STUDIO TKM ASSOCIATES
CONSERVATION OF FINE ART & HISTORIC WORKS ON PAPER

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June 21, 2019

18.78 Elihu Akin House (ca.1762) Parlor Wallpaper


The Elihu Akin House

The 1762 Elihu Akin House, located at 762 Dartmouth Street at the intersection of Dartmouth and Rockland Streets, Dartmouth, Massachusetts. Built in 1762, it is one of the oldest existing buildings in the town of Town of Dartmouth, Massachusetts, is listed on the State Register of Historic Places and is eligible for listing on the National Register. Built by house-wright Job Mosher for his wife, Amie Akin. A few years later the 18-acre property with house was purchased by a Captain Jonathan Delano who soon died at sea. In 1769, Elihu Akin, Amie's uncle, purchased the property from the Delano estate presumed as an investment for farming. As one of Dartmouth's founding families, the entrepreneurial Quaker Akins, who became politically active against the British Crown, owned a shipbuilding business and were instrumental in the economic development of the town. In September 1778, the British assisted by Loyalists raided the strategic coastal areas of old Dartmouth, destroying the Akins' shipbuilding business, great houses, a tavern and other holdings. Presumed to have lost everything, Elihu Akin and his family moved to his farm on Potter's Hill, less than a mile from the harbor where he died in 1794 at about 74 years old. What is now called the Elihu Akin House survived the invasion of the British during the American Revolution. The house remained in the Akin family for 241 years.

The house was in substantial disrepair in 2003, when Waterfront Historic Area League of New Bedford, Inc. (WHALE) purchased the property from Akin family descendants with funds provided by the Town of Dartmouth Community Preservation Fund. WHALE began post-and-beam stabilization and restoration on the property, addressing serious structural issues including exterior siding, the roof, and some interior repair work. WHALE then conveyed the property to the Town of Dartmouth acting through its Historical Commission on March 19, 2008. In May, 2008, the Historical Commission leased the property to Dartmouth Heritage Preservation Trust (DHPT). DHPT, through funds acquired by two grants (2008 and 2015) from the Community Preservation Fund, carried out a second phase and third phase of work to transition the house into a heritage center for the Town. As a rare example of the post-and-beam construction of the 18th century, the Akin House will be maintained as a working classroom for area residents and visitors. The house will be designed for self-guided tours with fixed and revolving exhibits and will serve as a venue for the DHPT in partnership with other groups to offer innovative ways to teach local history with hands-on workshops and other programming to provide a living history experience.

In July 2018, the National Trust for Historic Preservation awarded a $13,000 grant from the Cynthia Woods Mitchell Fund for Historic Interiors to DHPT for use in the South Parlor (Sitting Room) at the Akin House. These funds were applied in part to the examination and stabilization of the South Parlor wallpaper. (Cited from http://dhpt.org/history).

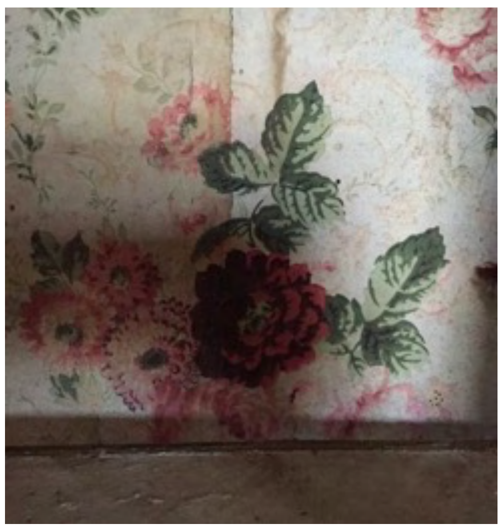
Historic Wallpaper in the Akin House
Numerous examples of historic wallpaper were discovered and documented in the North and South Parlors by Diane Gilbert, DHPT during the restoration of the Akin House. The accompanying photos are indicative of the range and stratification of papers on the walls of Akin House.

North Parlor (also referred to as the Formal Parlor)

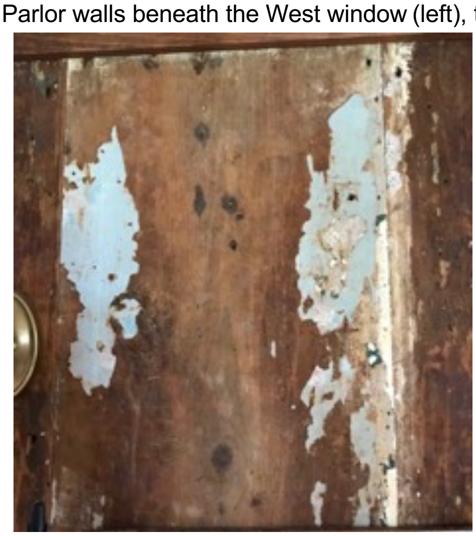
Wallpaper layers photographed by D. Gilbert prior to removal from the North Parlor walls.







Wallpaper remnants retained on the North Parlor walls beneath the West window (left), to left of the fireplace mantel (right)

Stairwell/Cupboard interior
Wallpaper fragments found in the interior of the cupboard to the left of the mantel in the South Parlor


Identified by DHPT within the collection of Historic New England, as GUSN-296581, WP368, maker unknown, ca. 1840-1860. Machine printed.

South Parlor (Sitting Room)
The wallpaper remnants within the South Parlor are the subject of this report.


Paneling covered walls of South Parlor, 2003 (left) & the most recent wallpaper installation, a rose-colored floral pattern paper (right).

Below are additional photographs taken by Diane Gilbert during the exploration and salvage phases of the Akin house restoration and are indicative of the layers of wallpaper and plasterboard that accumulated throughout the 20th century. At some point in the late 19th/ early 20th century, a plaster and lath surface wall was constructed atop the house's original plank walls. The approximately two inch sawn wooden lath spaced at approximately ½ inch was coated with a substantial thickness of lime-based horsehair plaster in the traditional fashion, a relatively thick brown coat, a skim white coat followed by paint. Upon removal of the plaster and lath, three layers of paper wallcoverings were revealed that were adhered directly to the original wide wood plank interior and exterior walls. These paper layers, two historic wallpapers with a newsprint intermediate layer, were the subject of analysis and conservation treatment as documented in this report.



Most recent wallpaper layering

20th century wallpaper stratigraphy

20th century wallpaper stratigraphy atop plasterboard

Underlying plaster & lath wall structure

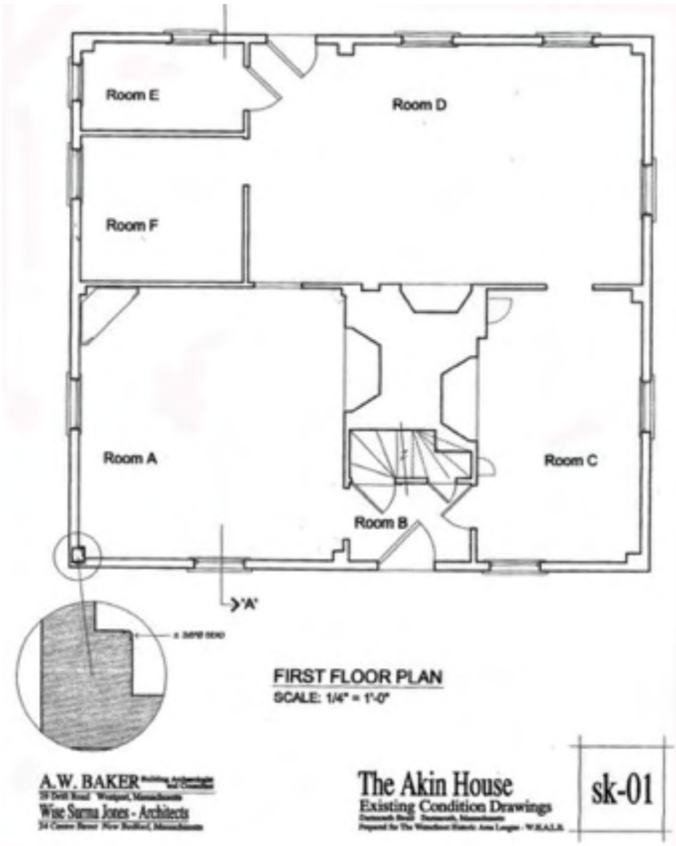
Wallpaper fragments revealed on the original wall surface upon removal of the plaster & lath surface wall.

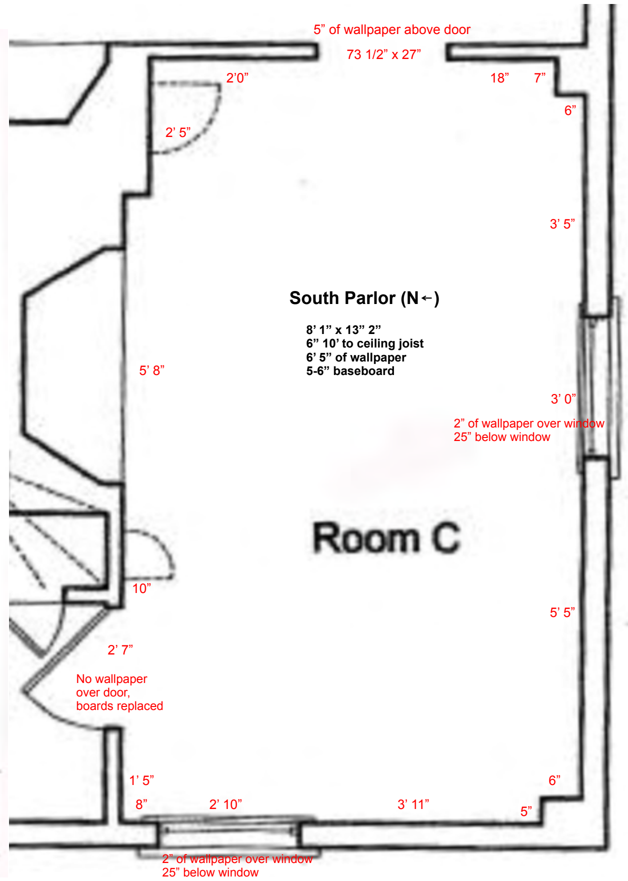
Earliest Wallpaper

Three layers of paper were revealed following the removal of 20th century wood paneling, plasterboard and early plaster and lath walls. The wallpaper is adhered directly to whitewashed wide wood plank interior and exterior walls. The wood planks range in width up to 15 inches. The wallpaper is installed from the floor to the ceiling joists for a height of approximately 6' 10" though it is covered by a painted flat profile 5-6" wood baseboard with a black ¼ inch round molding at the floor in some areas. Fragments of the earliest wallpaper are present on all of the wall surfaces with the exception of the north overdoor which appears to have replacement wood planks, totaling approximately 142 square feet of wallpaper.

The wallpaper proceeds under the left side of the north door, under the mantle at the left side and cabinet above, and continues under the trim of both windows indicating that a slightly different configuration of wood moldings was extant at the time of installation than at present.

South Parlor Floor Plans (not reproduced to scale)






Photographed with studio lights


Photographed with raking light to capture 3-dimensionality of layers

Extant Wallpaper Stratigraphy

Wood planks
White wash
Wallpaper Layer 1 (oldest) Palmette design, block printed in blue and red possibly on a beige background on light brown paper
Wallpaper Layer 2 (intermediate) Letterpress newsprint in black ink on off-white paper.
Wallpaper Layer 3 (newer) Stylized vine pattern roller printed in black and white on pale blue-green paper.

Layer 1 Palmette Offset Pattern Paper

Palmette design, block printed in blue and red possibly on a beige background on light brown paper (likely originally off-white).

Width of the paper is 19 ½ inches with nearly an inch underlap. The wallpaper design exposure measures approximately 18 ¾ inches wide with the vertical repeat every 16 inches. On the north side of the east wall, the largest vertical fragment measured 52 inches without a visible horizontal seam. Likewise, a fragment to the right of the window on the south wall measured more than 40 inches in height. This indicates that the wallpaper was printed on machine-made roll paper and not handmade sheets assembled into rolls, as was the convention prior to the invention of machine made paper. Therefore, the palmette paper most likely dates to 1820-30 or later.

<u>Pigment and binder analysis</u>

XRF analysis was carried out at the Isabella Stewart Gardner Museum (ISGM) by Objects Conservator, Jessica Chloros. A full description of the results is presented below. Though informative, the results were not definitive. Therefore, repeat XRF as well as follow-up instrumental analysis was carried out at the Scientific Research Lab of the Museum of Fine Arts (MFA), Boston by the Richard Newman, Head of Scientific Research. Attached are the reports of scientific analysis provided by the ISGM and MFA. A summary of the results of analysis follows.

Analysis by non-invasive x-ray fluorescence detected iron as the major element within the paper substrate, the blue colorant and the red colorant with calcium as the minor element. Traces of potassium, lead and zirconium were detected in all three areas, traces of titanium in the two colorants and a trace of sulphur in the blue colorant. Because similar elements were detected in paper and the colorants, no definitive conclusions could be drawn regarding the pigments from the XRF data. This is not surprising, as iron ions can solubilize and leach into the paper substrate over time. Fourier Transform Infrared analyses of samples showed that the blue pigment is Prussian blue and the red pigment is hematite (red ochre).

Prussian Blue

Prussian blue is considered the first modern synthetic pigment, and was first synthesized, through accidental discovery in 1706. The distinct blue hue proved an inexpensive alternative to the very costly natural mineral pigment lapis lazuli. Prussian blue quickly came into common use as a pigment in watercolor and oil paints as well as printing inks. The vivid, generally lightfast blue pigment is composed of synthetically produced ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$ forming an intermediate white, Berlin white, that is oxidized in air to produce Prussian blue. Prussian blue has a deep blue, insoluble colloidal crystalline structure. It has high tinting strength and can be stable to light when properly formulated. However, Prussian blue is sensitive to alkalis or heat, a defining feature, and will turn to brown upon exposure and eventually to white with extended exposure.

Discoloration & fading of Prussian Blue

Prussian blue is most readily distinguished from other blue pigments by its sensitivity to alkali and lack of reaction with acids. An alkaline or buffered environment causes Prussian blue images to lose detail and density. The images first turn yellowish brown before eventually fading to white. In theory, the blue color can be restored by adding acid.

Hematite (red ochre)

Hematite is a naturally occurring mineral form of iron(III) oxide and the principal colorant in red, brown and purple iron oxide-based pigments, including ochre, umber and sienna colors. The mineral is found in many places throughout the world, and trace chemical elements within the mineral are often indicative of the source.

The word *hematite* derives from Greek word *haima*, referring to blood, and was undoubtedly given the name because of its red color. Hematite is one of the earliest known pigments, first referenced as bloodstone by Theophrastus' *On Stones* (c. 315 B.C.E.). About four hundred years later, Pliny the Elder (c. 77 C.E, Book xxxvii) references hæmatite, in his widely cited *Historia Naturalis*. Its continued use throughout modern history, is well documented through scientific analysis.

Printing medium
Both colorants contain a water soluble medium whose FTIR spectra closely resembles a plant gum. This is a curious finding, as wallpaper printing is historically presumed to have employed a proteinaceous glue binder. However, this assumption often relies on the supposition of historians, and not chemical analysis. To further explore this finding additional instrumental analysis was carried out using peptide mass fingerprinting (PMF), which can identify specific proteins that have been historically used as binders (collagen in animal and fish glues; egg white; egg yolk; casein; etc.), and gas chromatography/mass spectrometry (GC/MS) for the identification of free monosaccharides and some non-carbohydrate materials (such as oils, natural resins and waxes). The full results are available in the attached *Scientific Research Lab Akin House wallpapers report 2*. The analysis was summarized by Richard Newman as follows:

> The detailed analyses for different major classes of paint binding media could not conclusively prove the identity of the binder. It is not obvious why the binder of the paints did not seem to dissolve, or chemically react, with either of the reagents used to prepare samples for GC/MS analysis. The best estimate is that the original binder was a carbohydrate, as the FTIR spectra had suggested.

References
Cameo, Conservation and Art Materials Online Database developed by the Scientific laboratory of the Museum of Fine Arts, Boston. Cameo.mfa.org
National Park Service Caring for Blueprints and Cyanotypes, www.nps.gov/museum/publications
National Gallery of Art. *Artists' Pigments: A Handbook of Their History and Characteristics*. Published 1986, 1993, 1997.

Central plank exhibits offset palmette pattern (left), Detail of palmette with laurel & cascading leaves (center), Wallpaper seam at the center of the palmette installed slightly out of alignment (right)


Measuring the roll width from seam to seam (south wall)


Measuring continuous paper height (east wall)



Rudimentary reconstruction of single palmette repeat (left) & palmette pattern (right).

Layer 2 Newsprint
Letterpress printed newspaper text in black ink on off-white paper. It is suspected that this layer was installed just prior to the installation of layer 3 in order to smooth and prepare the walls for installation of a new wallpaper.

Infrared photography was carried out in situ using a Sony Alpha 7II camera modified to take infra-red images using wavelengths up to 1150nm. This was not successful in penetrating the top layer of paper to image the newsprint below. In situ IR photography will require hardware that is capable of additional wavelength modification to optimize penetration and imaging of the underlying text. This is something that can be considered in the future, as budget allows.

Examination of text within the newsprint layer was carried out throughout the surface cleaning process. In three areas of paper, exposed text indicated the possible presence of dates. In those areas, the upper wallpaper was gently humidified and released to reveal the text below. Those areas are shown in the photographs below. Text reads “New Bedford, Jan 24, 1846” and Washington May, 18 31.”

Layer 3 Stylized Vine Pattern Paper
Stylized vine pattern printed in black and white on pale blue-gray paper.
It is difficult to measure the exact paper width, though it appears to be at least 18 inches wide. There are no visible horizontal seams and the paper is presumed to have been printed on roll paper. The small, simple offset pattern repeats every 4 ½ inches height and 3 ¼ inches wide.

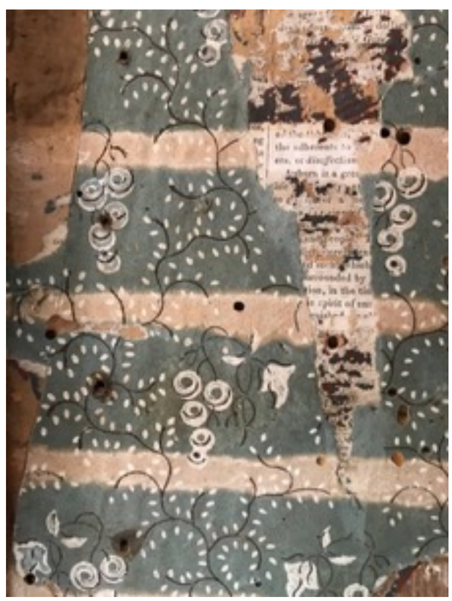
<u>Pigment and Binder Analysis</u>
As in the palmette wallpaper, XRF detected iron as the major element and calcium as the minor element in paper and colors. Traces of potassium, lead, and zirconium were detected in all three areas. In addition, silicon was detected in trace levels in the white ink and dark lines. Similar elements found in the paper and paint make conclusions regarding paint pigments difficult. FTIR and Raman analysis of samples identified the blue pigment as Prussian blue, the dark lines as carbon black with red ochre, gypsum and kaolinite (clay). The white pigment contains kaolinite. The inks contain a water-soluble medium while FTIR spectra resembles a plant gum.

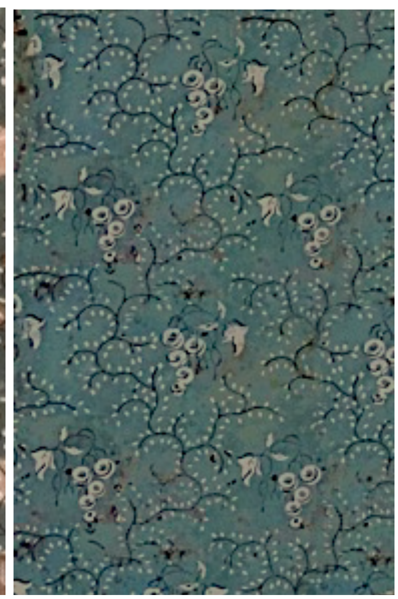
Prussian Blue
As described above. In this paper the Prussian Blue has been added to the papermaker's vat to produce an overall background tone for the printed image. And as seen in the lower paint layers, the sensitivity of the colorant to the high alkalinity of the plaster surface wall is apparent in the bleached horizontal linear pattern at two inch distances mirroring the plaster and lath wall structure.

Dark lines
The dark lines consist of a carbon based mixture containing red ochre, gypsum and kaolinite. Carbon containing black pigments were ubiquitous throughout history. As one of the earliest pigments known to man, carbon is produced by burning organic material either in an oxygen-free environment to produce charcoal residue, or in an oxygen rich environment as soot, smoke residue. Carbon black is usually a fine, soft, black powder, but some blacks contain mineral impurities that give it a bluish, reddish or brownish tinge, as in the case of this wallpaper. Carbon black is very stable and unaffected by light, acids and alkalis.

Kaolinite
Kaolinite is the primary constituent of naturally occurring kaolin clay. It is a hydrated aluminum silicate with a lamellar or plate-like crystalline structure which is white or off-white in color.


Representative wall section


Extant wallpaper fragment


Rudimentary wallpaper reconstruction

South Parlor Wallpaper Condition
The wallpaper remains in fragmented sections and a printed text interlayer is visible where the uppermost wallpaper is missing. The fragmentary sections of wallpaper appear damaged from prolonged exposure to light,

moisture and pollution, from the application and subsequent removal of covering layers and from extensive damage from silverfish feeding on the cellulose and starch in the layers of wallpaper.

The wallpaper layers exhibit extensive insect activity. Most damaging is the lacing effect on the paper around the design caused by the feeding of silverfish on the cellulose of the paper and the adhesive paste used for installation. Other insect activity is evidenced by the presence of webbing and egg casings throughout the room and on the wallpaper surface.

Detachment from the wood resulted from fluctuations in temperature and relative humidity, mechanical damage, as well as destruction of the underlying wall structure by softening and deterioration of the wood as well as the incidental activity of wood borers. The wood borers surfaced from beneath the paper resulting in small circular holes with clean edges. It is noteworthy that the woodboring insects often did not ingest the wallpaper, but remained below the wallpaper surface feeding only on the wood structure. This is distinct from the grazing insects that fed on the surface wallpaper and adhesive.

The discoloration and embrittlement of the wallpaper is a result of age and contact with the wood plank and may have been reduced in areas by the intermediary white wash. The alkalinity of the calcium-based white wash may have partially neutralized the acids migrating from the wood and retarded the wallpaper deterioration.

The fading or bleaching of the colorants in horizontal striations are a result of contact with the lime-based plaster between the lath of the surface wall.

Water staining is presumably from penetration of water through the exterior siding and along window trims.

Extensive accumulation of surface dirt and debris is due to the number of years that the wallpaper remained entombed as well as the heavy construction carried out for the stabilization of the building.

Photographic Documentation of Condition

Insect webbing and frass

Silverfish damage

Wood boring insect damage

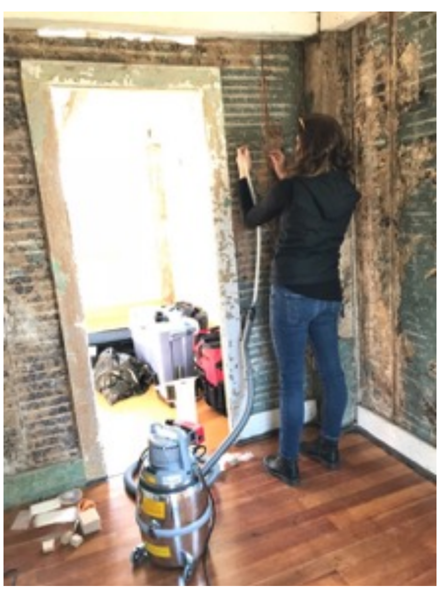
Silverfish damage, general surface accretions

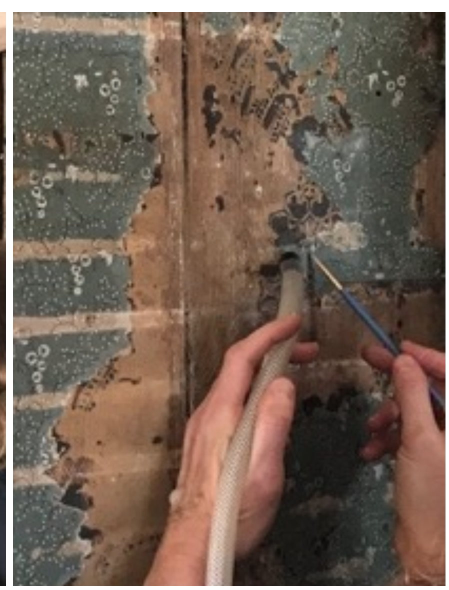
Fading of color due to contact with highly alkaline plaster

South Parlor Conservation Treatment

<u>On-site Cleaning & Stabilization of Wallpaper In situ</u>

Minimal intervention was undertaken with the goal to stabilize and preserve the existing wallpaper in situ. The wall surfaces were vacuumed with a variable suction HEPA-filtered vacuum to remove a heavy accumulation of insect webbing and frass, dust and fine construction debris. The wallpaper was then surface cleaned as possible with extruded latex fire recovery sponges to remove lightly affixed surface dust and dirt. Lifting wallpaper fragments were set down with precipitated wheat starch paste, Jin Shofu manufactured by Nakamura Co., Japan. The wheat starch is purified through precipitation to remove the insoluble glutamine in the starch which contributes to embrittlement and yellowing upon aging, thus producing a very smooth, water-soluble paste with a neutral pH with excellent aging properties. The wheat starch paste was applied very dry to the wood plank surface or the reverse of the wallpaper, as necessary, and dried with a tacking iron over hollytex or hairdryer to ensure fast drying and good adhesion without staining.





Removal of loose dust, construction debris and insect frass with a HEPA filtered variable suction vacuum

Before surface cleaning

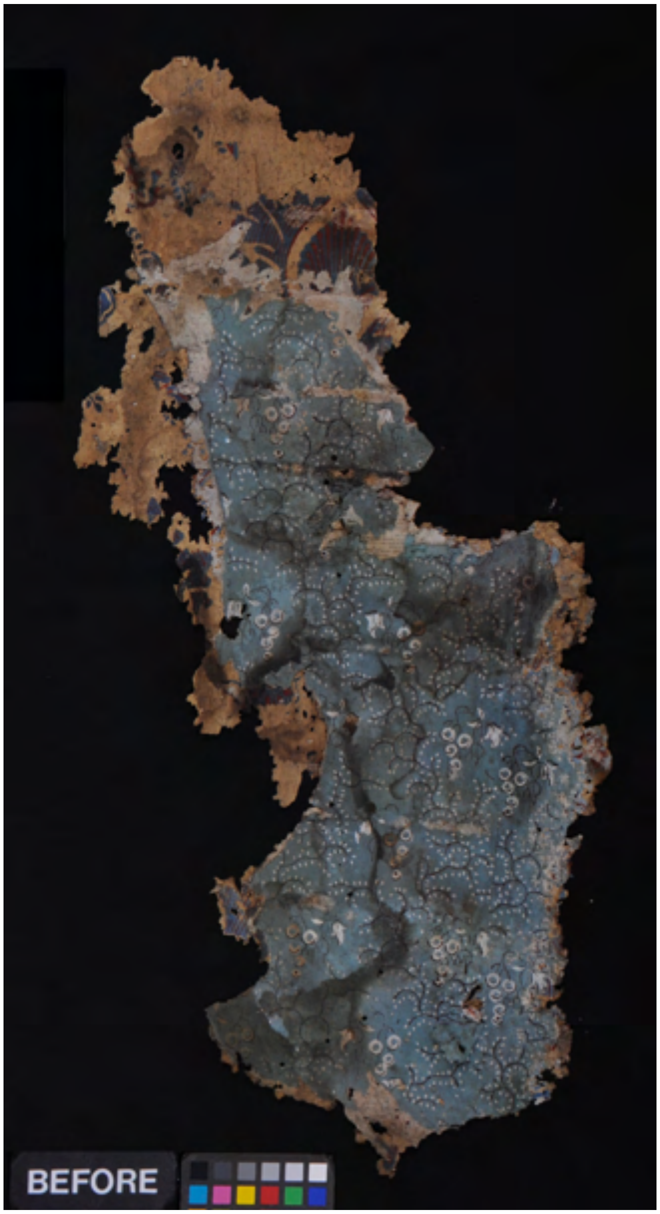
After surface cleaning

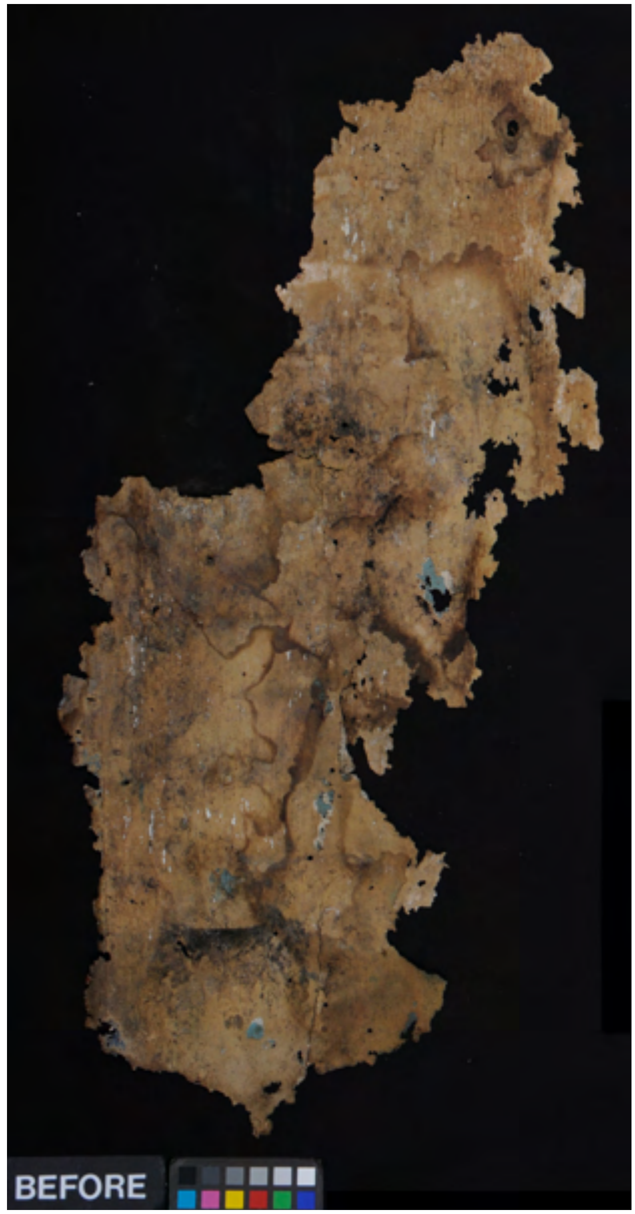
Setting down with wheat starch paste

Detail of setting down with wheat starch paste

In-studio Conservation of Wallpaper Sample

Conservation of a loose wallpaper fragment was undertaken in the conservation studio to separate the layers in order to preserve and individually exhibit the three earliest layers of wallcovering. The wallpaper sample was vacuumed with a variable suction HEPA-filtered vacuum to remove loose surface dust, dirt and mold. Further surface cleaning was carried out, as possible, with extruded latex fire recovery sponges. The wallpaper layers were then mechanically separated with the aid of steam, as necessary, to soften the interlayer adhesive. The individual wallpaper layers were washed on deionized water saturated blotter to reduce soluble discoloration and strengthen the intrafiber hydrogen bonding within the paper. To structurally support the fragile, aged paper, each layer was lined with lightweight Japanese paper of a sympathetic tone adhered with Jin Shofu wheat starch paste. The thin, but long-fiber lining paper adds support to the aged paper while still permitting visibility of the paper verso. The lined fragment layers were dried under heavy felts to maintain planarity. They can be trimmed to accommodate the final display format, once determined.






AFTER

AFTER

AFTER

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Recommendations for In-situ Wallpaper Preservation & Care
Maintain building envelope to ensure protection for the wallpaper from water and pests. Regularly inspect the wallpaper throughout periods of non-use of the building as well as open hours.

Climatic conditions should be stabilized as possible in order to mitigate large swings in humidity and prevent rapid spikes in temperature. The historic wallpaper no longer benefits from the climate buffer that the plaster and lath surface wall provided. With full exposure, the adhesive as well as the paper and pigments are more susceptible to changes in temperature and humidity. Evaluation of the annual climate within the space will help inform best recommendations for climate stabilization.

- Log climate data within the space over a representative period of time to inform the need to climate mitigate.
- Evaluate the need for dehumidification throughout rainy seasons.
- Monitor the use of heating equipment and measure low humidity levels throughout the winter to determine the need for the introduction of humidification.

Though relatively lightfast, the wallpaper pigments will eventually fade with exposure to light, and will fade more rapidly in the presence of ultraviolet light. Low, UV-filtered light levels are recommended.

- 100% ultra-violet filtering film should be applied to all windows.
- Solar shades should be installed.
- Curtains or scrims should be drawn when the room is not in use.
- Lights should be installed with a sensor for motion and dimness to minimize exposure during tour hours.

The wallpaper should be protected from mechanical damage such as scratches, abrasion, blunt contact. These are primarily caused by visitors, who very often cannot resist the urge to touch walls and house surfaces, or accidentally brush up against wallpaper when passing through narrow spaces. Restricting the path of visitors to the center of the room or limiting entrance into the space with stanchions, is an excellent way to reduce visitor damage, particularly when guided tours are not required. Installation of acrylic glazing is not recommended as this can create a microclimate that can be more detrimental to the wallpaper. If areas of vulnerability to visitors are noted, then the use of acrylic protection can be specially designed for set locations with these issues in mind.

Accounting

On-site conservation treatment (2 conservators/ 2 days)		
In-studio preparation & packing (1 hrs.)	$175	
Examination, documentation & photography (2 hrs.)	$350	
Surface clean & stabilization (25 hrs.)	$4375	
Travel (12 hrs.)	$2100	
Subtotal (40 hrs. @ $175)	$7000	
Mileage (520 miles @ 0.52/mile)	$270	
	$7270	
	-3070	
Total adjusted to meet estimate	$4200	$4200
In-studio conservation treatment		
Surface clean (1 hr.)		
Separation of layers (2 hrs.)		
Wash & line each layer (4 hrs)		
Storage in archival folder with appropriate interleaving		
Total (8 hrs. @ $175)		$1400
Instrumental Analysis		
Pigment analysis by SEM/EDX, Richard Newman, MFA Boston		$325
Portable XRF analysis including delivery and supervision		$450
Documentaion		
Preparation of comprehensive research and condition report. (1.5 days)		$2100
Total		**$8475**

APPENDIX

ISABELLA STEWART GARDNER MUSEUM

XRF ANALYSIS INTERPRETATION

DATE OF REPORT: December 16, 2018
ANALYSIS PERFORMED BY: Jessica Chloros
INTERPRETATION PERFORMED BY: Jessica Chloros
ANALYSIS CONDITIONS: 40 kV, 8 uA, no filter, air, 60 sec
EQUIPMENT USED: Bruker Tracer III-SD spectrometer with S1PXRF & ARTAX, 7.4.0.0 software

INVENTORY NUMBER: Outside Project - Studio TKM
TITLE DESIGNATION: Wallpaper sample
ARTIST: Unknown

The following elements are detected as a result of instrument artifacts and while they appear in the spectrum, they will not be reported here unless they are present in the material being analyzed: Ti, Fe, Cu, Ni, Zn, Rh, Pd.

Location	Color	Elements Detected[1,2]	Inferred materials/pigments	Notes
Spot 1 Plain paper on Plexi		S, Ca, **Fe**		
Spot 2 Plexi		**Si**, Sn(?), Ca, **Ti**		Sn Lα line is present, but not fully understood.
Spot 3 Lower paper layer	Dark blue	**Fe**, Ca		High Fe peak, greater than Spot 1.
Spot 4 Lower paper layer	Dark red & dark blue	**Fe**, Ca		Highest Fe peak of all spots analyzed.
Spot 5 Upper paper layer	Green	S*, K, **Ca**, **Fe**, Pb		
Spot 6 Upper paper layer	White decoration on green	Al*, Si, K, Ca, **Fe**		Lower Ca peak than in Spot 5, so Ca not necessarily related to white.
Spot 7 Upper paper layer, lifted section	Green	S*, K, **Ca**, **Fe**, Pb		Higher Fe peak than in Spot 5.

SUMMARY: Iron was the primary element present in all analyzed areas of the wallpaper, including an undecorated area of plain paper. Calcium was also present in all analyzed areas, which likely is attributed to filler in the paper. Four areas of color were analyzed and possible inorganic pigments will be suggested: dark blue, dark red, green and white. The dark blue area was iron-rich, which could indicate Prussian blue. The dark red area had the most significant iron peak, perhaps indicating the red is an iron earth color, such as hematite. The green areas were iron-rich, which could indicate a green earth (terre verte). There were also very small peaks

[1] Elements in **bold**, designate major elements present and/or elements of interest.
[2] Elements with an asterisk* after them indicate a minor/trace element.

SCIENTIFIC RESEARCH LAB, MUSEUM OF FINE ARTS, BOSTON

Analytical Report

Subject: parlor wallpaper adhered to wide plank interior and exterior walls, from Akin House (ca. 1762), Dartmouth, MA

Contact: Diane Gilbert, Dartmouth Heritage Preservation Trust, P.O. Box 87026, Dartmouth, MA 02748, d.m.gilbert@comcast.net

Request for analysis: Deborah LaCamera, Studio TKM Associates, deborah@studiotkmassociates.com

Introduction

This report presents results of further analyses, focused specifically on more detailed characterization of the binder(s) for the paints used on the wallpaper. The two wallpapers are shown in fig. 1. The lower layer consists of paper substrate, painted dark blue with overlying red-brown painted designs. The upper layer consists of a paper substrate covered with thin pale grayish blue paint. On top of this are thin dark-brown red lines (like stems or vines) and thick white oblong spots or circles (like leaves or flowers). The dark red "stems" were painted before the white elements.

Initial transmitted FTIR analyses of the colors were carried out on very small isolated bits of the paint, pressed on a diamond window. After initial analysis of some of the bulk samples, a small amount of water was added to the sample and evaporated under a heat lamp. If water-soluble material is present, it is drawn out of the solid sample and concentrated in a ring on the diamond. If concentrated enough, FTIR analysis of this ring provides information on the extracted material. Bulk sample FTIR spectra (fig. 2) suggest the presence of a carbohydrate binder, and water extracts (one of which is shown in fig. 2) closely resembles a common plant gum, gum arabic.

Fig. 1. Detail of wallpaper, showing the upper layer and some of the underlying lower layer.

Samples discussed in this report are:

1. upper layer (thin light blue paint, covering thin paper sybstrate)
2. upper layer (thin light blue, covering thin paper substrate)
3. upper layer (thin light blue paint, covering paper substrate, with some dark red paint from "stems")

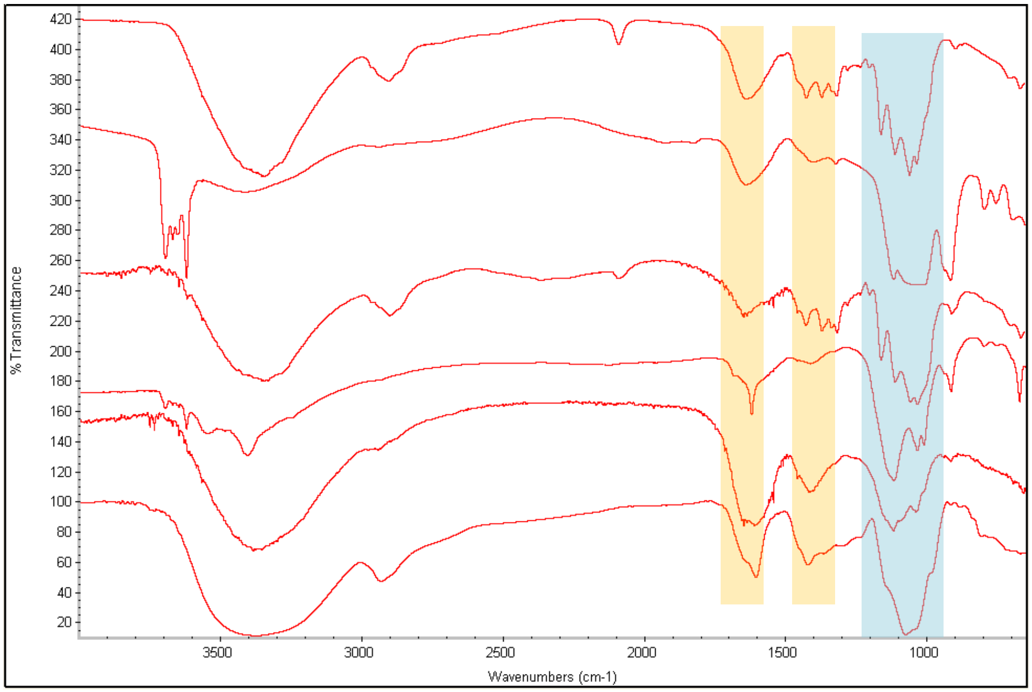


Fig. 2. Transmittance FTIR spectra of samples from the wallpaper (top five spectra) and reference gum arabic, probably *Acacia senegal* (lowermost spectrum).
Spectra numbered from top down:

1. Sample 3 (upper wallpaper layer; blue paint on paper).
2. Sample 4 (upper wallpaper layer; white paint).
3. Sample 2 (lower wallpaper layer; blue paint on paper).
4. Sample 4 (upper wallpaper layer; red paint).
5. Sample 4w (upper wallpaper layer; red paint, material extracted from paint by water).
6. Reference spectrum of gum arabic.

Yellow boxes and blue box highlight three characteristic absorption regions for gum arabic. Other materials (cellulose from paper and inorganic compounds in the pigments) also have absorptions in one or more of these regions, which may completely or nearly completely mask features from the (potential) gum arabic binder.

Spectra 1 and 3: the blue in both layers contains Prussian blue (small absorption band at ~ 2100 wavenumbers). Most of the features in the boxes are due to cellulose of the paper substrate, which could not be separated from the paint. There is no clear indication of the paint binder.
Spectrum 2 mainly shows kaolinite (the white pigment). There is a possibility that features in the two yellow boxes indicate a gum binder.
Spectrum 4 mainly shows kaolinite and gypsum. Some of the features in the blue box are due to cellulose. Spectrum 5, from the water extract of the sample analyzed in bulk in spectrum 4, very closely resembles gum arabic.

Analytical procedures

For the current project, specific analyses were carried out by three methods that focus on different classes of organic materials which are commonly used as binders for pigments: proteins; carbohydrates (such as plant gums); and oils, fats, natural resins and waxes.

Proteins. A solid sample is treated with an enzyme (trypsin), which breaks down proteins into smaller fragments (peptides). The peptides are then analyzed by matrix-assisted laser desorption ionization (MALDI) time-of-flight mass spectrometry. The method, called peptide mass fingerprinting (PMF), can identify specific proteins that have been used as binders (collagen in animal and fish glues; egg white; egg yolk; casein; etc.). Non-proteinaceous binders cannot be detected.

Carbohydrates. A solid sample is hydrolyzed in methanolic hydrochloric acid, then derivatized with a silylation reagent. The procedure breaks down carbohydrates into their constituent monosaccharides (and uronic acids), which are derivatized into forms amenable to analysis by gas chromatography/mass spectrometry (GC/MS). Free monosaccharides and some non-carbohydrate materials (such as oils, natural resins and waxes) can simultaneously be detected. Identifications of plant gums are based on types of monosaccharides detected and their relative quantities. Proteins cannot be detected.

Oils, fats, natural resins and wax. A solid sample is treated with a mixture of 'MethPrep 2' (a commercially-available reagent in methanol solution) and benzene. This reagent is commonly used to hydrolyze esters (such triglycerides in oils, fats and waxes) and to methylate acidic compounds. This is a convenient method by which several types of binding media can be simultaneously prepared for GC/MS analysis. Proteins and carbohydrates cannot be detected.

Results

No proteins were detected in any of the five samples analyzed by PMF (white paint and dark red paint from upper wallpaper; blue background with some paper fibers from upper wallpaper; blue background with some paper fibers from lower wallpaper; dark red paint, on top of blue background, from lower wallpaper). Had a protein-based binder (such as glue) been present in paint, or protein- based contaminant from paper substrate, these would likely have been detected, given the sizes of the samples analyzed.

For GC/MS analyses, sufficiently large isolated portions of the paint could not taken for analysis.

Thus all of the analyzed samples consisted of paper with some paint attached. Paper was usually the predominant part of each sample.

The solid samples being prepared for carbohydrate analysis were observed under a stereobinocular during the course of sample preparation. Previous experience in the lab indicates that solid samples of watercolor paints (whose binding medium is plant gum) generally break down into particles of pigments during heating in methanolic hydrochloric acid, and the polysaccharides are completely converted into their constituent monosaccharides (which would be in solution at this stage). Cellulosic materials (such as paper) partially break down but do not completely disintegrate. Wood (and paper products made from wood) contain significant amounts of hemicelluloses, which also usually only

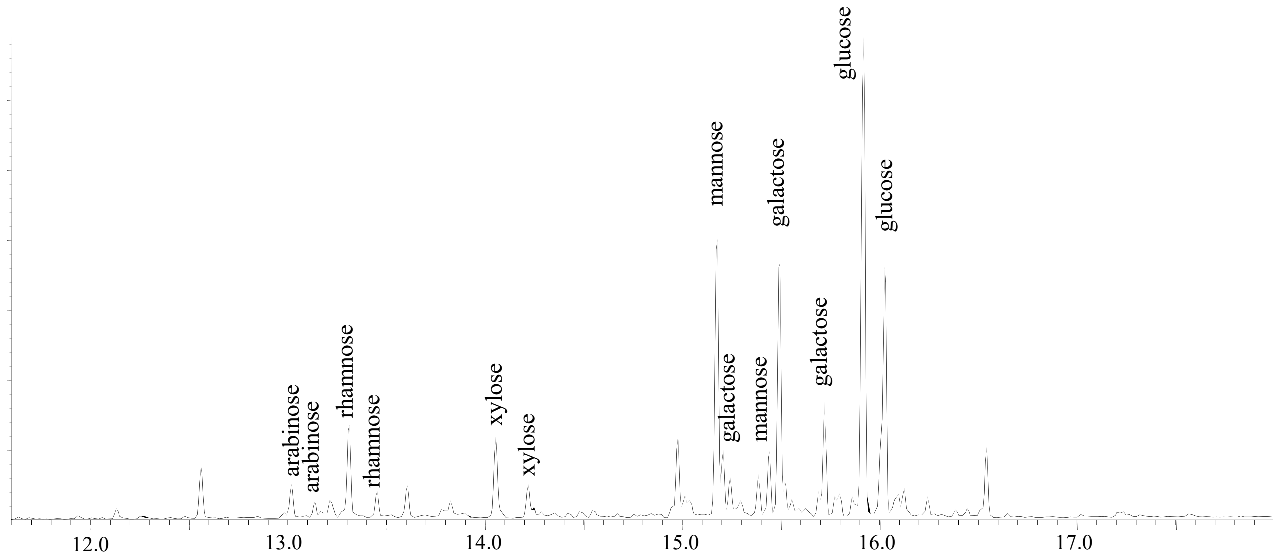


Fig. 3. Detail of reconstructed total ion chromatogram (TIC) from GC/MS analysis of methyl glycoside TMS derivatives of sugars from wallpaper sample 3, blue paint on paper (upper layer of wallpaper). X-axis: retention time (minutes). Major peaks for six monosaccharides are labeled. Unlabeled peaks are either minor peaks for these monosaccharides, or are unidentified compounds.

partially break down. After treatment with methanolic hydrochloric acid, the wallpaper samples had not noticeably changed in appearance—paper fibers seemed still to be intact and all paint was still adhered to the fibers. This suggested that the binder of the paint might not be a plant gum, although it is possible that aging may have made an originally water-soluble paint less soluble. A paper sample that contained no visible paint was also analyzed as a 'blank' to indicate the monosaccharide composition of the substrate. Significant differences between this 'blank' and the paper + paint samples could then be reasonably attributed to the paint binder.

In an attempt to better separate the water-soluble binder from presumably less soluble carbohydrates from the paper substrate, additional pieces of paper with attached paint were heated to 80C in water for two hours. The water was drawn off, the solution evaporated to dryness, then prepared for carbohydrate analysis. The solid sample, after water extraction, was dried and then also prepared for carbohydrate analysis. Even after extensive heating in water, the paint remained on the paper and did not seem to have undergone any readily visible solution. Some water-soluble material was extracted from the solid samples, however.

The analyses of several samples detected substantial carbohydrates in all. The same simple sugars were detected in all samples, with only relative amounts varying (one chromatogram is shown in fig. 3). The bar graphs in fig. 4 give indications of relative amounts of the several monosaccharides detected in each sample.[1] The results, unfortunately, do not prove that the paint binder contained a carbohydrate. Many of the sugars detected probably derive from cellulose and hemicelluloses in the paper substrate. One caveat is that glucose, which of course is present in the paper components, may also be associated with a sugar or starch, which could be components of a carbohydrate binding medium. But the relative level of glucose is generally higher in the samples that contain relatively more paper than those containing relatively less (in comparison with paint).

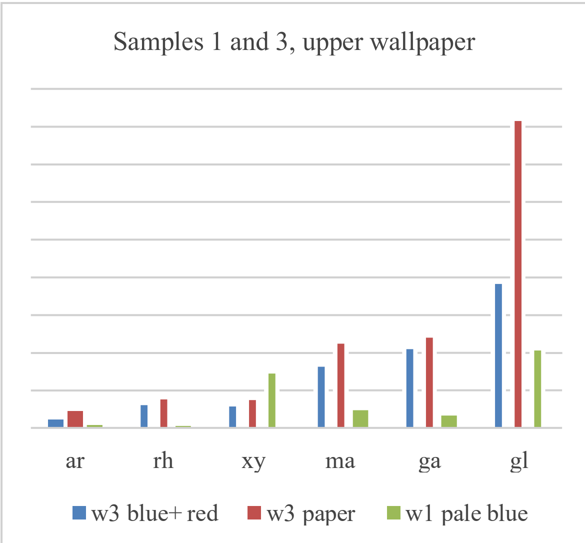
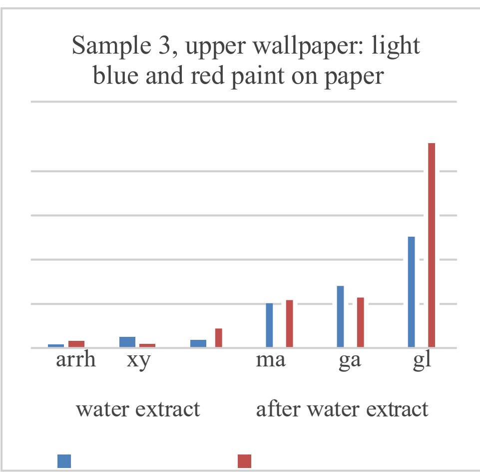


Fig. 4. Comparison of peak areas from six monosaccharides in samples 1 (upper wallpaper: light blue paint with paper substrate) and sample 3 (upper wallpaper: light blue paint and dark red overlying decoration, with paper substrate). Also shown are results from a portion of sample 3 that contained no visible blue or red paint.

Note that the paint-free part of sample 3 (red bars) contains more glucose than the paint-containing portion of the same sample (blue bars) relative to the other five sugars. The elevated level could be due to cellulose. The relative levels of the other five sugars are similar in both portions of sample 3. In sample 1, consisting of the very thin light blue paint on paper, xylose and glucose were the major monosaccharides detected. These two sugars are most likely to be associated with hemicellulose and possibly cellulose rather than a plant gum.



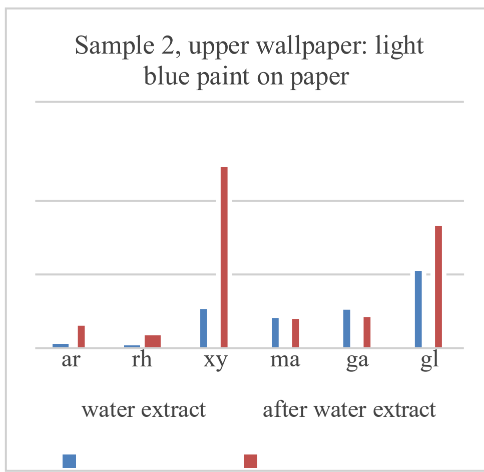


Fig. 5. Comparisons of peak areas from six monosaccharides in water extracts and residual solid Portions from sample 2 (upper wallpaper: light blue with paper substrate) and sample 3 (upper wallpaper: light blue paint and dark red overlying decoration with paper substrate). Xylose and glucose are notably present at higher relative levels in the sample 2 residual solid than in the water extract of the same sample. In contrast, only glucose is present at a higher relative level in the sample 3 residual solid than in the water extract of that sample.

Gum arabic contains substantial amounts of arabinose, rhamnose and galactose. These three can also be present in hemicelluloses, so their detection in the wallpaper samples is not indicative of the presence of that plant gum. Monosaccharide profiles of other common plant gums cannot be discerned in the samples either.

The solid samples (portions of samples 2 and 3) prepared for GC/MS analysis of oils, fats, resins and waxes were also observed after sample preparation. In no case did the paint appear to have dissolved. Heating in this reagent usually significantly dissolves natural resins and waxes. Oil-containing paints will at least partially disintegrate as the triglycerides are broken down. The analyses of two samples showed that small amounts of oil or fat were present. Palmitic, oleic and stearic acids, and smaller amounts of some other saturated fatty acids, were detected. Virtually no azelaic acid was found, indicating that the possible oil was not “drying” in nature. In addition, some compounds characteristic of conifer (most likely pine) resin were also detected. Since the paint did not appear to have been significantly separated from the paper (either going into solution or undergoing hydrolysis) during sample preparation, it seems unlikely that the paint binder was oil, or oil + resin. The “oil” detected could be contamination not associated with the original paint, as could also be the case with the resin.

Conclusions

The detailed analyses for different major classes of paint binding media could not conclusively prove the identity of the binder. It is not obvious why the binder of the paints did not seem to dissolve, or chemically react, with either of the reagents used to prepare samples for GC/MS analysis. The best estimate is that the original binder was a carbohydrate, as the FTIR spectra had suggested.

June 12, 2019

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Note

1. The carbohydrate analysis procedure gives two to four (or even more) peaks for each monosaccharide. For the bar graphs, the areas of the two or three most prominent peaks for each monosaccharide were added together.