a laser spot size of 1 μm, and, as noted above, usable spectra can be collected from particles as small as 0.75 μm.

The system is equipped with a motorized X-Y-Z stage. This stage is appropriate for specimens mounted on most substrates including normal microscope slides, the salt plates used for IR analysis and the beryllium or carbon planchettes used for EDS studies. The stage even allows a small amount of rotation for limited PLM studies. The stage can also be modified or removed for in situ analyses.

**Inorganic Pigments**

Raman is very well suited to the analysis of inorganic pigments. The spectra tend to be relatively simple and highly discriminating. Pigments which are stoicheometrically similar but crystallographically different can be readily distinguished with Raman; these include lead tin yellows type I and type II (1) and the two important polymorphs of titanium white pigment (see below).

The information provided by Raman for inorganic pigments represents the analytical ideal in that, in addition to providing reliable information in its own right, it correlates well with our other two commonly used methods, PLM and EDS. PLM provides color, morphology and a host of other crystallographic information, EDS provides elemental data and Raman provides additional structural data based on molecular vibrations.

**Titanium Dioxide Pigments**

Titanium dioxide appears in three common crystal forms in nature, as brookite, anatase and rutile. Brookite is not commonly used as a pigment, but both anatase and rutile are of great importance in all parts of the paint industry, from architectural paints to artists' colors. They are especially important when the goal is to authenticate a work of art, because each pigment form was introduced at different dates. In fact, the titanium dioxide pigments provide the microscopist with about a half dozen dates of first use, depending on which crystal form is present, and with or without co-precipitated extender pigments such as calcium or barium sulphate (2). Titanium dioxide pigments also appear mixed with various percentages of lithopone.
PLM provides the first indication that TiO₂ may be present: although the particles are white with reflected light, because of their high refractive indices, they appear black with transmitted light. The particles are also very small, many less than one micron. The rutile form also has very high birefringence, so that, under crossed polars, properly oriented particles may appear as tiny pinpoints of light. SEM/EDS shows the presence of titanium in the sample, although care must be taken to distinguish it from barium, an element with EDS spectral overlaps. A skilled polarized light microscopist may be able to sort out the two crystal forms (rutile has both higher indices of refraction and higher birefringence than anatase), but they can also look quite similar to one another. Distinguishing the two forms then necessitates some other analytical method to resolve the issue. X-ray diffraction is the most common method used to determine crystal forms, but McCrone Associates currently lacks the instrumentation necessary for single crystal studies. Another effective method is electron diffraction (selected area electron diffraction or SAED); the problem here is the fairly lengthy specimen preparation and instrument time: such analyses are expensive. Raman resolves the problem quickly, unambiguously and economically (Figures 17 and 18).

### Table 1
Raman Spectroscopy Compared with Other Analytical Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Specimen Prep. Time</th>
<th>Time: Analysis</th>
<th>Cost</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman Spectroscopy</td>
<td>None</td>
<td>15 min</td>
<td>$125</td>
<td>Fast, inexpensive, no extra sample prep, highly accurate</td>
<td>Results highly dependent on library; fluorescence</td>
</tr>
<tr>
<td>Polarized Light Microscopy (PLM)</td>
<td>5 min</td>
<td>5 min</td>
<td>$50</td>
<td>Fast, inexpensive</td>
<td>Low level of confidence in some cases</td>
</tr>
<tr>
<td>X-ray Diffraction (XRD)</td>
<td>0.5 hours</td>
<td>Several hours (unattended camera)</td>
<td>$600</td>
<td>Accurate results with high levels of confidence, even in mixes</td>
<td>Slow; moderately expensive</td>
</tr>
<tr>
<td>Selected Area Electron Diffraction (SAED)</td>
<td>0.5 hours</td>
<td>1 hour</td>
<td>$650</td>
<td>Advantages of XRD plus morphology</td>
<td>Time consuming, expensive, highly skilled analyst</td>
</tr>
</tbody>
</table>

#### Case Study: Impressionist Pastel

Raman spectroscopy helped in the solution of a difficult case involving a pastel drawing based on a well-known Impressionist painting. The well-executed work carried the signature of the famous artist. Sampling the work was rather difficult as the pastel color was generally thin, and the amount of chalk removed was quite limited. With PLM and EDS, we were able to identify a large number of the pigments present. The black chalk of the signature also contained fair amounts of a white pigment including, unfortunately, titanium dioxide in pigment form. This was not completely confirmed until AEM studies were performed, confirming TiO₂. Particle morphology and selected area electron diffraction suggested the anatase crystal form, and the limited size range of the particles suggested a precipitated product. Raman spectroscopy confirmed the anatase crystal form (Figures 19 - 20), but it also identified chrome yellow (Figure 21), which was only present in trace amounts and was not noticed with either PLM or EDS. It also confirmed the presence of Prussian blue and synthetic ultramarine blue (Figure 22).

#### Organic Pigments
Organic pigments represent a special problem for the analyst. Before the pigment explosion of the twentieth century, there were only a very few in common use, and most of them were readily distinguishable with PLM. Madder and alizarin, gamboges and Indian yellow, indigo and the inorganic blues all represented relatively straightforward identifications. The twentieth century, however, saw a virtual explosion of organic pigment invention.

EDS is of little help in identifying organic pigments, and PLM is rarely much better in that many of the organic pigments within a class all look pretty much the same. Today, the usual method for organic pigment identification is IR, for which we have a great deal of experience and excellent libraries. The only weakness for IR is that it requires its own careful specimen preparation: the appropriately thin sample must be placed on a substrate that is totally transparent to IR such as alkali metal halide salts; NaCl and KBr plates are both popular.

However, as noted earlier, Raman spectra can be obtained directly from the PLM specimen slide; this can represent a considerable time savings. But just how reliable would Raman be for organic pigments? In order to study the question further, we investigated two classes of organic pigments, a selection of the most common organic red pigments, all of which are chemically quite different, and a selection of the Hansa yellows, all of which are members of a chemical family with only minor chemical differences between them.

**Organic Red Pigments**

We compared spectra from four organic red pigments in common use in contemporary artists' colors: theofast red (PR88), quinacridone red (PV19), parachlor red (PR4) and perrindo red (PR224). All were clearly distinguishable, although care would have to be exercised in distinguishing between PR4 and PR224 as their spectra share a number of important lines (Figure 23).

**Hansa Yellow Pigments**

Probably the most important contemporary yellow organic pigment is Hansa yellow 10G (PY3). We found that we could clearly distinguish between PY3 and PY75 (Figure 24).

**Case Study: Possible Rubens Painting**

This painting was submitted to McCrone Associates as possibly made by Peter Paul Rubens, the famed 17th century painter. All the materials identified up to that point proved to be appropriate to the period, but in several samples, small amounts of very small blue pigment particles scattered randomly throughout the preparation were visible when viewed with high magnification. Morphological and optical characteristics were difficult to determine by PLM from such small particles, and it would have been difficult (and very expensive) to isolate the particles for further analysis with EDS or IR. Yet, the identification was of the greatest importance, because the possible pigments ranged from the earliest to among the most recent (Figure 25):

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultramarine blue (natural)</td>
<td>Ancient</td>
</tr>
<tr>
<td>Indigo ancient</td>
<td>Ancient</td>
</tr>
<tr>
<td>Prussian blue</td>
<td>1705</td>
</tr>
<tr>
<td>Ultramarine blue (synthetic)</td>
<td>1824</td>
</tr>
<tr>
<td>Cobalt blue</td>
<td>1802</td>
</tr>
<tr>
<td>Phthalocyanine blue</td>
<td>1935</td>
</tr>
</tbody>
</table>

Raman spectroscopy was performed by analyzing the blue particles in the light microscope slide itself, aiming the laser through both the glass cover slip and the Aroclor™ medium itself. The result? Indigo! (Figure 26). This finding was significant, not only due to the ease of analysis (The entire analytical procedure took approximately 15 minutes, including library research and documentation) but because indigo is not only an ancient pigment, it also provides the analyst with a date of last use: it disappeared from oil paintings about 1800. Furthermore, this pigment was also accompanied by lead-tin yellow, a pigment with an even earlier terminal date of about 1750. Interestingly, lead tin yellow comes in two different phases, classified as Types I and II – crystallographic distinctions discernable by Raman spectroscopy (see Clark, 1997).

**Graphite Pencil Lead Discrimination**

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In addition to forgery, in which a work is created with the purpose of deception, works created as honest copies or imitations of a particular master (often by talented students) are occasionally misrepresented as works by the master by the addition of a spurious signature. If the work in question is a pencil drawing, the analyst is faced with only two items for analysis, the substrate and the graphite pencil marks. Pencil lead is relatively simple material, consisting of a molded mixture of ground graphite, carbon black and clay. Neither PLM nor EDS provide much help, but we found that subtle variations in the Raman signal can distinguish these differences with clarity (Figure 27).

Our experimental procedure was as follows: We collected several different brands of pencils and wrote with each onto a bond paper substrate. Raman spectra of each were collected in situ. Our findings were as follows:

1. Raman spectra of a single pencil were consistent with one another (Figure 28).
2. Raman spectra of different pencils showed distinguishable differences (Figure 29).

Natural Red Chalk Analysis

Natural red chalk was a popular sketching material used in 18th century France by Watteau, Bouchet, Lancret, Robert and other artists. McCrone Associates has been providing some analytical services to the Art Institute of Chicago in a study of the red chalk drawings of Watteau and his contemporaries. The natural red chalks consist of little more than iron oxides hematite (Fe₂O₃) and goethite (FeO(OH)) in a natural clay matrix. Each of the different chalks consists of different relative amounts of hematite and goethite, subtle differences that can be studied with Raman (Figure 30). Besides Raman, each sample was also studied with PLM and EDS.

One specific goal of this study was to determine whether two anonymous red chalk drawings (Figure 31) tentatively attributed to Watteau (A1 and A2) may have been made by the master, or whether a different attribution was more likely. The PLM and EDS data showed all the samples to be very similar in composition. The Raman data, showing variations in the relative amounts of goethite and hematite, was more specific: it showed that the two anonymous pieces were very similar to one another, possibly from the same batch of chalk. It also showed a fair amount of variation among the known Watteau drawings, but at least one of the known Watteau pieces was very similar to the two anonymous drawings (Figure 32). This project is ongoing.

In Situ Watercolor Analysis

Raman microscopy has been employed for analyzing paints and pigments in situ on illuminated manuscripts, pottery and oil paintings (3 - 5). Based on these previous successes, we applied the technique to the analysis of watercolor paints in situ. Watercolor paints spread pigment particles in a thin film directly onto fibers of the paper substrate. When the paint is thick, sampling is generally not problematic, but, when very thin, it is difficult or impossible to sample without tearing fibers. Because of this potential of damage and the subsequent impact the damage could have on the painting's value, we decided to try Raman for examining pigment particles directly on watercolor paintings, avoiding the particle isolation step and potential damage to the paper substrate.

Ms. Kathleen Brahney, watercolor artist, provided us with samples of her palette on a good quality paper (Figure 33). Her palette consists of Windsor Newton™ watercolor paints exclusively, and she fully documented each sample. These samples of watercolor paints were analyzed using the Raman microscope to generate a reference set of spectra for comparison to particles on an actual painting. A painting by the artist from the author's collection (Figure 34) was used as an evaluation sample.

After collecting our reference set of Raman spectra from the watercolor paint palette, we proceeded to analyze the painting directly. Microscopic examination of the painting showed that we could clearly irradiate pigment particles or pigment areas that would not be interfered with by the paper fibers of the substrate. In situ Raman analysis was able to identify all of the pigment present on this painting (Figure 35).

Although the palette for this evaluation sample was limited, we have shown that Raman spectra can be collected directly from the surface of a watercolor painting with sufficient spatial resolution to avoid spectral features from surrounding pigment particles or the fiber substrate, and we can get good quality spectra of multiple pigments that can be interpreted. A full discussion of this study has been recently published (6).

We also encountered a number of difficulties:
1. Without the aid of a mechanical stage, positioning the artwork under the microscope can be difficult and
tedious, especially for analysis of small or unique particles.
2. The paper fibers tend to shift position due to thermal expansion under the laser beam. However, after the
fibers reach an equilibrium thermal state and the fiber has expanded as much as possible in the paper,
maintaining focus becomes easier.
3. Another limitation of in situ analysis is the size of the piece of art. The microscope stand only permits a 4.5”
distance from the center of focus the inside arm of the stand. For areas within the 4.5” distance, conventional
sample removal would have to be done.
4. We lose some of the PLM information available with transillumination. While we retain morphology and
color, we lose important crystallographic information such as refractive index, birefringence and optical
sign.

Limitations of Raman Spectroscopy

No analytical technique is useful for every kind of sample, and Raman is no exception. Some of the factors limiting
its use are listed below (Figure 36):

1. Fluorescence. If the exciting radiation is too energetic, the electrons may be raised to electron energy levels
that result in fluorescence. When this occurs, the large fluorescence signal greatly overpowers the much
weaker Raman signal. Fluorescence can frequently be controlled by using a laser with longer wavelength
such as the near IR 782 nm laser.
2. Raman inactive material. Fortunately, many Raman inactive materials are IR active.
3. Some organic materials, especially those of a color complementary to the color of the laser, are charred by
the laser; this changes the spectrum. This can usually be seen through the microscope; the solution is to
change to a longer wavelength laser or to lower its brightness. Thus, a red pigment stimulated by the 514
nm argon ion laser is a likely candidate for charring, whereas the 782 nm diode laser might be a better
choice.

Raman’s Role in the Art Authentication Process: Some Final Thoughts

If Raman is so wonderful, why not use it routinely on all samples taken from a painting?

One of several answers is, of course, that occasionally we do, when that is our only option, such as when analyzing a
watercolor. However, we do not use the method routinely, and the reasons for our approach spring from our overall
strategy in painting analysis and, indeed, all analyses of this sort: our strategy is to provide the most complete and
accurate and definitive analysis possible, in the shortest time possible, for the most reasonable cost. If we used
Raman on all specimens, we would have to either increase our fees per project or decrease our use or replace one of
our two other routine analyses, PLM or EDS.

With PLM, we are able to identify most if not all of the pigments in our samples, and, as a minimum, provides us
with good information about all of the pigments visible in a mounted sample. This information, that is size, color,
relative refractive index, birefringence, and so forth, helps us narrow down the possibilities enormously. If PLM has
a disadvantage, it is the ability of small amounts of important pigments to hide among others with which they share
some optical characteristics. For example, a sample of white paint might contain mostly lead white but contain small
amounts of zinc white, lithopone or titanium white in the anatase form.

By performing EDS analysis on relatively large amounts of material, we get an elemental profile of the entire
sample, so if we see zinc or titanium or barium in the spectrum, we can take measures to identify the extra pigments
present. With EDS we can also analyze individual particles, but they must be isolated and mounted onto a suitable
substrate. Thus, specimen preparation can add as much as an hour or more per particle to the analysis. If the
specimen turns out to be an organic pigment, the EDS provides very little useful information, and the efforts are
largely wasted.

With Raman, we are able to simply go to the PLM slide, find the particle of interest, and analyze it directly through
the cover slip. However, when analyzing a mixture of pigments such as is commonly found in a paint sample,
Raman’s great virtue of high spatial resolution becomes a handicap when the method is used as a bulk screening
method. The resulting spectrum of a complex mixture can be quite confusing, and, while specific spectra can be
subtracted from the mix, complex mixtures are less than ideal candidates for analysis. It is best to consider Raman as the technique of choice for single particle analysis rather than a bulk screening method (Figure 37).

References


Techniques for Identification of Unknowns

- Morphology (appearance, shape) (PLM)
- Elemental Analysis (EDS & WDS)
- Molecular Vibrational analysis (types of chemical bonds, functional groups, symmetry) (IR and Raman)

Protocol for Painting Authentication

- Receive Painting
- Inspect Painting
- Sample Painting
- Measure PLM, EDS, IR
- Analysis PLM, EDS, IR
- Select suitable method of analysis
- ID all important components
- Raman
- Generate Negative Report
- Generate Positive Report
- All available at time of original creation?
- No
- Yes
- Yes
- No
- Yes

Raman Spectroscopy

- What is it?
  - Type of vibrational spectroscopy based on the interaction of a monochromatic light source and the electron structure of a sample (scattering), a complimentary technique to infrared

- How does it work?
  - Elastic collision between a photon and molecule

Figure 1. Shroud of Turin
Figure 2. Basic Protocol for Art Authentication
Figure 3. Techniques for Identification of Unknowns
Figure 4. Protocol for Painting Authentication
Figure 5. Raman Spectroscopy
Figure 6. Raman Spectroscopy
Raman Spectroscopy

Sample

Rayleigh

Stokes

Anti-Stokes

Raman

Detector

Frequency

μ = αE

E = E_0 cos 2πν t

α = α_0 + (δα/δQ)Q + ... α = constant (polarizability of bond)

Q = Q_0 cos 2πν t

μ = dipole moment of bond

E = electric field energy

α = constant (polarizability of bond)

Q = internuclear separation

Figure 7

Raman Vibrational Bands

Rayleigh scattering (Same λ as source)

μ = α_0 E_0 cos 2πν t

+ 0.5 (δα/δQ)Q_0 E_0 [cos (2πν + ν)] + cos (2πν - ν)]

Raman scattering (Anti-Stokes) (Stokes)

Shorter λ than source Longer λ than source

Figure 8

FTIR vs. Raman

- FTIR: Energy absorption
  - dipoles
  - asymmetric vibrations
  - Mid IR (4000 - 6000 cm⁻¹)
  - 10 μm min. spot
  - IR transparent substrates or reflection
  - opaque samples

- Raman: Energy emission
  - polarizability
  - symmetric vibrations
  - Shift from laser (10,000 - 50 cm⁻¹)
  - 1 μm beam size
  - exposed sample, or through optically transparent material
  - fluorescence & photodegradation

Figure 9

Molecular Vibrations

IF | Raman Anti-Stokes | Raman Stokes | Raman Scattering | Rayleigh Scattering | Infrared Absorption

V = 0 | V = 0 | V = 0 | V = 0 | V = 0

ν = 0 | ν = 0 | ν = 0 | ν = 0 | ν = 0

ν' = 0 | ν' = 0 | ν' = 0 | ν' = 0 | ν' = 0

I = 0 | I = 0 | I = 0 | I = 0 | I = 0

Figure 10

Molecular Vibrations

Figure 11

Figure 12
**Raman Spectroscopy**
- What can it do?
  - Provide spectra of organic and inorganic materials.
  - Gain information about symmetric molecules
  - Structural (crystallographic) information

**"Ideal Analytical Method for Pigment Analysis"**
Clark et al, 1995
- Reliability
- Sensitivity
- Non-destructive
- Relatively immune from interferences
- Adaptable to *in situ* application

**Practical Advantages of Raman Spectroscopy**
-McCrone Associates
- Microscopic method
- Integrates well with other analytical techniques such as PLM, EDS and IR
- Spatial resolution
  - 1 micron using a 50X objective
- Sample preparation
  - None, Be stub, glass slide, IR salt plate
- In situ analysis

**Renishaw 1000 Raman Spectrometer Olympus BH2 Microscope**
- Dispersive Raman
  - High sensitivity
  - Suited to microscopy
- Lasers
  - Easily switched
  - 514 nm
  - 782 nm

**TiO₂ Crystal Form: AEM**
- Elemental information with EDS
- Crystallographic information
  - Morphology
  - Electron diffraction (SAED)
- Expensive sample preparation
- Expensive instrument time
"Impressionist" Pastel

- PLM: Very small, very high ref. index white particles
- EDS: C, Ca, P, Ti, Ba, S
- WDS: Confirms Ti
- AEM: Confirms Ti; anatase; size distribution consistent with pigment
- Raman confirms anatase

White Particle

Yellow Particle

Blue Particle

Some organic reds

Two Hansa yellows
**Application: Blue Pigments**

- Problem
  - Very small, scattered blue particles
  - PLM ambiguous
    - Ref. Index < 1.662
  - Chelsea filter dark gray
  - Too small for microchemical tests
  - Isolation for EDS or IR difficult or impossible

- Possible pigments:
  - Ultramarine - Ancient
  - Indigo - Ancient - 1800
  - Prussian blue - 1704
  - Phthalocyanine blue - 1935

  Possible Rubens 1577-1640

**Possible Rubens**

**Application: Pencil Analysis**

- Carbon phases
  - graphite
  - carbon black
  - wax

**One Pencil Over a Page**

- Consistency

**Four Different Pencils**

- Discrimination

**Iron Oxide References**

- Hematite (Fe₂O₃)
- Goethite (FeO(OH))
Anonymous red chalk drawings - possibly Watteau?

Raman spectra of red chalks

W & N Pigment References

Watercolor by K.J. Brahney

Raman and PLM Analysis

Limitations of the Method

- Fluorescence
- Raman inactive material
- Charring of sensitive samples
Conclusion

- Has been used successfully at McCrone Associates to distinguish small amounts of very small pigment particles in works of art
- Raman competes and integrates well with alternative analytical methods
- Best used for single particle analysis
TECHNICAL STUDY AND RESTORATION OF AN EARLY 17TH CENTURY LANDSCAPE PAINTING BY ESAIAS VAN DE VELDE

William P. Brown, Chief Conservator, North Carolina Museum of Art

Introduction

In this talk, the restoration of a small Dutch ‘winter scene’ by Esaias van de Velde will be discussed. This small panel, dated 1614, is one of the earliest painted by Van de Velde, who was an important contributor to the development of Dutch 17th century realistic landscape painting.

Rarely, is the restoration of an old master painting straightforward and this treatment was no exception. A complex restoration history and an unorthodox painting technique presented difficult restoration challenges.

History

Van de Velde was an accomplished painter, draughtsman and etcher. His earliest training was received in Amsterdam presumably from his father as well the Antwerp painter Gillis van Coninxloo. Esaias became a member of the Haarlem Guild of St. Luke in 1612, as did Hercules Segers. During Van de Velde’s Haarlem period, he taught Jan van Goyen. By 1618, he had moved his family to The Hague where he died in 1630.

The work of Esaias’s teacher Coninxloo represented the last of the Mannerist tradition, in which landscapes were constructed in a fantastic and unrealistic manner. In contrast, Esaias’s landscapes during his Harlem period, especially his early etchings, were truer to nature. His earliest landscapes already show his characteristic low horizon, open foreground and tonal coloration which was a realistic recreation of the monotonous Dutch landscape. E. Melanie Gifford has written at length on this topic. Her observations on Esaias’s choice of materials in the North Carolina panel and their visual analogy to his etchings were important to understanding the artist’s intent and guiding restoration choices.

Conservation Background

The painting was cleaned before 1990 (fig. 1), but left unrestored until the current restoration was undertaken by the author in 1997. The original panel support is poplar, confirmed in 1986 by Dr. Peter Klein. The choice of poplar was unorthodox for Van de Velde as well as for
other Northern European Artists, although Rembrandt paints on poplar around 1640. Oak additions to the panel were added much later to the top and bottom edges to extend the sky and landscape (fig. 2, radiograph). Most of the sky is a later addition. At the time of the additions, considerable damage to the original panel already existed, especially along the top edge. In addition, there was insect damage to the paint and wood further into the composition in the house, at the left. New damage was likely caused from the joining of extensions to the old panel. The full extent of loss to the top and bottom of the original panel is unknown. The original panel was thinned, mounted onto Masonite, and cradled in the 1940’s.

Conservation Questions

Two restoration questions proved to be the most challenging.

The first question posed was should the painting be displayed in its original format. Two options were proposed—remove the later oak additions or the more feasible choice—conceal them in a frame with a wide hidden rabbet. To ‘frame out’ the additions would require a custom frame that would cover all but about an inch or so of the added sky. Was there another option?

The second question posed was to what extent should abraded passages in the landscape be inpainted. Presumably, Esaias used the tone of the wood, modified by a thin translucent ground, as part of the final image. To what extent was the tone of the wood intended to show through. Has the ground become more transparent with age? The most problematic area was the very thinly painted ice passage at the bottom right corner. To get the effect of buildings reflected in the ice, Van de Velde took advantage of the tone of the wood and gray striations in the ground. The area was visually confusing due to paint abrasion.

Treatment Solutions: question one

The first question was answered by considering the later addition to the panel as a permanent part of the history of the painting. An understanding of why and when the additions were added would help in justifying this approach.

Other known examples of 17th century Dutch paintings, which have been added to for the purpose of creating large skies, include three panoramic views by Seghers. Like the original composition of the North Carolina Esaias, these paintings originally had an elongated horizontal format with a relatively narrow sky. Stechow in his book Dutch Landscape Painting of the 17th Century reports that the additions were made just after the artist’s death in 1640 to appeal to the fashionable taste of the day for high skies. FTIR analysis of a sample of blue pigment from the added sky of the North Carolina painting identified Prussian blue. This dates the additions to the late 18th or early 19th centuries—definitely not to van de Velde’s lifetime or to the 17th century, as in the Seghers.

The North Carolina panel was thought originally to have been painted for inclusion in a cabinet. In George Keyes monograph on Van de Velde there is mention of one other painting on a soft
wood support, *Road before Farms*, dated 1623. Because of its small size and unusual support, Keyes proposed that it could be a furniture inset. The North Carolina painting was thought also to fall into this category for the same reasons. However, at this time, cabinets were more of a Flemish, not Dutch taste.5 Also, Van de Velde is not known as a cabinet painter. There are many 17th century panels which were originally apart of a cabinet, especially Flemish paintings on copper.

To summarize what we have learned about the North Carolina Esaias, our painting probably was intended for sale to hang on a wall—not in a cabinet-- the additions were added several hundred years later, and the technique and original elongated format were influenced by etching.

After several hundred years in the larger format why would we now consider displaying the painting differently? Visually the expanded composition of the North Carolina painting doesn’t work very well. *Winterscene* painted by Esaias in 1624, in the Royal Picture Gallery Mauritshuis, is almost the identical size as our painting, but the vertical framing of the tree and tall house is in proportion to the format. For Van de Velde, this is the type of exaggerated perspective composition you would expect to see in his square format paintings. The original pronounced horizontal format of the North Carolina panel, which is similar to his etchings a year or two later, does not allow for a higher sky. In the expanded North Carolina composition, the sky is largely extraneous and painted in an inappropriately dramatic style. Our painting with the expanded sky works neither as a square formatted composition like the 1624 *Winterscene*, nor as a panoramic composition like the Seghers mentioned previously.

Despite this compositional incongruity, we decided to leave the expanded format as a permanent part of the history of the painting and to restore the painting as a whole. The decision was strongly influenced by the extent to which the original sky had been altered and the uncertainty of how much of the original panel was removed, if any. A closer look at the sky of the original section reveals considerable damage to original paint and extensive overpaint. To integrate the two skies into one, the restorer overpainted most of the original, very placid sky. Applying a light rose tint, he negated the original subtle gradation from buff-color at the horizon to smalt blue higher up, typical of Van de Velde’s paintings. The original sky is now the lower horizon for the larger sky. To help tie together the landscape with the enlarged sky the restorer extended the blasted tree, rather crudely, into the upper section. In addition, he sketched in limbs out from the top of the truncated tree to give a vertical bracket similar to the composition in the 1624 ‘Winterscene.’ In an apparent attempt to simplify the composition, the limbs were painted out by the restorer, as well as an original horizontal limb lower down. Removing the two hundred year old overpaint from the much-abraded original paint was not considered a prudent option. The sky is not as Van de Velde intended whether displayed in its original elongated format or left in its expanded format. The later additions are noted in the wall label and the original section has been reproduced in print (fig. 3, additions masked out for photography).

Although the decision was made to treat the painting as a whole, as a compromise the repainted top of the blasted tree was modified to bring it back into the original composition. The restoration was in keeping with Van de Velde’s style based on the study of other trees by the artist. Most useful for comparison was the etching *Shepherd Standing to the Left of a Curving.*
Truncated, Deciduous Tree, printed in 1613, just before our painting was completed in 1614. The bold and simply stated design is remarkably similar. This tree was most useful in understanding the shape, twist and play of light and shadow up the tree trunk. Many more examples of blasted and truncated trees can be found in Van de Velde's paintings. The top of the tree was inpainted over existing overpaint using dry pigments ground in PVA-AYAC/AYAA and the limb painted back in with watercolor.

Treatment Solutions: question two

On to the second restoration question, to what extent should the abraded passages in the landscape be inpainted? This required an understanding of how Van de Velde used the ground in the North Carolina painting. In Winterscene, Van de Velde apparently used the tone of the wood, modified by a thin translucent ground, as part of the final image. To what degree was this effect intended and how was it different from conventional usage? To help answer these questions cross-sections were taken from undamaged areas to identify the composition and medium of the ground. In addition, a comparison/contrast was made between the technique of the Raleigh panel and panels at the Fitzwilliam Museum, Cambridge and the National Gallery, London to help understand Van de Velde's different approaches to painting, which were apparently based on his choice of ground.

The thin, continuous translucent ground is clearly seen in cross-sections taken from the building to the left and the blasted tree. These are undamaged areas. The use of a thin translucent ground is unorthodox, like the choice of poplar for the support. Typically, chalk with and oil imprimatura would be applied producing a thicker and more opaque ground. Because of its unusual nature, the ground is likely artist applied. As well, the Haarlem guild archives mention primers only from 1631 onwards. The ground is thicker where it is packed into the wood grain therefore it appears gray and opaque only in the grain. Stack process white lead is clearly seen in the interstices. Between the wood grain, the ground is very thin, thus visually transparent. The alternation between thin and thick accounts for the striation pattern.

Cross-sectional analysis identified the ground as a combination of white lead, black, earth color (ochre) and probably some chalk. Oil was estimated as the binder (confirmed with Rhodomine B). The lead white, chalk combination used by Van de Velde in his ground, and possibly the white in the ochre layer on top, may have been the commercially available white called lootwit, frequently used in grounds and underpaints of the day. If chalk were present in the ground, it would be somewhat transparent in oil medium because the refractive index of chalk and oil are close. How transparent is difficult to say, as the proportion of chalk was not established by the testing. However, the thinness of the ground would certainly give a translucent effect, allowing the tone of the wood to come through. It appears that Van de Velde used what amounts to an oil imprimatura containing lead white and chalk, applied directly to the wood, not over a more traditional white glue ground. It's my feeling, that the overall translucency of the ground would have been somewhat lesser pronounced at the time Van de Velde finished the painting.

To help understand how Esaias used the ground in his painting technique, visits were made to Cambridge and London. The ground in Winter Landscape, dated 1614, in the Fitzwilliam Museum, Cambridge appears to be a more traditional and usual preparation for Van de Velde—
an oak support with a light colored ground, which is more opaque and thicker than the North Carolina ground. The neutral light gray color imparts a general higher-key tone than the North Carolina panel—the tone of the wood does not show through the ground in the Fitzwilliam painting. However, the exposed ground serves as the general light gray color for the landscape and patchy snow. Thin dark washes applied over the ground form shaded areas around the base of the trees to the left and below the grouping of figures. White brush strokes pick up highlights and indicate where the snow has perhaps not melted. In the North Carolina panel, the snow and ice are not colored by the ground as in the Fitzwilliam panel, but by white or gray vehicular paint applied onto the ground. In addition, in the North Carolina painting, the tone of the wood modified by the translucent ground, is closer to that of shadows or half tones producing a darker tonal effect. The North Carolina and Fitzwilliam panels were both painted in 1614 but demonstrate very different tonal approaches.

The ground observed in Winter scene, dated 1623, National Gallery, London is very thin and translucent, similar to the North Carolina panel, although somewhat lighter in tone. White striations are created where the ground fills in the wood grain, instead of gray as in the North Carolina panel. The ground is applied much the same way as the North Carolina ground. The color of the oak support shows through the ground creating a slightly orange or blond color. As in the North Carolina panel the tone of the wood serves as the color basis for the areas in shadow such as the line of trees in the background below the horizon, the right side of the house, and the stand of trees and areas of grass to the left of the curved road. The use of the wood tone in the final image is seen to a greater degree in the National Gallery painting than ours, but generally served the same purpose as a half tone and as a unifying warm tone. The National Gallery painting served as a useful comparative reference for the restoration of the North Carolina panel. A color transparency of the National Gallery painting was on hand during the restoration.

In the North Carolina panel the trunk of the blasted tree was the best inpainting reference. The translucent ground was intact and not abraded. Thin grayish PVA glazes were used to inpaint areas of abrasion up to the level of translucency observed in the tree trunk. The painting was brush varnished with MS2A (fig. 4, after treatment).

**Conclusion**

The key to this treatment was an understanding of the artist’s technique, particularly the function of the ground. Painted almost four hundred years ago, it was difficult to make a clear distinction between the effects of aging, restoration and artist intent. I felt fortunate to have had so much technical information and expertise to draw from in guiding treatment choices, but the choices made were not cut and dried.
Acknowledgments

I am grateful to David Findley for his artist insights and Noelle Ocon for her expertise in Photoshop. Thanks also to colleagues who shared their understanding of the subject, with special thanks given to Melanie Gifford.

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6 Ibid.
7 cross-sections analyzed at Williamstown Conservation Center by Kate Duffy. Samples were coated with conductive carbon and examined for elemental content with a scanning electron microscope. X-rays were collected separately for each element, providing x-ray dot maps or density maps for each element.
Figure 1. Esaias van de Welde, *Winter Scene*, 1614.
Before 1997 restoration (varnish removed before 1990)

Figure 2. X-radiograph.
Notice oak additions top and bottom.
Figure 3. Later oak additions masked out for photograph.

Figure 4. After treatment.
Acrylic artists’ paints were received with much fanfare and excitement in the 1950’s and 60’s. The materials were inherently stable against ultraviolet degradation and could produce films with great clarity and phenomenal elasticity. They were easy to manipulate, could be painted directly onto supports, dried quickly and were thinned with just water. However, the period of excitement was soon tempered with concern as some of these newly painted works began to require cleaning and repair. Much of the concern focused on the lack of knowledge of the acrylic systems, the complexity of the formulas and the lack of information coming from the manufacturers of both the raw materials and of the artists’ paints. In 1974, one of the earliest articles suggesting the inherent conservation problems with the materials was published by Margaret Watherston in an article called, "The Cleaning of Color Field Paintings." Not until the early 1990’s did one of the first critical studies of acrylic paintings in museum collections appear, authored by Stringari and Pratt, in the conference and publication called Saving the Twentieth Century.

Acrylic dispersion paintings present great challenges to conservators, yet very few studies of these materials are published. Before we can move on with the critical research, it is essential that we have a common starting point. For this reason, a review of existent literature was compiled by the authors, but is beyond the scope of this presentation. Instead, three broad areas will be discussed: the general concerns with the conservation of acrylic paintings, the components and drying process of acrylic as they relate to conservation issues and, finally, suggestions for future research.

General Concerns with the Conservation of Acrylic Dispersion Paintings

Very few conservation treatment cases involving acrylic paintings can be found in the literature. Instead, the concerns tend to be communicated through informal discussion. Most of these discussions surround two central issues: the sensitivity of acrylics to water and other organic solvents and the thermoplastic nature of acrylics. Sensitivity to water and other solvents limits the choice of cleaning techniques, consolidants, inpainting materials, and options for varnishing and varnish removal. Temperature sensitivity raises problems particularly during storage or transit of paintings. High temperatures and relative humidity can cause packing materials to stick to a painting’s surface. Low temperatures and relative humidity can contribute to cracking, if the painting sustains a blow or if it is rolled. At room temperature acrylic paintings can be tacky and therefore attract dirt and airborne pollution. The conservator must consider all of these issues during conservation procedures. Future researchers will need to define the proper environment in which to conserve acrylic paintings.

Some other typical problems during conservation include the following: difficulty in removing embedded grime, such as fingerprints, difficulty in matching color and gloss during inpainting and the temporary swelling of the surface with water, if water is tested as a cleaning agent. Solutions to these problems are few, but include: mechanical cleaning of the surface, encouraging preventive conservation, such as framing and glazing and redefining acceptable degrees of degradation, as in accepting the yellowing of exposed, unprimed canvas that can be found in color field paintings. A more radical position would be to accept the slight, temporary swelling during cleaning with water, when nothing else will remove grime.

Components of Acrylic Dispersion Paints

The properties of acrylic paintings during storage, transit and conservation are also determined by the formula of the paints. There are many different formulas for acrylics which can be grouped into two major categories: acrylic dispersion paints and acrylic solution paints. Only the acrylic dispersion paints will be discussed in this paper. These are water-borne and are more commonly known as "acrylic emulsions." Acrylic dispersion paints contain a
host of additives that govern their wet- and dry-handling properties. Among these additives are: raw polymer binder, the pigments, and additional additives which can be categorized as volatile and non-volatile.

The raw polymer binder is created by the polymerization of acrylic monomers. Some of the more popularly used monomers are: acrylic acid, methacrylic acid, ethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, i-butyl methacrylate, n-butyl acrylate, n-butyl methacrylate, i-butyl acrylate, 2-ethyl hexyl acrylate and styrene. The type of monomer, the method of polymerization and the additives required all affect the properties of the final raw polymer and, thus, the paint. Raw polymers exhibit a variety of degrees of clarity and tint. They have different properties, viscosities and accept pigments and other additives in different ways. The paint formulator must build the formula accordingly to achieve the desired properties of the paint.

Pigments, the second most important additive, are dispersed into the polymer. Each type of pigment has its own sensitivity to water and other solvents. This sensitivity, the volume concentration within the paint formula and the size and shape of the particles all affect the properties of the dried paint film.

The volatile additives contribute essential qualities to the formulation and drying process, and for the most part leave the paint during the drying, though residual amounts may still be present in the dried film. These include the coalescing agents, ammonia, and freeze-thaw agents. The non-volatile additives, equally necessary to achieve the desired properties of the paint, will remain in the dried film; these include surfactants, thickeners, defoamers and preservatives. Their presence in the dried film may affect conservation and needs to be addressed in future research.

Drying Process or Film Formation Process of Acrylic Paints

While conservators do not usually see the artwork until long after the paint has dried, it is still important to develop a consensus as to the stages of drying and the impact of that process on the properties of the film and resultant conservation issues. Watching paint dry can be very interesting given the correct context.

For our purposes, the drying process can be divided into four stages. But it is important to remember that these stages may be occurring simultaneously in different places within the paint film; this depends on the thickness and shape of the paint film and ambient conditions during drying.

In Stage I, the paint has just been applied and is still easy for the artist to manipulate. There is an abundance of water in this very mobile system; though it is evaporating rapidly, along with the volatile additives, and is being absorbed into the substrate or any layers of paint or ground underneath. Moving in the flow of water may be some of the water-miscible additives, such as surfactants and coalescing agents. The mobility of these additives depends on their affinity for the polymer and their size and shape: a strong attraction would anchor them to the polymer and large or awkward molecular structures would not flow very easily with the water.

As the water and water-miscible additives are absorbed into the substrate, they can wet-out components in the substrate such as size, dirt particles and degradation products. As the water evaporates back up through the paint, these materials can be pulled into the paint and discolor the film, causing Support-Induced Discoloration. When the paint is applied to highly absorbent substrates, such as blotting paper, the water and water-miscible additives can be drawn away from the acrylic binder too quickly leaving the binder unable to deform and coalesce. The binder then cracks to alleviate the stress. The result resembles mechanical cracking in oil paint films, but is accomplished by a completely different process.

In Stage II, the paint is sticky, more viscous and a little more difficult for the artist to manipulate, with more drag on the brush. This drying occurs sooner at the edges and surface of the film where there is more surface area. There is less water in the system, so the film is denser and the polymer particles are drawn together more closely and begin to deform. Part of this deformation produces capillaries through which the water moves to the surface of the film, where it can evaporate. The water-miscible additives may also be drawn through the capillaries along with the water, though this remains to be studied. The importance for conservation is that these additives would then be deposited at the surface. Such hygroscopic additives on the surface of the dried film are prone to attract dirt and pollution and could be removed by conservation cleaning.
In Stage III, the drying is further along at the edges and surface, forming a skin or semi-permeable membrane. This skin probably closes off the system of capillaries, forcing the remaining water and volatiles to escape by diffusion. The skin is thicker at the edges of the film than at the surface. The interior of the film is still mobile with water and volatiles. As a result, the tension between the thicker skin at the edges and the mobile interior may cause the film to split. This 'acrylic traction cracking' resembles traction cracking common in oil paints. Also, the surface skin may retain craters from foam created in applying the paint or present in the original paint formula. And finally, clear acrylic media may appear milky or cloudy at this stage until the water has completely left the film.

At last, in Stage IV, the film appears to be dry, though water and volatiles are still slowly escaping; this process can go on for up to 50-60 days or longer, depending on the thickness of the film and ambient conditions. The coalescing agent film is formulated to remain in the film for a short time after the water evaporates. This allows the polymer particles to continue their compaction as the polymer attempts to achieve a lower surface energy state. The molecular chains of each polymer particle have entangled with those of its neighbors and full mechanical properties are achieved.

Pores or microvoids can easily be left within the dry film. In fact, the porosity of acrylics was known and utilized early on in the coatings industry; acrylics were used as coatings for wood because they allowed water vapor to pass through, reducing the risk of delamination. Of course, a porous paint film in artwork has many implications for conservation. A porous coating may trap air pollution, dirt and foreign matter, encouraging biological growth and, of equal importance, may trap conservation cleaning agents via capillary action, leaving highly concentrated pockets of solvent that can interact with the paint film on a long-term basis, causing weakening.

Current and Future research

The end of Stage IV achieves the dried film and it is at this point that a conservator would see the painting for the first time and study its properties. There are only a handful of published studies in conservation on specific aspects of acrylic dispersions. Some of these include: studies of the general characteristics of acrylic dispersion media during natural and accelerated aging; studies of the mechanical properties of the film upon exposure to variations in temperatures and relative humidity; a study of the stresses that can occur during the drying of the film; and a study of the haziness that can sometimes be observed on clear acrylic dispersion media.

Based on our review of the literature we have some suggestions for the direction of future studies. Short-term studies could provide fundamental information, starting with a visual characterization of the paint surface. The films could be observed while altering temperature and relative humidity during drying and cleaning and on a range of substrates. Also, it will be important to vary the paint formulas and pigment types. The most critical long-term study will be to determine the effects of removing additives from the paint film during cleaning. This would include an observation of which additives are removed and how each would affect dirt pick-up, changes in gloss and mechanical properties of the film. Additionally, it would be useful to study the effect of repeated cleaning on the acrylic film. If we can demonstrate that removing some of these additives can actually improve the properties of the film, it will then be left to conservation to decide if this is an appropriate course of action.

In our current research we began to investigate some of these questions, specifically, the role of surfactants. Surfactants are added to the raw polymer to initiate polymerization and they are added to the paint formula to help disperse pigments into the polymer, ease coalescence and help the paint wet-out the substrate upon application. A series of studies in the coatings industry and two of our own informal studies suggest that surfactants are present at the surface of the dried paint film, rather than (or in addition to) being locked within the film. The house paint industry acknowledges that surfactants in outdoor paint will be washed away by the rain when the paint is young and that this is a positive scenario. Washing away the surfactants will reduce dirt pick-up and staining and will even-out the surface gloss. In another series of industry studies, the distribution of surfactant in dried paint films was monitored using an infrared surface technique. Through analysis of cross-sections of paint, surfactants were found at both the surface of the film and at the paint/substrate interface.

An informal study was conducted in the Technical Department at Golden Artist Colors to investigate some unexpected varnish adhesion failure. The failure was isolated to cases where the acrylic paint had been applied to a non-absorbent substrate and had dried at least 30 days prior to varnishing. It was suggested that non-absorbent substrates permit only one-way drying, in which the water and water-soluble additives cannot be absorbed into the
substrate, but can only move toward the film surface to evaporate. During the 30 days or so of drying, the surfactant is deposited at the paint film surface in critical concentration, enough to inhibit the adhesion of varnish to the paint surface. In some tests, the paint film was washed with water before varnishing which greatly improved varnish adhesion.

In another informal study, through a joint project between Golden and Rohm and Haas Company, testing consisted of carrying out mock conservation cleaning on two different pigmented films: naphthol red light (10 years old) and cerulean blue (12 years old). Warmed distilled water, ethyl alcohol, and mineral spirits were swabbed onto the paint surfaces. The swabs and the paint films were then analyzed to determine if anything was removed from the paint films. A look at the preliminary results for the swab analysis suggests that nonionic surfactants were sometimes removed from the paint films, especially by the more polar solvents.

Although we are just at the beginning of our research on these topics, the implications for developing new conservation processes are extremely exciting. As well, artists continue to engage in the possibilities of this medium. It seems that at this time in our history there is enough interest among conservators to begin to study these issues. We will be challenged to find effective and acceptable ways to work on these materials.

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References


"THERE MIGHT BE MURALS...":
THE CONSERVATION OF THE ROBERT S. DUNCANSON MURALS

Helen Mar Parkin, Conservator of Paintings*

Introduction and Background

This talk concerns the recent treatment of a suite of murals, located in the Taft Museum of Art in Cincinnati, Ohio, painted in oil on plaster between 1850 and 1852 by Robert S. Duncanson, the first African-American landscape painter to achieve international fame. The murals represent the largest commission of Duncanson’s career and, according to Joseph Ketner, they are “the most ambitious and accomplished domestic mural paintings in antebellum America, combining the traditions of wallpaper fashions, domestic mural decoration, and...landscape painting”1. The focus of the talk will be the history of the murals and how they were affected by the architectural and decorative changes the building has undergone over the past 150 years. The technical part of this presentation will be given at next year’s meeting by my colleague, Frederick Wallace, who also worked on the project.

The building that is now the Taft Museum of Art was erected in 1820 as a private residence. In 1829, it was purchased by Nicholas Longworth, a wealthy landowner and businessman, who named it Belmont. In 1869, Longworth’s heirs sold the house to David Sinton, a widower, who took up residence with his daughter, Anna. In 1873, Anna married Charles Phelps Taft, the older half-brother of William Howard Taft, the 27th president of the United States. Anna’s father gave the property to the couple as a wedding gift. After Sinton’s death in 1900, the Tafts began collecting European paintings, Chinese ceramics, Limoges enamels and other decorative arts, for the purpose of making great works of art available to local artists and craftsmen. In 1927, Mr. and Mrs. Taft deeded their house and collection to the people of Cincinnati to be preserved intact as a museum.

Robert Duncanson was born in New York State, the great-grandson of a Virginia slave owner, and grew up in Monroe, Michigan. There is no record of formal education, but his surviving letters show that he was well read. He began working in the family business of housepainting, carpentry and interior decoration, then established a painting and glazing business with John Gamblin in 1838. In 1840 his ambition to be an artist drew him to Cincinnati, the “Athens of the West”2 in the mid Nineteenth Century and a haven for free persons of color, where he could enjoy greater artistic opportunities in an intellectually liberal environment. He opened a housepainting business and began taking commissions for portraits, historical paintings, and so-called “fancy pictures”, while traveling back and forth between Ohio and Michigan, working as an itinerant artist.

Duncanson’s first important commission, “Cliff Mine, Lake Superior”, 1848, changed the direction of his career toward landscape.3 Although he was self taught as an artist, Duncanson knew and was influenced by the work of other renowned contemporary Cincinnati painters such as Worthington Whittredge and William Sonntag, as well as by the paintings of Hudson River School artists exhibited at the local Western Art Union.4 In the 1850s and 60s Duncanson’s rapidly developing skills equalled and then surpassed those of other local artists. In 1861, the Daily Cincinnati Gazette called him “the best landscape painter in the West”.5 Because of the encroaching Civil War, Duncanson emigrated to Canada in the early 1860s, where he helped to found a national landscape painting school. He traveled to Europe several times throughout his career to exhibit and sell his paintings and was particularly interested in the Scottish highlands. Later in life, he suffered from mental illness, perhaps brought on by exposure to lead-based paints as a young man,6 and died in 1872 at the age of 51.

The Belmont Murals

Around 1850, Duncanson’s skill as a landscapist caught the attention of Nicholas Longworth, an abolitionist and strong supporter of the arts, who hired him to paint a suite of imaginary landscapes for the foyer of Belmont. The murals were probably painted with the help of assistants over a two year period during the winter months when...
Duncanson was not on sketching trips. There is no documentation of the commission, but we know Longworth was acquainted with the artist, since Duncanson painted his portrait in 1858. Longworth had commissioned work from several other local artists, including Worthington Whittredge and Hiram Powers. It was Longworth who would later send Duncanson on the first of several trips to Europe to study the Old Masters. By the time Nicholas Longworth’s heirs sold Belmont to David Sinton in 1869, the house had undergone many decorating changes. In keeping with the fashion of the times, the walls were covered with wallpaper, so the murals disappeared from view and were nearly forgotten. Between 1900 and 1927, Charles and Anna Taft added more layers of wallpaper and hung paintings on the walls. Before her death in 1931, Mrs. Taft mentioned that there might be murals, which she had never seen, under the wallpaper. During the renovation of the house to a museum in 1932, the wallpaper was removed, revealing eight large murals, four in the entrance hall, measuring approximately 9’ x 7 ½’, and four in the interior long hall, measuring approximately 9’ x 6 ½’ (Fig. 1). Four small overdoor paintings were also discovered, two flower still lifes, also believed to be the work of Duncanson, each measuring 31” x 60”, located over the parlor doors, and two paintings of large birds, painted by an earlier artist, each measuring 33” x 80”, located over archways in the interior long hall. These birds are probably turkey vultures, the closest thing in Ohio to American eagles, symbols of the new republic and appropriate decoration for a Federal house built in 1820. On the walls below the large murals were found false-grained dado panels, probably painted around 1851 by a craftsman named Hamilton Cummings, who was known to have done fine graining work for Nicholas Longworth in this house and for his son-in-law across the street.7 Removal of the wallpaper above the Music Room Door revealed fragments of three more overdoors (Figure 3). When the house was built in 1820, there were evidently two narrow doorways leading into the Music Room, instead of a single large door, and the three small overdoors spanned the top of the double doorway. During the late nineteenth century, when the murals were hidden by wallpaper, the two doors were replaced by a tall, arched Victorian doorway, resulting in the almost complete destruction of the overdoor painting in the center and substantial loss to the other two. Around 1932, the doorway was changed again. In keeping with the Tafts’ wish to return the house to its original appearance, a Federal style door was installed and is still in place today.

**Treatment of the Murals in 1932**

The architects responsible for the renovation of the house in 1932 felt that the newly revealed murals bore no relationship to the way the house looked in the 1820s and should be recovered with wallpaper of that period. But Walter Siple, the first director of the Taft Museum, felt they were historically important and, with the exception of the badly damaged overdoors over the Music Room door, should be allowed to remain visible. Siple hired the well known restorer, William Suhr, to clean and restore the murals in the summer of 1932 (Figure 2). Suhr was born in Germany in 1896, studied painting in Berlin and Hannover, and by the early 1920s had learned art restoration. He was brought to the United States in 1927 by William Valentiner, Director of the Detroit Institute of Arts. While at Detroit, he undertook a number of freelance projects at other institutions around the country, primarily in the midwest. He would later establish a practice in New York City in 1935, when he was appointed conservator to the Frick Collection and where he remained for 41 years until retirement.8 Surprisingly, no written records remain of Suhr’s treatment of the Duncanson murals, but there are black and white photographs, which he may have taken. Some of the correspondence between Siple and Suhr has survived, so we know the work took place between mid-June and early October, 1932, and was finished in time for the opening of the museum to the public. In his report to the Trustees, Siple wrote,

> “Mr. William Suhr of Detroit, probably the most important expert with regard to the cleaning and repairing of paintings, has done an excellent piece of work with the frescoes in the hall. During the summer we discovered that these frescoes [a term which Siple was using loosely] were by a Cincinnati artist—R.S. Duncanson—who worked here between 1840 and 1850. It is remarkable how well Mr. Suhr has brought these back to life.”9

Newspaper reports at the time announced that the murals were “so well preserved that little restoration was necessary”.10 While it was certainly true that the wallpaper had protected the murals from the harmful effects of light, coal smoke, and malicious mischief, considerable damage had been done unwittingly throughout the nineteenth century by the installation of gaslight fixtures and chair rails and by the hanging of framed pictures. Suhr may have encountered other problems as well. In a letter to Siple in January, 1933, Suhr described the treatment of the murals as “a work which had been such a strain upon all my energies and into which I had really put all I had to give…” and he alluded to the “difficulties in the way of restoring the pictures at all.”11 In the course of Suhr’s treatment, the small overdoors on either side of the Music Room door were painted out and the missing mural in the center was reconstructed.
Recent Conservation Treatment

Unfortunately, the materials available to even the most conscientious restorer in the 1930s were not as stable as those we have today. We know that the varnish began to yellow almost immediately and by the early 1990s, it was so dark that it obscured the colors and many of the design elements of the paintings. In 1994, the museum decided to undertake another treatment to bring the murals closer to what the artist intended. The treatment was fairly straightforward. The heavy, black grime and streaky, darkened varnish were removed with Acetone mixtures, revealing the fresh colors and details of the designs that had been obscured for over sixty years, and revealing as well the damages visible in the 1932 photographs. Large areas of tenacious overpaint were also found covering abrasion and old damages. The abrasion was particularly severe in the darks, but it was also found in some of the sky passages. Small areas of weak plaster were consolidated with acrylic dispersions or resins. The brush applied, isolating varnish used overall was MS2A®, with the addition of 2% Tinuvin® 292 Hindered Amine Light Stabilizer. Holes were filled with vinyl spackling putty. Areas of raised, dislocated paint along structural cracks in the wall were consolidated as much as possible by introducing Beva® 371. The museum has consulted an architectural conservator to determine whether the cracks pose an ongoing threat to the murals. Inpainting of abrasions and disfigurements was carried out with dry pigments ground in a 1:1 mixture of PVA AYAA and AYAC (Union Carbide), applied in thin, lean washes. For reconstruction of missing areas we referred to similar areas in other murals. Interestingly, the artist took into account the light sources in the hallways when painting the shadows on the trompe l’oeil frames. In the front hall, the light source would have been the west-facing exterior door, so all the shadows in the frames fall toward the east. In the interior hall, the light source was evidently a ceiling fixture in the center of the hall, so two of the murals have shadows on the north side and two have them on the south. To reconstruct an area of missing design, we photographed the corresponding area with identical shadows on another mural, enlarged the image, and copied it onto the fill. The final spray varnish for the murals was stabilized MS2A, applied lightly to achieve a semi-matte appearance.

Discoveries During Treatment

In one of the murals we found a large area of very old, resinous overpaint filling the entire lower right corner and covering extensive damage. The overpaint may be seen in the 1932 photograph as a dark triangular shape, obscuring part of the horizontal chair rail damage. Since it was present at the time the wallpaper was removed, the overpaint must have been there when the wallpaper was applied, giving us clear evidence of a previous and rather harsh restoration sometime between 1852 and 1869. Discovery of this area must have been an unwelcome surprise for William Suhr and perhaps the cause of what he referred to as the “strain upon all my energies” during the project, considering the short time frame for completion of the treatment. When we removed the old overpaint in this mural, remnants of another structure were discovered beneath the teepee. Inpainting of abrasions and stains revealed a crude shelter which we believe is closer to what Duncanson originally painted and perhaps changes the subject matter of the painting in a subtle way. (Figures 5 and 6 show the appearance of this painting before and after treatment in the late 1990s.) We also made a number of discoveries about the way the murals were constructed. The surface of the wall appears to consist of a thick layer of coarse aggregate containing fine, crushed stone and horse hair with a thin layer of smooth plaster on top. A large, rectangular area of white paint was applied to each wall as a ground. A continuous, raised, horizontal edge of ground may be seen along the top of each wall, even those with an overdoor between the large murals, indicating that the artist prepared the entire wall at one time. In some cases, vertical lines may also be seen defining the width of the large murals. A very thin layer, possibly a sealant, may have been applied over the ground. Next, the rectangular shape and curved upper edge of each landscape were laid in with white paint, applied in broad, sweeping strokes. Strokes and swirls of grayish-brown paint were applied for the underlayers of the frames. The sky area was roughed in using thin layers of blue or green paint, with spaces for the trees sometimes held in reserve. A reddish-brown wash was applied to the foreground and to the reserved areas, sometimes overlapping the sky color. Once the tonal balance was established, the composition was completed and other design details were added in low to medium impasto. At some point in the process, details such as foliage and bridges were sketched in roughly with graphite pencil. The finished design does not always follow the drawing. The final layer of paint in the sky was intended to fill in the gaps between the curved upper edge of the design and the inner edge of the frame, where the white ground was exposed, but because it has become more translucent with age, this paint no longer matches. Since the trompe l’oeil frames overlap the designs, they were probably the last areas to be completed. The presence of small, black dots suggests the use of cartoons to transfer the frame designs to the wall. The frame motifs were probably adapted from French wallpaper designs of around 1850. The eight large trompe l’oeil frames show a consistently high level of skill. In looking at
the landscapes, however, it is obvious that the complexity of the compositions and the technical skills vary from one to another, suggesting that Duncanson's mastery of painting was still developing during the two year period of the commission. The four paintings in the interior hall depict picturesque views of unidentified American landscapes, resembling the Ohio River Valley and recalling the artist's work of the 1840s. (See Figures 5 and 6 for example.) Those in the entrance hall represent idyllic European scenes, based on classical landscapes, resembling his more accomplished work of the 1850s before his first trip to Europe. (See Figures 7 and 8.) The painting called the Sunset mural is the most distinctive of the group and is thought by some to be the most accomplished because of its sensitive use of color and light.

The scope of this project did not include treatment of the reconstructed overdoor or the recovery of the hidden overdoor murals. Since no isolating varnish was applied in 1932, it is very difficult to separate the green wall paint from the original, but we were able to uncover a small area (Figure 4). It appears from this test window that the hidden murals matched the floral overdoors in the entrance hall. A section of one of the false-grained dado panels was partially uncovered by architectural conservator Brian Powell. Again, there is no isolating varnish, so recovery of the original surface, which consists of thin resinous glazes over a white ground, is very difficult. Brian's tests also revealed that the white painted molding in this part of the house was false-grained in the past. This evidence suggests that the hallway had quite a different appearance in the early 1850s; the paneling and dark woodwork around the murals might have enhanced the illusion that the murals were distant landscapes viewed through carved sandstone openings, rather than framed paintings hanging on the walls.

Comparison with Another Painting by Duncanson

Several of our discoveries about technique are similar to findings made by Pamela Betts during her treatment of an oil painting on canvas by Duncanson, a view of "Loch Long" in the Scottish highlands, dated 1867, in the Indianapolis Museum of Art. In this painting, a reddish-brown imprimatura, applied as glazes and scumbles in the foreground, valley, and closest mountains, has been left unpainted in some areas. Cross-sections of "Loch Long" reveal a two part ground with a thin, possibly resinous size layer on top. When stained with TTC (triphenyl tetrazolium chloride), the ground layers show a strong positive reaction for carbohydrates. Infrared examination reveals an underdrawing in pencil or charcoal.

Plans for Further Study

The recent treatment has given us the first opportunity to look comprehensively at the Duncanson murals since the restoration of 1932 and to gain a greater appreciation of their place in the artist's work and in the history of American art. The Taft Museum of Art is planning a major renovation in the near future, part of which will involve returning the hallways to their appearance circa 1850. This project will include recreating the false-grained dado panels and woodwork surrounding the murals and uncovering and reconstructing the hidden overdoors. The murals will be available for viewing through November 4, 2001, after which the museum will close for eighteen months. At next year's AIC meeting Fred Wallace will present Part Two of our continuing research on Duncanson's materials and techniques, based on samples and cross-sections taken from the murals and comparisons with other paintings by the artist.

The author would like to thank colleagues Fred Wallace, Andrea Chevalier and Betsy Geiser for their help on this project, Pamela Betts for sharing her research on Duncanson, and Henriette Suhr for providing the photographs of her husband. The conservation treatment of the Duncanson murals was made possible by The Greater Cincinnati Foundation, The J. Paul Getty Trust, grants from several other foundations, and a number of private donations. The illustrations of the murals accompanying this text are the property of the Taft Museum of Art.

2 Ibid., 1.

3 Ibid., 27.

4 Ibid.

5 Ibid., 84.

6 Ibid., 2.

7 The following entry appears in Charles Cist, *Sketches and Statistics of Cincinnati in 1851.* Cincinnati: William M. Moore and Co., 1851, 224.: “Hamilton Cummings, corner of Walnut and Baker streets, executes graining in a style that cannot be surpassed. Fine specimens in that style of painting may be seen at N. Longworth's and Larz Anderson's mansions, on Pike street.”


10 Cincinnati Plazette, January, 1933, 17.

11 Director’s correspondence, January 15, 1933. Cincinnati Art Museum-Art Academy of Cincinnati Archives. During this time, Walter Siple was director of both the Taft Museum and the Cincinnati Art Museum.

12 Ketner, Ibid., 56.
Figure 1. View of two large murals and overdoor in entrance hall in 1932. Note false-grained dado panels below murals, chair rail damage, and old repairs.

Figure 2. Restorer William Suhr and two assistants (father at left and sister in law at right) working on the murals in 1932.
Figure 3. View of the wall to the right of the Music Room door in 1932, showing large mural and fragment of overdoor. The outline of a previous doorway may be seen below the overdoor.

Figure 4. Test cleaning in the interior long hall during recent conservation treatment, revealing upper right corner of the overdoor seen in Figure 3.
Figure 5. Mural in interior long hall, before treatment in 1994, showing Suhr restoration.

Figure 6. Mural shown in Figure 5, after treatment in 2000. Note crude shelter at lower right.
Figure 7. The Sunset mural (entrance hall) after treatment in 2000. Compare to Figure 1.

Figure 8. Another large mural in entrance hall after treatment in 2000. Compare to Figure 1.
HEALING THE COMMUNITY: A COLLABORATIVE PROJECT FOR COLUMBINE HIGH SCHOOL

Victoria Montana Ryan, Conservator of Paintings*
D. Hays Shoop, Conservator of Paintings**

In the aftermath of the shootings that took place at Columbine High School in April 1999, spontaneous memorials to the victims appeared in the park adjacent to the school. In seeking healing, the community made the decision, as a lasting memorial, to renovate and rededicate the part of the school where the tragedy occurred. Bringing together the conservation team with the artist, the architect, the contractor and the community representatives enabled the vision of a new, uplifting and inspiring space to be completed.

As conservators, we are there to support the art, appropriately behind the scenes, whether saving artifacts, preparing exhibitions, or carrying out installation. We were integral to the success of this project, and so contributed to the healing intentions, but we were certainly never the story. We want to discuss the process, and the deadlines and complications that at times tested our spirit of benevolence! This is not a presentation about innovation, but rather a story of accomplishment and support, of collaboration and healing -- a human-interest story with a soaring spirit.

In the days after the tragic shootings expressions of grief began to appear. Simple heart-felt memorials such as single flowers or cards were left on cars of the victims and in the park adjacent to the school grounds. The grief of the community continued to be expressed with more memorials, as parked cars and tents became “shrines” to the victims. The outpouring of support continued until there were literally memorial mounds, several feet deep, in numerous locations in the park around the school.

Materials in the memorials included flowers, posters, cards, stuffed animals, banners, and personal momentos. Inclement weather brought rains and snow - obviously not ideal conditions for such ephemeral materials. Deterioration of, and damages to, the materials came from rainwater that soaked cloth and paper and caused ink inscriptions to bleed. Other damages included fire damage that resulted from burning candles, from mud several inches deep and from organic matter such as straw and grass that became embedded in the materials that were soaked to the consistency of pulp.

With jurisdiction for the physical materials not completely clear, politics and discussions continued for sometime as to whether these materials should be preserved. Finally a decision was made to “save” or preserve the memorial materials including fifteen hand-made large wooden crosses. These crosses were a point of contention with community members who felt that thirteen crosses representing the thirteen victims of the shooters were appropriate, but that the two crosses representing the shooters were totally inappropriate. In fact when the fifteen crosses were first erected two of the crosses disappeared the first night, and community members were vocal in their objections to the fifteen. This issue of fifteen continued to be of importance throughout the project.

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Friends, families, and community members wished to do something, to contribute in some small way to help with the healing process. The conservators in the area also wanted to contribute in whatever way they could. As the
conservation community in the Denver area joined the efforts, conservators used their expertise to organize and guide people and to arrange for the site and equipment necessary for an undertaking of this magnitude. The business community also donated time, people, and equipment. An example of this is the trucking firm that donated use of their trucks and people to remove more than fifteen truckloads of memorial materials from the park and school grounds. Another business, Professional Restoration, provided the dehumidification equipment that would be used to dry out the collected materials. Government agencies pitched in and provided the site - the Denver Federal Center provided a vacant building where the trucks would deliver all the materials.

At the Federal Center the conservators helped to "triage" treatments and help guide the efforts of the many volunteers. A large room in the Center was set up as the initial treatment area where the dehumidification equipment was placed. The water soaked materials were then sorted onto a series of shelves allowing most pieces to achieve a stage of slight dampness or dryness. When materials reached a drier state they were separated and moved into individual rooms within the Center. Shooting victim, general memorial, or material type defined the room designations at the Center. For example, several rooms were dedicated to the more than five truckloads of teddy bears which, if not for a specific victim, were cleaned and eventually recycled for use at children’s hospitals.

While new truckloads of materials continued to be unpacked, dried materials that had been sorted now received the attention of volunteers. Conservators worked side by side with volunteers to clean away caked on mud and debris so that materials could be identified and further sorted (e.g. types of materials, like cards, for each victim). The entire facility was put to use, including an old chemistry lab where wet banners were laid out to dry before being rolled up and sorted. Sorting the written cards, banners, and messages required reading the heartfelt expressions of grief and sympathy and will forever remain in our memory. Victim’s families were allowed to keep as much of the memorial materials as they wished. Some materials were just in too poor a condition to keep and these were discarded. Materials not kept by the families were distributed to local history collections.

This project included the collaboration of conservators, government agencies, businesses, organizations, and community volunteers who donated, served, and helped in the healing process. Our assistance in preserving the materials was complete, and though deeply touched, we thought we’d moved a year beyond the initial healing. The organization Healing of People Everywhere (H.O.P.E.) engaged in a project to begin the re-building of the Columbine community --- and one day we received a call for assistance on this new project.

On July 18th, 2000 artist Virginia Wright – Frierson, contacted us. Ms. Wright – Frierson volunteered her time to paint murals to be installed in the newly renovated space at Columbine High School. Despite assurances by the project architect, Ms. Wright – Frierson, had concerns about the installation of the murals, and initially contacted conservator David Goist who referred her to the Conservation Center. When she spoke with us she was asking for advice on the installation and / or a couple of days of assistance.

We were sent a blueprint of a reflected ceiling plan of the atrium. With just the reflected plan it was difficult to visualize the artist’s intent, so we asked Ms. Wright – Frierson to email us a digital image. She sent an image of the murals in the pattern she had envisioned, laid out on the floor of the local gymnasium. The scheme involved a large central area for murals and numerous “floating cloud” forms that were to hang around the central area. It was the artist’s and our understanding that murals would be installed on these clouds at ground level, then hoisted and suspended by cables. We told Ms. Wright – Frierson that we wished to be of assistance, but that we were concerned about the lack of time to problem-solve, gear-up, and test materials.

On July 20th we met with project supervisor Ryan Thompson of Turner Construction and project engineer Greg Johnson at Columbine. Imagine our surprise walking in and finding the clouds already hung. We were then
informed that the contractor refused to lower the clouds, to allow us to marouflage the murals, due to the weight (each cloud weighs over 500 lbs.) and the risk of damage to the structures. The clouds, constructed of a steel curvilinear armature covered with painted gypsum board, have either a concave or convex curvature. Turner Construction committed whatever resources were necessary to allow us to do our work (30 feet up in the air!) around obstacles and deadlines. We were given a deadline for completion of August 14th, the beginning date of classes at the school.

Initially the architect had envisioned the center panel murals being on stretchers mounted to the ceiling. We were asked for advice on how to design and build this suspended system. After discussions involving the architect, artist, conservators, and construction crews we all agreed that installing the center panels would be done in the same fashion as the rest of the murals. We advised that marouflageing the murals directly to the gyp-board panels, (especially given the force of gravity) would likely be the best option for the long-term stability of the paintings. We became more concerned about the increasing complexity of installation and lack of time, but we committed to the project knowing that the artist would need much more help than she had planned on.

After advising Ms. Wright - Frierson on the necessary packing procedures, she contracted with ARTEX to ship the murals to Denver, and we were informed that the murals would not arrive until August 1st. The construction firm then advised us that the installation must be completed by August 7th in order to allow time for flooring to be installed. Our deadline had closed by one full week, and with seven days available to install nearly twenty mural pieces, we began to feel a bit of panic set in.

In the interim, while waiting for the murals to arrive, we procured painted canvas samples from the artist and sections of the painted gyp-board from the contractor to begin testing. In addition to testing the materials and constructing mock-ups we consulted with colleagues. Due to the number of people working in the atrium space, from the construction crew, to visiting family members, to sub-contractors of all types, we needed to find an adhesive that provided the strength necessary with the least amount of toxicity. The use of strong solvents was not a viable option. We ruled out Beva 371® as an adhesive option due to the toxicity (given the quantities required), precise heating requirements, and possible bonding problems induced by the solvents on the subjacent acrylic paint already on the clouds. Starch paste was also ruled out owing to a critical window of tack, generally low humidity levels in our region, and no clear advantage over other adhesive options. Beva Gel® was tested on the samples for application thickness, tack window, and removability. Based on results of tests and mock-ups this seemed the most viable adhesive option. We calculated the square footage and ordered, via Federal Express, the amount of Beva Gel® required based on Berger’s recommended usage.

August 1st the murals arrived, properly packaged and on schedule. We chose a staging area in an adjacent auditorium for unpacking the murals (ironically, strobes and alarms going off all day due to a malfunction of the system gave us a sense of the noise and confusion endured by people trapped in the building the day of the tragedy). We assembled our crew and were prepared to work 24/7 if necessary to complete the project in the allotted time. The artist was frustrated that we wanted to start without her there (she kept telling us “We don’t have to rush too much”) and wasn’t confident that we could configure the murals without her. We were able to convince her of the need to start installation immediately with 19 murals ranging in size from 6’ x 4’ to 24’ x 20.’

Although we discussed plans for installation procedures, we understood that until you begin you are never sure of what adjustments may be necessary. We installed the first “cloud” mural and developed a working system, taking into consideration working time of the adhesive (and still through the whole installation more adjustments would be necessary on particular murals). Each mural was draped over an 18” diameter Sonotube® and lifted near to the panel using scissor - lifts (sometimes as many as five lifts were necessary at one time). Using the lifts, the mural was then pressed up against the “cloud” panel, still draped over the tube. Adhesive was applied to the panel on one
side of the tube, and the mural was pulled tightly to the edge of the panel and stapled on the vertical edges of the "clouds". The mural was then pressed by hand into the adhesive and smoothed out using rollers and hands. Heat (from hand irons) was applied as necessary to edges, bubbles and any areas of poor adhesion. The lift was then lowered, allowing the tube to be rolled back toward the adhered side, and the procedure was then repeated on the other side. We often worked frantically due to the quick drying time of the Beva Gel® in the dry Colorado climate. We found that it was possible to mist the gel with water during the application process to buy more time and extend the tack window.

It was important to plan each installation logistically to minimize the time required to rearrange lifts for access to the entire surface. We realized that we must be able to operate lifts and maneuver them around, over, and under various obstacles in the atrium. While most of the contractor's people were a great help they couldn't always be counted on to be available, as everyone was scrambling to meet completion deadlines. One day we received an extra helping hand from a quiet, but friendly young man we had previously seen assisting in the demolition of the old cafeteria wall. This person turned out to be Dan Steepleton, one of the students shot in the attack. Despite his own injuries (he still has a bullet fragment in his knee that can't be removed), he wanted to assist in the new project. We also shamelessly took advantage of Ryan Turner and Greg Johnson, both of whom are about 6'4", for their "wingspan". In a "spirit of cooperation" we managed to tie up most of their time during the week.

The biggest obstacle to overcome was the light fixtures. We pleaded with the contractors to hold off on their installation because it would complicate access to the clouds (already difficult to access). Again, we were told we would just have to deal with the situation. We had to position the lifts around, over, and under the fixtures and supporting guy-wires without damaging the adjacent walls. We not only had to be able to operate the lifts, but to operate them with finesse!

We used a chalk-marking tool to blue-line the area for registration of the center panels. There was one slight complication - a fire sprinkler, not at the center where the murals would meet, but slightly off-center, necessitating the cutting of one mural to accommodate the sprinkler head. As we started installing the center panels, another crisis began to brew. H.O.P.E. members didn't want any derivations of 15 (the total number of fatalities including the shooters). There were fifteen cloud paintings. Subtract a cloud and there would still be 14 clouds plus the central panel area, again equaling the number 15. We knew this discussion would need to involve both the community and the artist, whose arrival we were awaiting.

On August 4th the artist arrived on site and began retouching the seams of the central montage. After all the discussions, she finally decided to paint a 16th mural directly onto one of the gyp-board clouds. This required her to spend a very long day painting directly overhead from an elevated scissor-lift. Additional clouds were painted in flat colors (blues and gray) to further weave color and design throughout the space. The completed murals and configuration of clouds provide an ant's eye view to the sky through the Colorado forest (note that the sprinkler head is virtually invisible).

On August 6th conservators Ryan and Shoop spent the day "flying" around the clouds and central murals in Genie lifts, trimming canvas edges, finishing late at night. The August 7th deadline was met. On August 19th a "Media Day" was held and the school opened to the media and the Columbine community. Dawn Anna, the mother of one of the victims, emerged as the spokesperson for the families of the victims and the H.O.P.E. organization. She said at the unveiling that they wanted people to walk into the atrium and not be able to resist looking up. Instead of seeing the library where so many of their classmates died, the students look into light streaming through windows and a mural of forest and clouds. All are in agreement as their heads turn upwards that it is now a wonderfully inspiring and comfortable space.
During the remainder of the early fall, prior to school re-opening, the construction company completed the new library space, adjacent to the new atrium space with a connecting entry between. Just inside the connecting entry is a simple panel with the names of the thirteen victims. Outside the entry there is a large rock called "Rachel’s rock" (after victim Rachel Scott) where students can sit and view a small bronze floral-design plaque set into the wall; much as Rachel herself might have done, for she liked to sketch flowers, and they can remember. These new spaces indicate not only new beginnings, but are manifestations of the spirit of the Columbine community.

We would like to thank the following for their cooperation and assistance:
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Figure 1. Installing the mural, above a light fixture, with the aid of scissor lifts.
Figure 2. Atrium interior space showing clouds, cables, light fixtures, guy-wires, and surrounding walls.

Figure 3. The center mural panels providing an ant's eye view up through the Colorado forest.
THE CONSERVATION OF THE FOUNDING OF SAUGUS MURAL BY ELIZABETH TRACY MONTMINY

Gianfranco Pocobene, Conservator of Paintings

Introduction
In 1935, Elizabeth Tracy Montminy (1911-1992), a young artist with little experience painting murals was commissioned, under the Works Progress Administration Program, to paint The Founding of Saugus for the town of Saugus, Massachusetts (fig. 1). The image was painted by Montminy in the years 1935-36 and measures 8 feet, 10 inches in height by 17 feet, 4 inches in width. Its narrative depicts the arrival of the first settlers in Saugus in 1692 and includes scenes of the settlers bartering with native Americans and the establishment of a settlement on the Saugus river. The work was commissioned by the town of Saugus to decorate the courtroom of the then newly constructed police station. Contemporary art critics acclaimed the mural after its completion but over time it suffered physically from neglect and ultimately became inaccessible to the general public. This paper describes the history of this WPA mural, its recent conservation treatment, and relocation to a new public space.

Tracy Montminy was born in Boston on June 5, 1911 and she attended schools in Cambridge, MA. She graduated from Radcliffe College with a BA in Fine Art in 1933 and studied art at the Art Student’s League in New York in 1934-35 under Rico Lebrun. Montminy painted the mural at the age of 24, and although it is the first mural project that the artist undertook in her artistic career, it is a confidently executed work. In subsequent years she went on to paint murals in public buildings throughout Massachusetts, Maine, Illinois, Missouri and Mexico City. From 1948 to 1981 she was a professor of art at the University of Missouri-Columbia.

History and Technique of the Mural
The mural, which is painted on cotton duck canvas, was originally mounted to the rear courtroom wall using a flour and water, paste adhesive. According to Montminy, the canvas was first primed with a water-based, chalk ground layer. She made preparatory drawings which were then traced onto the ground to create the composition and a range of gray tones were applied over the surface using a thin, turpentine medium to establish the predominant light and dark patterns throughout the mural. The painted image, lacking impasto but painted with solid colors combined with delicate glazes was executed with what the artist described as “an almost straight varnish medium”. Most likely she was adding varnish to a commercially prepared paint, possibly an emulsion type paint. In written comments about the technique, the artist stressed that a varnish layer was not applied to the mural but rather that the “varnish was part and parcel of the colored pigment”.1 It is unclear, however, how saturated or glossy the paint layers were because of the use of the varnish medium. Forty years after painting the mural Montminy returned to Saugus in 1975 to clean and retouch the work which, according to contemporary accounts, was covered with grime. Commenting on the murals condition after the visit she noted that “it had darkened and cracked because of my use of a varnish medium – a huge mistake”.2 She further indicated that in spite of cleaning the mural it nonetheless remained dark.

By the late 1980’s, the state of the mural deteriorated considerably and the conditions in the police station where it was housed were atrocious. The room where the mural was located had been converted into a policeman’s exercise space where the exercise and weightlifting equipment was used and stored. In 1988, a steam pipe burst in the room filling the space with steam and this along with a leaky roof further degraded the mural. The appearance of the mural at this point was described as “white and ghostlike” (fig. 4). An eight foot high, temporary wall was subsequently placed in front of the mural to prevent further physical damage. This covered all but the upper foot of the work but nonetheless provided some degree of physical protection to the paint surface. In 1988, a mural committee was formed to restore the mural and find a more appropriate location for the display of The Founding of Saugus. After studying the situation, the committee determined that two approaches could be taken for its restoration. One option was to have the work carried out by a paintings conservator. The conservator Linda Tucker was hired to examine the mural and make recommendations for its treatment. Tucker concluded that the mural could be removed from the police station and that much could be done to restore its surface. The other option was to have the artist, who was living in Missouri, perform the restoration. At the invitation of the committee, Tracy
Montminy returned in 1989 to assess the mural’s condition after which she expressed considerable interest in undertaking the restoration herself. The artist felt that she could repaint the image by building up the colors that at the time she believed had been permanently damaged. Furthermore, the artist offered to restore the mural at no charge. While there was some merit to having the artist rework the mural, some of the mural committee members expressed concern that the work might be significantly altered and its value diminished.

After some debate but to the dismay of the artist, the committee indicated that it was inclined to have the mural conserved by a paintings conservator. Montminy expressed considerable reservation about this course of treatment and wrote strongly worded letters to the members of the committee. The artist remarked that “professional conservation is by its nature insensitive and mechanical, an alternative which is uncalled for when the original artist’s knowledge and touch are available”. This passionate reaction is understandable since, as many of us are aware, damage has resulted when works of art are subjected to restoration treatments. We are also well aware, however, that conservators are capable of carrying out their work in a manner that respects the integrity of the work of art. As I became involved in the discussions in 1992 I made efforts to educate the committee about conservation and to assure them that, in this case, their inclination to have the mural treated by a conservator was correct. I also suggested, however, that the involvement of the artist at some level might be desirable during the treatment.

The initial examination of the work, though limited by the temporary wall covering, indicated that much of the mural remained extant below the severely blanched and grime-laden surface and that the prospects for rescuing the image were good. In March of 1992, I was fortunate to have a telephone conversation with Tracy Montminy and we discussed at great length the condition of her mural and the issues that concerned her about having a conservator restore the work. I told her that, if the stabilization and cleaning of the mural were undertaken by a qualified conservator, much of the mural surface could be safely recovered without any major re-constructive intervention by either the artist or a conservator. I also proposed that if significant portions of the mural were indeed found to be irreparably damaged after cleaning it would be prudent to have her consult on the project and possibly participate in the re-painting of those areas. She was satisfied with this possible course of treatment but sadly, the issue of involving the artist in the future restoration of the mural became a mute point as Tracy Montminy passed away on October 23, 1992 at the age of eighty-one.

Mural Removal
In the fall 1992 I was contracted to begin work on the mural and carry out the first phase of work. The treatment began in November of that year with the dismantling and removal of the temporary wall that covered the mural. In short, the first phase called for the removal of the mural from the police station and its placement in temporary storage until funds for the actual treatment and relocation to a new space could be secured. Examination of the mural revealed a surface that was in a poor state of preservation and aesthetically compromised. The term “ghost-like” was indeed an appropriate description of the mural’s appearance (fig. 4). Curiously, the lower third of the painting was not blanched to the same degree and this appears to have been caused by structural variations in the wall that altered the effect of the steam damage on the paint surface. Numerous areas exhibited cracking and cupping of the paint layers and severe blanching, drip marks and staining disrupted the image. Scratches and scuff marks were also present over the lower portions of the image. An uneven but significant layer of yellow-gray colored grime also covered the surface. Scattered over the mural in areas of old paint loss were retouchings made by Montminy during her cleaning of the work in the mid-seventies. Ironically, these had not been affected by the steam damage and remained conspicuously darker and more saturated against the blanched original paint layers. Upon closer examination it became evident that although some paint loss had occurred, most of the cracked paint was stable and well adhered to the underlying canvas support. At this point, localized areas of severely lifting paint were consolidated with warm sturgeon glue and set down with a warm tacking iron to prevent paint loss during the detachment process.

Once the condition of the mural was documented and stabilized the detachment of the canvas from the wall was begun. Our intent was to detach the mural except for the top six inches of the canvas. The mural would then temporarily hang from the wall while it was rolled onto a large diameter Sono-tube. The detachment was carried out with long, thin Teflon and metal spatulas which were slipped between the canvas support and the plaster wall (fig. 2). The process was begun from the bottom of the mural and worked off the plaster by sliding the spatulas upward along the wall. The work was proceeding well but, as we gained confidence removing the canvas, a vertical split, originating from the bottom edge approximately two feet from the right edge rapidly shot up the canvas. After recovering from the initial panic that we had accidentally torn the canvas, it became apparent that the split was
actually a canvas join from the mural installation. The initial examination of the mural surface suggested that only one section of fabric had been used by the artist. In fact, the mural was composed of four canvas sections that were adhered to the wall. Apparently this was done in such a manner as to avoid any gaps or overlaps between the canvas sections. In effect, they were carefully butted together by the artist during the gluing process and the thick, smooth chalk ground that was applied to the canvas covered the joins making them undetectable through the painted image layers.

Although the strength of the adhesive paste varied across the surface, the four canvas supports that comprised the mural were remarkably strong and were safely detached with little trouble. The four canvas sections varied considerably in width. The left most section measured just over 4 feet in width, the two middle sections both six feet in width, and the right most section just over a foot in width. Rather than rolling the mural onto a tube as originally intended, the sections were instead packaged in a flat folder constructed with paper honeycomb sheets and double wall cardboard for rigidity. The mural sections were placed in the folder inter-leaved with Glassine and polyethylene sheets. The entire folder was then taped shut and sealed in a polyethylene envelope for storage in a safe location in the Town Hall which was located next door to the Police Station.

Conservation Treatment

Securing funding for the second phase of the conservation treatment and finding a new home for the mural proved to be especially time consuming for the town officials. Finally, in the summer of 1998, six years after the mural was removed from the police station, the Town of Saugus put out a request for proposal for the conservation of the mural. I was fortunate to be selected to carry on with the project and the four murals sections were transported to my studio where the second phase of the conservation treatment was begun. Space limitations prevented us from hanging all four sections of the mural side by side and thus the sections were treated one at a time. The next step in the conservation treatment of the mural was the consolidation of all of the cracked and cupping paint layers. As mentioned earlier, the worst areas were consolidated before the mural was detached in 1992. Here again, warm sturgeon glue was used as the consolidant and the paint layers were secured with a warm tacking iron.

Once the consolidation procedure was completed, a number of clean tests were carried out to develop at a cleaning solution that would safely remove the heavy layer of grime and the severe blanching on the paint surface. Initial tests carried out with citrate based solutions indicated that much of the blanched material could be removed and would greatly improve the appearance of the work. The majority of the disfiguring surface material was removed from the mural with a 2% diammonium citrate in water solution adjusted to pH 7.0. For more sensitive passages the concentration was reduced to 1% citrate and thickened with methyl cellulose to keep the cleaning solution on the paint surface. Because each of the murals sections was being cleaned one at a time, we resisted the temptation of cleaning the surface as thoroughly as possible. The concern was that we could not judge the level of cleaning between each canvas section and that the visual relationships between the various components of the composition could not be assessed as a whole. Therefore, the surface was not thoroughly cleaned, leaving the decision to remove all of the grime until the mural was re-assembled in its new location. During the cleaning procedure, it became apparent that the retouching that the artist had carried out in the mid-seventies to cover areas of loss would also need to be removed. Although these were applied by the artist in the seventies, they were dark, poorly matched the original surface and in many areas covered over large areas of the original paint layers. The unsightly over-paint was readily dissolved by rolling cotton swabs dampened with iso-propanol and acetone mixtures over the surface.

As the cleaning process was reaching completion, the mural committee and town officials were finally coming to a decision about where to relocate and re-hang the mural. One option was to install the mural in the stairway lobby of the town's new public library. The interior space was visually attractive and featured a space flooded with natural daylight. Unfortunately, if hung there, portions of the mural would be exposed to direct sunlight during the morning hours. Another option was to install the mural in the historic Victorian Town Hall whose interior and exterior were undergoing a major restoration. The proposal for this location was to place the mural on the stage wall of the second floor auditorium. In the end, the restored auditorium was selected as the permanent home for the mural as it would be accessible to the general public and would provide a relatively stable environment for the mural. The other significant issue regarding the re-hanging of the mural being discussed at this time was the type of structural mounting system for the canvas. The mural committee was given two options to consider. The first was to attach the mural directly on the auditorium stage wall in a manner similar to the original installation. The second was to attach the mural onto an aluminum honey-comb panel support. The rigid panel support interested the town because it meant that the painting could be removed from the wall and moved from the building if necessary in the future.
The only problem with the rigid panel support, which would have measured almost 9 feet by 17 ½ feet, was that it would not fit in the stairway between the second floor auditorium, where the mural was to be installed, and the first floor exit. Budgetary constraints also precluded this type of mounting system and in the end it was recommended that the mural be re-attached directly to the stage wall.

The mural installation was undertaken in the summer of 2000 and in preparation for re-attachment, the wall was measured for the centering of the mural on the wall. The individual canvas sections were measured and the two middle canvas sections were temporarily raised onto the auditorium stage wall and their edges traced to ensure accurate placement on the wall. During this phase of the work the town officials indicated their intent to the attach a frame around the mural after its re-installation. My recommendation was that the frame chosen for this be kept as simple and unobtrusive as possible. BEVA Gel®, which has been used successfully on other mural re-installation projects, was chosen as the adhesive to attach the mural to the wall. This dispersion is used as a contact adhesive and dries by the evaporation of the water phase. The mural is affixed to the wall before the BEVA Gel® dries which remains slippery long enough to allow for the position of the canvas to be adjusted on the wall. As recommended by the manufacturers and to facilitate any future removal, a release layer of BEVA 371® was applied to the back of the mural canvas sections using paint rollers and then allowed to dry for 24 hours. The mounting of the mural sections began with the application of the BEVA Gel® with paint rollers to the wall and this procedure was begun with the left middle section of the mural (fig.3). The adhesive was allowed to dry for 20 to 25 minutes until slightly tacky to the touch. At that point the canvas section was raised, positioned on the wall and adhered using hand pressure and rollers. Any loose pockets that appeared on the surface as the mural was being mounted were set down with a warm iron through cotton canvas sections. The other three mural sections were then carefully aligned and reattached following the same procedure.

After the re-installation was completed, the remaining grime and overpaint layers were removed using the citrate cleaning solution and solvents discussed earlier. While the cleaning had dramatically improved the appearance of the paint surface many passages remained bloomed and unsaturated in appearance. It was evident that it would be necessary to saturate the dulled paint layers. To accomplish this, the affected areas were reformed using iso-propanol delivered to the paint surface with a spray gun. After the iso-propanol had completely evaporated the mural was then spray varnished with a thin coating of Acryloid B-72® 10% in a (1:1) mixture of xylenes and CycloSol 100® (Shell). Minor paint losses and the seams between the canvas sections were filled with Polyfilla Spackling® compound and in-painted with Golden MSA® colors.

Conclusion
The conservation treatment of the mural resulted in a dramatic structural and aesthetic improvement of The Founding of Saugus (figs. 4 & 5). Although the project spanned some eight years from beginning to end, which included uncertainties about the relocation of the mural, the treatment was highly successful. The only regret is not having had the opportunity to meet and work with Tracy Montminy, to learn more about her technique and to discuss with her the ethics of conservation and the effect of the treatment on her mural. One aspect of the discussion would certainly have been the issue of varnishing the mural, which she executed with a varnish medium, but apparently left unvarnished. The artist’s views would have been invaluable in these matters. In an interview in May of 1936 as she was working on the mural, Tracy Montminy stated that “This has been my life long ambition. I have always wanted to paint a large mural. I hope the people of Saugus will be pleased with the results”. Were artist alive today, one would hope that she would be pleased with the result of the conservation treatment.

Acknowledgments
I would like express my gratitude and thanks to my colleagues who participated in the treatment of the mural. Lorraine Biggig and Glenn Samson brought their wallpaper conservation expertise to the first phase of the project removing the mural from the courtroom wall. In the second phase Jan Cavanaugh, David Colombo, Catherine Maurer and Peggy Waldron were invaluable in the cleaning, re-installation and restoration of the mural. Special thanks to the people of Saugus their determination to complete the project and ensure the preservation of the mural.

Endnotes
1. Montminy letter to Saugus Mural Committee February 15, 1990
3. Montminy letter to Saugus Mural Committee February 15, 1990
4. Lynn Daily Item, May 13, 1936
Figure 1. The *Founding of Saugus* by Tracy Montminy as it appeared shortly after its completion in 1936.
Figure 2. Detachment of mural canvas section from plaster wall by Lorraine Bigrigg and Glenn Samson.
Figure 3. Application of BEVA Gel by Kae Maurer Smith and Peggy Waldron during the re-installation of the mural. The first remounted section of the mural is visible on the right.
Figure 4. Before treatment detail of the mural showing the blanched and grime covered paint surface.

Figure 5. After treatment detail.
Imagine that you are a young airman in your early twenties or maybe just out of high school, overseas, probably away from home for the first time and assigned to a minimum of 25 combat missions before you can return back home, to safety, to the only life you knew before combat in a war. You are the pilot or crewmember in a group of bombers who are assigned the task of dropping bomb loads day or night in enemy territory which means at some point you will be attacked. Your chance of not returning home is one out of four.

Your physical situation is not comfortable to say the least. In the safe, high altitudes of your mission your unheated airplane will fly in sub-zero temperatures. There is little to no cushioning for your stressed and wearied body. At higher altitudes you must breathe through an oxygen mask just to keep from passing out. The constant odor of fuel, oil, grease and metal becomes one with the odor of fear, your own and that your crewmates. This odor becomes locked into your memory and any part of it can activate fear in a crewmember by the mere act of climbing aboard.

What can protect you during an attack, from running out of fuel or oxygen, from becoming numb from the cold, from exhaustion, from lack of enough nerve to ensure that you will not become the one out four who does not return? Faith and trust in God and prayer to be sure, good training, well-built airplanes and weapons and trust in your crew both on board and at your base. But something else is activated; your trust or a crewman’s trust in a talismanic device. This device is a forward placed decoration; symbol or figurehead meant to be a guardian spirit or to be a taboo to the enemy and it has a rich historical tradition. It was empowered by its crewmen to bring them home safely.

The following is from The Ancient Mariner, http://www.seagifts.com. “The figurehead embodied the spirit of a ship and was originally believed to placate the gods of the sea and ensure a safe voyage. Almost every prow had a carved figure looking down at the waves, and the variety was immense. From the earliest times the stems of vessels have been decorated with some form of figurehead and the seaman attached great importance to it.”

The most recent non-aviation use of this device was found on the bows of the Clipper Ships of the 19th century. Its use traces back through our country’s revolution, back through the Renaissance, the Middle Ages, and the Norman Conquest. Before then it was used by the Vikings, the early Romans, the Phoenicians and the Ancient Egyptians. Perhaps there is a universality or near universality in the talismanic use of ship decoration as exemplified by uses of it in still other cultures such as those of native Pacific peoples specifically in the Solomon Islands and New Zealand.

Nose Art is the copyrighted name given to the talismanic decoration painted by war theater servicemen onto the forward fuselage of combat aircraft. It is the continuation of the naval figurehead talismanic folk art tradition and a new application of this “universal” need. Its conservation treatment is the subject of this paper.

Painting the fuselage of airplanes began in the First World War and took the form of symbols or nicknames that the crew believed was instrumental in their safe return. It blossomed in World War II and in the Korean War. It was used in Vietnam, and the Gulf War.

In the beginning of this blossoming, during World War II, the themes of this folk art were similar to that of the figureheads of vessels of history, i.e., political or royal figures, Indians, animals, symbols and the always popular female figure. A 20th century addition was the cartoon character, which was the most common. The second most common was the female figure: a wife, a girlfriend, a nurse, Lady Liberty, but most often an anonymous woman copied from a calendar or magazine.
The most copied images were those produced by Alberto Vargas who worked for Esquire Magazine. Although some of the images were done by artists most were not, thereby keeping them in the realm of folk art. All of these images including those of low necklines, form-fitting clothing, suggestive posturing and sexy messages, again evocative of at least some of their 19th century counterparts, should be valued for their contribution to history and folk art. For these evoke memories of a time past, which is full of great patriotism, courage and the lost innocence of 20th century America.

This paper deals specifically with my treatment of various pieces of Aviation Nose Art that are from B-17 flying fortress bombers and B-24 liberator bombers. The B-17’s were used in the European Theatre and the B-24’s were used in the Pacific Theatre. They are all circa 1940-1944. However some history of the pieces is important before addressing their analysis and treatment.

The following information was gleaned from the owner’s collection research.

Virtually concurrent with the manufacture of the last planes the U. S. Congress passed the Surplus Property Act and created the Surplus Property Administration. Within a year or so George and Herman Brown created the Aircraft Conversion Company that salvaged the 20,960 airplanes that returned to the US after World War II. This gigantic company both in size and revenue (almost twice of what was spent to build this number of planes, $3.9 million that was gained from the resale of the salvaged metals and fuel) committed to a special ‘guillotine’ what could not be removed in advance such as magnesium, silver, copper and platinum.

George Brown’s brother-in-law, Minot T. Pratt Jr., general manager of the company thought that the Nose Art should be saved so he had his men take fire axes and chop the artwork off the planes in 1946. They were taken to Fort Clark, a historic U.S. Cavalry post near Bracketville, Texas that was purchased by the company when the Surplus Property Administration sold the bases. They were scattered throughout the Guard House and even in cells that formerly housed prisoners. In the mid-1960’s, after seeing several Confederate Air Force shows, Mr. Pratt’s son talked his dad into donating the 33 panels to the (CAF). Taking possession of the panels in the mid-1960’s the CAF, then located in Harlingen, Texas, stored the panels in an open-air bomber hanger. The panels remained there until 1991 when they were moved into the American Airpower Heritage Museum operated by the CAF in Midland, Texas. While in Harlingen the panels were cleaned with Bon Ami fine abrasive to remove spots and missing paint areas were filled in with artists’ oil and sign painters enamel paints.

The panels were exposed to the marine air environment of Harlingen for 26 years. They were moved to the AAHM in open lattice wooden crates and were given a conservation survey by Mary Frederickson. The museum immediately began planning for conservation and display. I began the conservation in 1997. Since that time I have completed the treatments on five panels and am working on a sixth and the museum expects their new facility expansion for display and conservation to be completed soon. The panels are shipped twice annually on urethane ester cushions in the mornings of a two day trip in the Spring and Fall; thus avoiding temperature extremes. The drive between Midland and Canyon takes about five hours.

The objects vary in size 8-9 feet wide X 6-7 feet high with depths ranging from 15-30 inches due to the vertical curvature. They have very sharp edges since they were just cut out of the fuselage in 1946. They weigh approximately 25-30 pounds although some can weigh twice that depending on the volume and type of original equipment that is still attached to the reverse. This equipment includes conduits, pulleys, electrical wires, switches, and other attachments. I found asbestos attached as some sort of fire proofing on part of the reverse of MAMA FOO, and also on some conduit on FOREVER AMBER. The design of each piece is painted in oil including artist paints, enamels, lacquer and house paint (owner information). However I found an occasional admixture of tempera (positive test results for protein). The paint was put directly onto the Alclad sheets that are riveted together to form the fuselage.

Alclad (an ALCOA product) is pure aluminum bonded to duraluminum, which has a very minor copper alloy. They are reinforced with structural ribs on the reverse and sometimes will have steel screws in them, which were used for attachments on the inside of the plane. Some of the paint suffers from flaking and loss of varying degrees. The objects are covered with dirt and some staining. Some of the dirt contains precipitate from the marine air.
I saw a single colorless cubic crystal on TARGET FOR TONIGHT, which I assume has a good possibility of being NaCl (which makes up 80% of seawater). They also have overall dents and scratches. The unpainted aluminum suffers from scattered exfoliation corrosion. Exfoliation corrosion is a type of corrosion that progresses approximately parallel to the outer surface of the metal, causing layers of the metal to be elevated by the formation of the corrosion product; in this case, aluminum oxide. Aluminum is a very durable material except when it is put in uninterrupted contact with a salt-water environment for a prolonged period of time. Studies in Conservation printed an article in 1983 by Ian D. Macleod which dealt with the examination and treatment of a duraluminum seaplane float which was in its littoral environment for 46 years. Pitting corrosion was found there but in these panels, only exfoliation corrosion was found. The Nose Art panels were not in salt water but they were in a marine air environment for 26 years. The degree of corrosion was slight to moderate on the visible scale and negligible if properly treated on the structural scale. The presence of chlorine in various amounts was confirmed by scanning electron microscopy and by using an energy dispersive spectrometer. The tests on my samples were done by my brother David who is currently a metallurgist with Aircraft Braking Systems Corp. in Akron, Ohio. The samples were from both corrosion and corrosion free areas. His findings are as follows: “The Nose Art aluminum base metal samples were examined using a scanning electron microscope. The metal particles were examined using X-ray micro spectroscopy and an energy dispersive spectrometer. The particles that were taken from a corrosion-free unpainted area were shown to be typical of an aluminum clad 2000 series alloy, probably 2024. This is consistent with the manufacturing information.

Examination further revealed a great deal of aluminum oxide corrosion product (very high peaks for aluminum and oxygen) and a high chlorine peak. This would represent salt water or an ocean environment exposure. Calcium, possibly calcium carbonate was also detected. Again, this is a common sea water mineral.” The findings for chlorine were consistent on four of the five objects that I have treated. The fifth, FOREVER AMBER had a lower chlorine peak. “Since the Nose Art is not intended to be stored in highly corrosive areas, no chemical corrosion coating, such as the typical dichromate (pea green in color), is necessary. A clear coat of polyurethane or equivalent should prevent any further contact with water exposure. Typically 70% or more relative humidity is required for aqueous corrosion. Once a moisture proof barrier is applied, further corrosion is prevented.”

The treatment for the corrosion is three fold. The primary treatment is cleaning. This was done while the object was in a vertical position. The non-painted areas especially the reverse were cleaned using deionized water and ammonia water. This was preceded by dirt removal by air hose as needed. The individual areas were first sprayed with deionized water via a Dahlia sprayer. This was followed by wiping with a large cotton swab, small sponge or large round brush (3 1/2” bristles) with 50% ammonium hydroxide reagent mixed with deionized water. Then the area was sprayed again. This was repeated three more times. The cleaned area was dried with cotton wool and air hose as needed. SEM sampling subsequent to the cleaning revealed virtually no trace of chlorine. Secondly the object is sealed. Three coats of 10% Paraloid B-72 were applied by spraying to the reverse. Thirdly the temperature in which the object is kept should not be low enough to cause any condensation on the surface. The object should be kept away from relative humidities above 69%, liquid water, or condensation.

The treatment of the painted surfaces was always done while the object was in a horizontal position usually on a low platform. Beginning with a four-step consolidation, it is as follows. The flaking paint was re-attached via application of Acrysol 200 (step 1); activation of the adhesive by low heat ~130-135 degrees F. via Leister hot air gun or Torchlamp and using finger pressure albeit through an isolating transparent spun polyester sheet (step 2); repeat step 2 and/or application of Paraloid B-72 (step 3); confirmation of consolidation as needed by Willard heated spatula (step 4). The use of the Torchlamp required using protective aluminum sheets (foil) in areas not being heated. All completed areas were isolated with transparent spun polyester sheet followed by polyurethane ester foam or moving blankets as a protection while the adjacent areas were treated. Paint layer cleaning followed consolidation.

The paint layer was cleaned by using small rolling cotton swabs with triammonium citrate. But for some areas of the images (and for one in particular this was virtually the whole image), the paint was too sensitive for even using a rolling cotton swab in water. For these areas cleaning was done by a light misting of deionized water and cotton wool dabbing. These sensitive areas were painted with the tempera/oil mixture, which is made by mixing the two while they are heated.
For the balance of the treatments the object was in a vertical position. The obverse was then sealed with two coats of 7% Paraloid B-72 by spraying. Color compensation was done with Maimeri, Magna, PVA and sometimes Shiva casein. Final spraycoating of 7% Paraloid B-72 followed.

As a matter of treatment sequence the obverse was treated first save for the compensation. After the reverse was completely treated then the obverse compensation and final sealing was done.

Additional treatments are sometimes necessary. I had two such cases. The first involved the fire extinguisher box lid, which was bent over on itself, on the obverse of MAMA FOO FOO. This had to be cold worked without removing it. The second was a small panel, which needed to have a structural wooden mount made and attached for exhibition.

My comments and recommendations to the owner are as follows. The object should not be stored or exhibited in a relative humidity below 40% or moved when in a temperature below 65 degrees F. The temperature should not be low enough to cause any condensation on the surface. The object should be kept away from relative humidities above 69%, liquid water, or condensation. Temperatures above 90 degrees F. should be avoided. The exhibition or storage environment should be dirt free. Any loose dirt on the object should be removed in a timely fashion by compressed air.

This is the most stable environment for both the paint and the Alclad. Although the exfoliation corrosion, the only corrosion present, is stable, it should be observed over time to see if there is any progression. If a progression is found an inhibitor such as Incralac should be applied by a conservator. An inhibitor coating was not part of this treatment since there was no identified need, i.e., there is no pitting or filiform corrosion, no meaningful history of marine immersion, and only a few traces of copper in the SEM testing of the corrosion.

Currently the untreated objects are in the museum housed in a poly tent in which the humidity is kept at 40%. This uses five gallons of water per day in dry Midland. The objects will be displayed on scaffolding like rectangular towers at a height, which corresponds to their original position on the aircraft from which they were taken. The new environmentally controlled exhibition area will be completed this October. And the CAF plans to change their name soon. The entire preservation effort on behalf of these objects by the American Airpower Heritage Museum is a Saving America's Treasures designated project.
MISSION COMPLETED raking detail before treatment showing flaking, loss, damage, exfoliation corrosion and deposits.

FOREVER AMBER raking detail before treatment showing flaking, loss and damage.
MAMA FOO FOO reverse after treatment.

MAMA FOO FOO obverse after treatment.
The small leather purse pictured in the two figures below is part of the Alexander Ramsey House collection, which is part of the collection of the Minnesota Historical Society. Alexander Ramsey was a major political figure in early Minnesota History, and one of the founders of the Minnesota Historical Society (MHS). For many years, it had been assumed that this object was a change purse or calling card carrier used by Alexander. However, the silver plate originally riveted to it had long ago had fallen off and become separated from the purse, and the two parts were stored in separate locations within the MHS collections. Recently, a thorough reassessment of the entire Ramsey House collection discovered that the two parts were associated, and after the two parts were reunited, the initials “AEF” were discovered engraved on the plate, indicating that this actually belonged to Anita E. Furness, Governor Ramsey’s daughter. Further research into the MHS archives discovered that Anita had purchased this purse outside the Paris Opera House in 1885 and had discussed it several times in her diaries, and in correspondence to her family in Minnesota (incidentally begging her father for more money to pay for such luxuries). What had been an object with a largely unknown provenience suddenly became one of the items in the collection with the best-known provenience, and it also became very important to ensure that the two parts would not again become separated.

However, the separation of the two parts was actually fortuitous for conservation treatment, because the tarnished silver plate was cleaned with a paste of precipitated calcium carbonate, water and ethyl alcohol, and if this cleaning paste came in contact with the leather of the purse, it could potentially have damaged it. After cleaning, the silver plate was coated with Agateen #27 cellulose nitrate lacquer, which should ensure that the silver will not tarnish for perhaps as long as 10 years. However, what is certain is that eventually the lacquer will have to be removed, probably with a solvent such as acetone. If the silver plate was permanently reattached to the leather purse, it could become difficult to remove the Agateen without damaging the leather of the purse. Ideally, a method needed to be devised by which the silver plate could be reattached to the purse securely, but which also could be easily and safely removed. Book conservators commonly use self-adhesive, flexible plastic films impregnated with magnetic material to make easily resealable book enclosures. For years the 3M Company has made such films with stable self-adhesive acrylic backing. One of these strips was adhered to the back of the silver plate (the silver was protected from the adhesive by the lacquer), and another magnet (with the self-adhesive removed with solvents) was inserted inside the front pocket of the purse. Thus the plate was held in place, but was also easily removable.

There were a couple of drawbacks to this technique; the magnets are strong, but still can only penetrate through relatively thin films, and rapidly lose their holding power when required to do so. Also, recently the 3M Company sold its magnetic products division to another company. However, finding these magnetic films should not be hard; they are made by several different manufacturers today, but they should all be tested with the Oddy test before using them, to ensure that they do not release compounds or vapors that could be harmful to the object.

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Figure 1  Coin purse before treatment

Figure 2  Coin purse after treatment
MORE VIRTUAL CONSERVATION WITH ADOBE PHOTOSHOP

Tom Braun

This tip is related to the publication by Getty Museum furniture conservators Joseph Godla and Gordon Hanlon in JAIC Volume 34, in 1995. The copper jewelry box pictured in the images below is part of the Alexander Ramsey House collection, which is part of the collection of the Minnesota Historical Society. Alexander Ramsey was a major political figure in early Minnesota History, and one of the founders of the Minnesota Historical Society. While in Paris, Alexander’s daughter, Anita Furness, purchased this French jewelry box. This is a very important artifact in the collection of the Minnesota Historical Society, and it has excellent provenance, as there are several mentions of the jewelry box in the correspondence and personal diaries of the Ramsey family. It is prominently displayed on a fireplace mantel in the bedroom of Anita Furness at the Alexander Ramsey Site. Unfortunately, like many parts of the Ramsey collection, this object suffered from overzealous cleaning, possibly by servants in the early 20th century, or by well-meaning but untrained site staff. Upon disassembly and cleaning of this object, remnants of previous gold and silver plating were discovered. Small remnants of the original plating can be seen in the deep crevices, as pointed out in figure 1. Much of the original gold and silver plating unfortunately has been lost from polishing.

Interestingly, the Ramsey Site interprets many objects damaged in such a way as evidence that the Victorians were obsessed with cleanliness as a result of becoming aware of germ theory and communicable disease. As a result, the site has often asked conservators working on their collections to preserve such damage as it illustrates a story. During treatment, it was realized that while the final appearance of the object would be much improved, it would not reflect the probable original appearance of the jewelry box. Additionally, replating the jewel box was not really an enticing prospect because it presents questions about reversibility and appropriateness. However, it was felt that it would be interesting to visualize what it might have looked like originally. Figure 2 is an illustration of how Photoshop was used to "virtually replate" the copper with what appears to be the original gold or silver plated surface, by simply removing the red color, to make it look golden, and removing the yellow color to make it look silver.

Unfortunately, the impressiveness of this photograph is best seen in a color format, which was not possible for this publication. Regardless, this process was completed within the Photoshop version 5.0 program by selecting "Adjust" from the “Image” menu, and selecting “Hue/Saturation”. A window appears that will allow modification of the hue and saturation. There is a “Master” selection that allows all the colors to be modified at once, or individual colors can be fine tuned by selecting individual colors; red, yellow, green, cyan, blue, and magenta can be selected. Of course, infinite variations are possible, and to get the best results, consultation with someone who is skilled in the manipulation of Photoshop is recommended.

Mainly this turned out to be an interesting exercise, but it could have numerous applications, and these images may soon be placed on the Minnesota Historical Society’s website. Hard copies will be kept in the permanent curatorial and/or conservation files. Additionally, these images could be used as Godlon and Hanlon suggested, to show a Curator, prior to treatment, what the object would look like after treatment. Also it could be used in a teaching exhibit to show an object in its current damaged state, with an accompanying picture of what it probably looked like originally. The display could include discussion on the mistreatment of the artifact that leads to the present damage.

Also, it is very important to note that these altered images should always be carefully labeled in writing as having been digitally altered, so that confusion does not result later when the enhanced digital image might be confused with the actual condition of the object at the time. In this case, someone seeing figure 2 could assume that the object was in that condition in August of 2001, when in actuality the last time it looked like this was probably in the 1930’s.

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Figure 3  Jewelry box image before alteration with Photoshop

Figure 4  Jewelry box image after alteration with Photoshop
Studio Tips

*Is that silicone release Mylar getting in the way?*

- *Try* kneadable, “thermal-conductive” RTV-2 silicone rubber - ELASTOSIL® M1470 / T40
- *Coat* the tip of your heating spatula and/or *configure* the “tip” that suits your needs
- *Eliminate* the need for silicone release Mylar

ELASTOSIL® M1470 / T40 (hardening paste) was introduced by Professor Winfried Heiber (University of Dresden School of Fine Arts) at the “Tear Repair Seminar” organized by the Paintings Specialty Group and hosted by the Art Institute of Chicago in September of 2000. ELASTOSIL® is a registered trademark of Wacker-Chemie GmbH.**

Tests were carried out on the ELASTOSIL® M1470/T40 for presentation here with product purchased through contacts in Germany.

A manageable amount of ELASTOSIL® M1470 was weighed out as well as 2% of the hardener paste T40. As noted in the technical data sheet, a 2% addition of hardener paste enables a working time of ca. 70 minutes while the addition of 3% T40 brings the work time down to 50 minutes, 4% to 30 minutes and 5% to 20 minutes. The components were mixed with a spatula, kneaded, rolled out onto 5 mil Mylar and cut into sections. These sections were then kneaded around the shaft of a steel picture hanging nail that has exactly the same diameter as the Engelbrecht welding needle in order to make several tips with the amount of silicone mixed; 3 grams goes a long way! In the preparation of different “tips” for the welding needle, it was noted that the working time of 70 minutes was far too long; the modeled “tips” did not maintain the desired shape and needed re-forming. The sterling silver “tip” that was purchased as an attachment for the Engelbrecht tool was also covered with the kneadable silicone. The interchangeable “tips” of the Willard heating spatula were coated and pressed against 5 mil Mylar on a flat surface and allowed to set. These “tips” soon found their way into the objects and paper studios for projects facilitated by directly heat-sealing without the interfering aspect of the silicone release Mylar.
Suggestions:

- When the “perfect tip” is made, it could conceivably be cast into plaster and recreated by pressing the silicone into the plaster (negative) rather than kneading from anew.
- Both ELASTOSIL® M1470/T40 and ELASTOSIL ® M4370 (Parts A, B) could conceivably be used for taking impressions (isolating resin where needed) from surface textures of paintings. These negative impressions can then be heat-sealed into thermoplastic fill materials to create the positive surface texture desired. **Note:** Using a silicone such as Dow-Corning® Sylgard 184 that is relatively transparent allows for precise placement during surface manipulation of a thermoplastic fill. If cast into a very thin film it adequately transfers heat from a hot spatula (with some heat loss) to the fill material.

Note:

- Silicone does wear with repeated use and should be replaced at the user’s discretion. The kneadable ELASTOSIL® M1470/T40 does not seem quite as hard nor tear as quickly as ELASTOSIL ® M4370 (Parts A, B), which is more fluid and absolutely accurate in reproduction.
- ELASTOSIL® M1470 is a slightly pinkish color while the ELASTOSIL® M4370 is the color of iron oxide red. **Caution** is recommended that the user be aware of pulverization of the silicone after extended and aggressive use - the particles of colored silicone could deposit onto the object.

**Availability: only through KREMER PIGMENTS, Inc., 228 Elizabeth Street, New York, NY 10012, Phone 212.219-2395, FAX 212.219.2395**

The kneadable, heat-conductive silicone is indispensable for point sealing in the reweaving of torn fibers with the adhesive mixture recommended by Prof. Heiber (wheat starch paste/sturgeon glue) *. This silicone also greatly facilitates in the re-tensioning of tears with adhesive-coated fibers that are heat-sealed to one side of a canvas tear, pulled across and heat sealed to the opposite side and conversely to recreate lost tension and prevent lifting at the site of the tear as described by Tomkiewicz at the AIC meeting in St. Louis, MO in 1999 (AIC PSG Postprints).

The silicone was dripped onto the hot spatula tips at least three times, allowing it to flow and evenly distribute itself within the 80-minute processing time listed in the WACKER Silicone Corp. “general information” sheet. The Teflon was used as a separating agent, since the silicone covers were originally conceived as removable “slippers”; however, there is no reason to remove them until wear demands replacing them.

**ELASTOSIL® M4370**

RTV-2 Silicone Rubber

- The tips for the above-depicted Willard (any hot spatula can be used) were wrapped smoothly in Teflon® cut from sheets and coated with **ELASTOSIL® M4370**. These silicone-coated tips were successfully tested for efficacy in directly heat-sealing BEVA®371 onto 5 mil Mylar with no silicone release Mylar → no sticky residues on the tip. The advantages of eliminating the sometimes awkward silicone release Mylar are self-evident.

**Note:** Contact has been made with TAYCHEM INDUSTRIES, LTD. in Atlanta, Georgia - Randy Schneider (866) 794-0004 has expressed interest in working with professionals in the field of Conservation to help answer questions concerning this and other silicone materials for mold making. Most importantly, he is willing to supply kits of the above-mentioned product in manageable 1 or 2 pound quantities, at a price yet to be determined.

Carolyn Tomkiewicz, Brooklyn Museum of Art, 200 Eastern Parkway, Brooklyn, NY 11231
tel. (718)638-5000 Ex. 274

**PARAFILM®**

*American National Can™ / MENASHA, WI 54952*

- Since silicone will not set up properly when in direct contact with Plasticine or Clean Clay, **PARAFILM®** might be helpful as a release agent.

- This product was successfully used by Carolyn Riccardelli, who should be contacted for further information (AIC Directory). It was applied to the surface of a mosaic to which it conformed exactly by heating with a hot air tool. The subsequent bed of silicone needed to hold the surface in place during the removal of a rigid backing set up against the **PARAFILM®** from which it easily released.