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Initial Characterization of Wall Map Varnishes Using UVA, Solubility Tests, and ATR FTIR

INTRODUCTION

Reducing the varnish layer is sometimes part of a treatment for varnished wall maps, particularly when the varnish has discolored to the point that it obscures information. This article discusses an investigation into varnish layers carried out following the AIC Varnished Wall Maps Symposium with the intention to better understand the varnishes used on maps in order to inform treatment decisions and provide historical context.

A major part of the symposium discussion focused on techniques and solvents for removing the varnish layer, although the actual compositions of the varnishes remained unclear. The most common solvent mentioned was ethanol for dissolving the varnish, but ethanol was not successful in every case. An online survey of conservators who treat varnished paper objects indicated that about half of respondents found that ethanol was the most effective solvent, whereas the other half found that a different solvent or solvent mixture was required to remove the varnish layer.

This initial investigation of varnish layers on varnished wall maps attempts to identify historically used resins with nondestructive or minimally invasive methods commonly available to conservators: Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) and longwave ultraviolet-induced visible fluorescence photography. The goal is to provide a path for more targeted approaches to varnish reduction.

BACKGROUND

Varnished Maps

The New York Public Library (NYPL) collections include more than 400,000 single-sheet maps. NYPL does not note whether a map is varnished during cataloging, so the number of varnished maps and exact dates can only be guessed without a thorough survey. At least 5% (or 20,000) of those maps are varnished. Anecdotally, most of the varnished maps date to the 19th century, so we have chosen to focus on that time period for this research.

The primary reason for varnishing a map was to provide a protective coating, ease of cleaning compared with unprotected paper, and a more refined appearance. The varnishing (or "finishing," which might also involve hand coloring, linen backing, and attaching wooden rods) may have been done before purchase by the customer, or the customer could bring it to a map finisher after purchase (Brückner 2017). It is likely that map finishers and customers knew that the varnish could deteriorate and yellow but probably assumed that this would happen long after the map's useful lifetime.

We found historical varnish recipes in artist, technical, and household manuals that could have been used in the 19th century. Varnishes are resins dissolved in a solvent to make a film, which is applied to a surface in a thin layer. The solvent volatilizes over several hours or days, leaving a solid layer. There can be other ingredients added, such as a drying oil, dimethyl ether, benzene, borax, or zinc chloride. A mixture of more than one resin can also be used (Lillard 1884; Dick 1900; Fenner 1904, 1510). When a drying oil is added to the varnish recipe, it is known as an "oil-resin type varnish" (Feller 1985; Mills and White 1987). There are many factors that could affect the properties and analytical results for a varnish, such as cooking time, impurities, or additives. There were imitation varnishes made during the 19th century, called "factitious" varnishes (Dick 1900), although it is unclear if these would have been used by reputable mapmakers.

Resins are water-insoluble sticky exudates of trees and plants (or insects, in the case of shellac) produced as a by-product of metabolic systems in the plant. "Resin" is a nonscientific term referring to materials that become amorphous when mixed with a solvent and form a film when the solvent evaporates. Because natural resins are obtained from nature, their exact composition can be variable, but they are largely composed of compounds belonging to the chemical class known as terpenoids (Mills and White 1987).

Proceedings from the AIC-sponsored event, "Varnished Wall Maps: A Collaborative Seminar to Investigate Treatment Methodology," September 14–16, 2022.

Common resins used were copal varieties, dammar, mastic, sandarac, shellac, Canada balsam, and Venetian turpentine. Many older varnish recipes call for distilled turpentine, spirit alcohol (from wine: 80%–90% pure ethanol), mineral spirits, "rectified spirits" (generally about 97% ethanol), or "oil of turpentine" (a.k.a. camphene) as the solvent to dissolve the resin. Turpentine is a liquid derived from distilling the resin from trees, usually pine trees. Mineral spirits are derived from crude oil. Both are a variable mixture of compounds with a boiling point range (rather than a specific boiling point) and vary in composition. In this study, we used pure ethanol to dissolve the resins in order to limit variables.

It is likely that a sizing layer was commonly applied to the paper before varnishing to protect the paper, limit penetration, and prevent the paper from becoming transparent. Materials used for sizing in the 19th century include gum arabic, gelatin, albumen, egg white, isinglass, alum, and parchment size. In this study, we used gum arabic because it was readily available and simple to make.

History of Varnished Map Treatment

Removing the varnish from a paper object is a drastic treatment but is sometimes necessary because varnished paper, especially when also mounted to fabric, can crack and flake, causing losses of the paper and the media. The varnish may also become darkened to the point that the map is unreadable. These effects are variable, likely depending on the past conditions the map has endured. Even when these conditions are present, there can be good arguments for choosing not to remove the varnish layer, such as the presence of annotations added to the varnish layer by a user or concern about loss of its material history.

Alternative treatments for varnish removal include "reforming" the varnish to smooth out craquelure (Feller, Stolow, and Jones 1985; Treacy 2006), pasting down flaking segments, or backing with a stiff material to prevent flexing.

From 2016 to 2018, NYPL conservator Denise Stockman treated six multisheet varnished maps. She developed a technique for treating and lining the maps on a suction table to keep the fractured pieces intact. This method was presented at the AIC Annual Meeting Tips Session and published in the *Book and Paper Group Annual* (Stockman 2018). In all six maps, ethanol was effective in dissolving the varnish layer.

In January 2024, we conducted a survey of conservators who treat varnished paper objects. Of 29 respondents, 16 found that, in their experience, ethanol was the most effective solvent; 11 found that a different solvent or solvent mixture was required to remove the varnish layer in some cases; and 2 did not use solvents for the treatment of varnished paper. A better understanding of historic varnishes could help clarify whether it is the resin used to varnish the map, aging characteristics of the resin, or additives such as a drying oil that affect whether ethanol can be used to effectively remove the varnish.

SAMPLES

Known Samples

Seven resins were applied to discs of Fisherbrand Filter Paper (grade P2) to use as references in comparison with historic (unknown) samples. The resins used were selected from historic recipes compiled in unpublished research by Jim Flatness, which was included as a resource for the AIC Varnished Maps Workshop. Solid resins were mixed with ethanol, as recommended by the AIC Wiki (Samet 1997). Premixed, bottled varnishes were applied unaltered, with the exception of Venetian turpentine, which was heated and thinned with Stoddard solvent. The preparation of each varnish is summarized in table 1.

Some resins mentioned in historic recipes, such as Canada balsam and copaiba balsam, could not be obtained for this study. Canada balsam is still produced but could not be found in the New York City area at the time of the study. Copaiba balsam was excluded, as it could not be found in retail except as an essential oil.

Gum arabic was prepared in a 1:4 w/w mixture with deionized water at 140°C, brushed onto half of the filter paper discs, and allowed to dry fully. Each of the seven varnishes was applied by brush to both sized and unsized discs of filter paper. A sample of filter paper sized with gum arabic

Kremer varnish name	Abbreviation	Product #	Solvent used/Notes
Venice turpentine	VT	62010	Stoddard solvent (20-mL varnish mixture in 8.5 mL of solvent); the product comes as a viscous liquid
Sandarac	SA	602	Ethanol (3.19-g resin in 21.4 mL of solvent)
Mastic varnish for Claude Yves gel	MA	79351	Turpentine oil (premixed in the bottle with about 40% solids)
Shellac	SH	60453	Ethanol (donated to the laboratory premixed)
Dammar varnish, glossy	DA	79301	Turpentine oil (premixed in the bottle with about 50% solids)
Manila copal	MC	6015	Ethanol (3.46-g resin in 30 mL of solvent)
Congo copal	CC	6016	Ethanol (2.79-g resin in 20 mL of solvent)

Table 1. Summary of Reference Samples and Preparation Method

only (no varnish) and a sample of plain (no size, no varnish) Fisher paper were retained.

This resulted in 16 samples, which were cut in half. One half of each was placed in a south-facing window for 45 days to encourage light aging. The other halves were stored in the dark in anticipation of differing analytical results between light-aged and dark-aged samples.

A smaller set of oil-resin varnishes (four total: mastic, Congo copal, shellac, and dammar) was prepared later in the study when preliminary FTIR data indicated that some of the unknown samples may contain drying oils. To prepare this set, the filter paper discs were sized with gum arabic, and the varnishes were applied by brush as mentioned previously. There were no unsized samples prepared for this set because drying oils are known to saturate and transparentize paper, so it is unlikely that an oil-resin varnish would have been historically applied without sizing.

For each mixture, the premixed varnish product or varnish (as prepared previously) was mixed in a 2:1 v/v ratio with linseed oil. The Congo copal and sandarac mixtures were immiscible at room temperature and were heated slightly before application to the sized paper. After air-drying in a fume hood, the samples were placed in the window for 37 days.

Unknown Samples

On the hypothesis that the varnish recipe used by a mapmaking firm would have been consistent within a given year, we decided to note the mapmaking firm and the date rather than other details such as what the map depicts, who designed it, the reproduction method, the paper type, or any other variables. It is our hope to broaden this sample set in the future.

Varnished maps stored in Mylar sleeves were examined for loose pieces inside the package. If the original location of the loose piece could not be determined (and could therefore never be set back into place), the piece was collected for testing. In this manner, we were able to obtain the following 10 small samples:

- J. H. French (Philadelphia) 1860. eBay purchase
- John E. Gillette (Philadelphia) 1854. NYPL MapDiv 16-5990 (note 1)
- J. W. Canfield 1860. NYPL MapDiv 17-5072
- A. Pomeroy (Philadelphia) 1867. NYPL MapDiv 17-5146
- Sidney & Neff (also S.B.Brown) 1851. NYPL MapDiv 16-6-40
- J. H. French & E.A. Balch (Philadelphia) 1858. MapDiv 16-5988
- A. Blondeau 1814, NYPL not cataloged
- H. F. Walling (D.R. Smith & Co.) 1857, NYPL not cataloged
- F. W. Beers (Mecklenburg, N.C.) 1877, NYPL not cataloged
- Carhart, Mead & Co. 1860. NYPL MapDiv 17-5071

TESTING

UVA-induced Visible Fluorescence Examination and Photography

For UVA-induced visible fluorescence photos, samples were illuminated with an Ultra-Violet Products 3UV-38 3UV Lamp set to 365 nm. Images were captured with a Nikon D750, using an AF Nikkor 50mm f/1.4D lens filtered with a Kodak Wratten 2E pale yellow filter and PECA 918 visible pass filter. Images were processed in Capture One using the UV Innovations Ultraviolet Photo Standard Target for white balance and exposure adjustment. All images were adjusted using the lightest gray swatch on the "low" fluorescence target so RGB values equaled 200/200/200.

FTIR Instrumentation

A Bruker Optics ALPHA I compact FTIR benchtop/portable spectrometer equipped with an ATR diamond probe was used. Each spectrum was accumulated from 32 scans with a resolution of 4 cm^{-1} in a range of 400 to 4000 cm^{-1}. The spectrometer was fitted with a permanently aligned interferometer based on a Bruker Optics patented RockSolid design and a DLATGS detector operating at room temperature. All spectra were collected with the varnish layer directly in contact with an ATR diamond probe.

Solubility Testing

Blotting the varnish with solvent-saturated Evolon was selected as a cleaning method for consistency of application. Samples of Evolon (1-cm squares) were placed in sealed jars for one hour with four times the Evolon's weight in solvent, assuming a 100% "solvent load" (Tauber et al. 2018). The solvent selection was based on availability and having been mentioned by survey respondents: Stoddard solvent, xylene, acetone, isopropanol, and ethanol.

Saturated Evolon squares for each solvent were applied to the sized, light-aged varnish samples for 60 seconds while covered with Mylar and rolled lightly with a swab. The efficacy of cleaning was evaluated visually under normal and UVA lighting conditions.

RESULTS

UVA Examination and Photography

The prepared known samples generally showed a blue-green fluorescence (fig. 1). The exceptions were the unsized shellac and Venetian turpentine samples, which fluoresce orange and yellow under UVA, respectively. The sized shellac and Venetian turpentine samples are much bluer in color and more difficult to distinguish from the other varnishes. The fluorescence of the light-aged shellac samples was less intense than that of the dark-aged samples.

The four oil-resin samples are overall less intensely fluorescent than the other prepared samples. These samples are

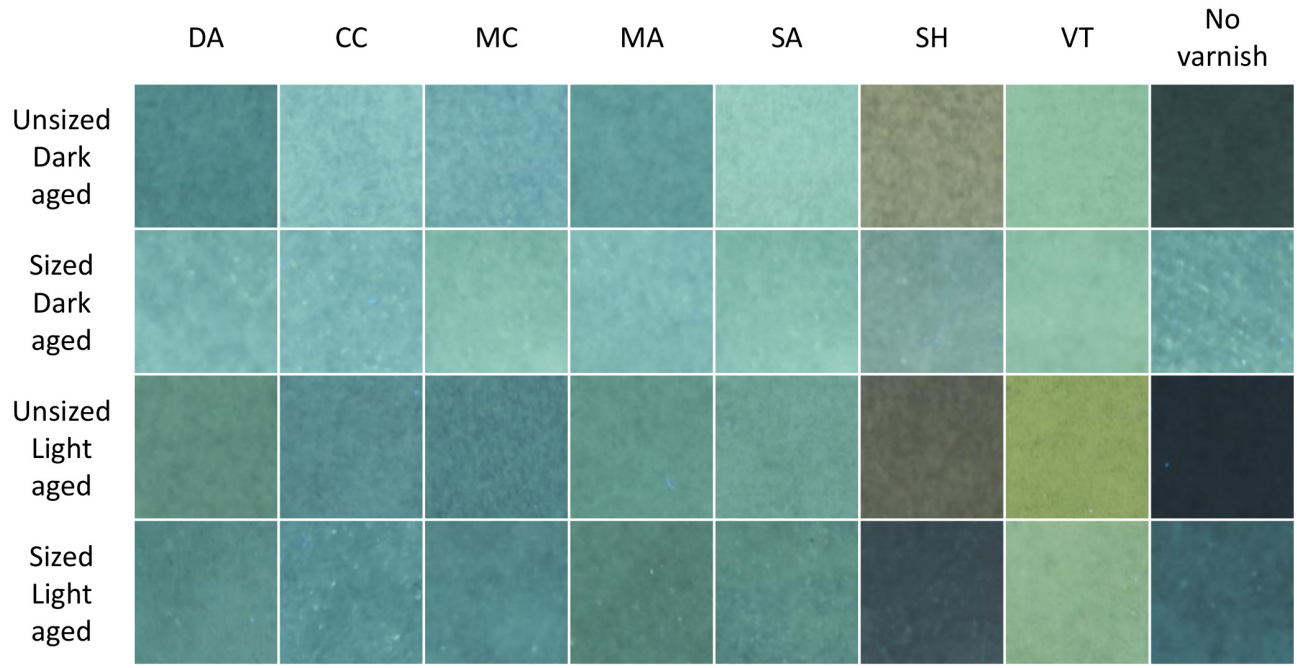

Fig. 1. Details of UV-visible fluorescent photographs captured of known samples. Most of the varnishes show a similar blue-to-green color under UVA with the exception of shellac and Venetian turpentine.

slightly translucent, assuming an error in preparation that would not have been made by professional mapmakers but a factor that affects their appearance in UVA illumination.

The historical samples are very small, making visual comparison difficult. They generally had a yellow fluorescence of medium intensity under UVA, although the Blondeau and Neff samples were darker and more orange (fig. 2). The paper, sizing, and past storage conditions are additional unknowns which may contribute to the perceived fluorescence of the samples. The unvarnished areas of the historic

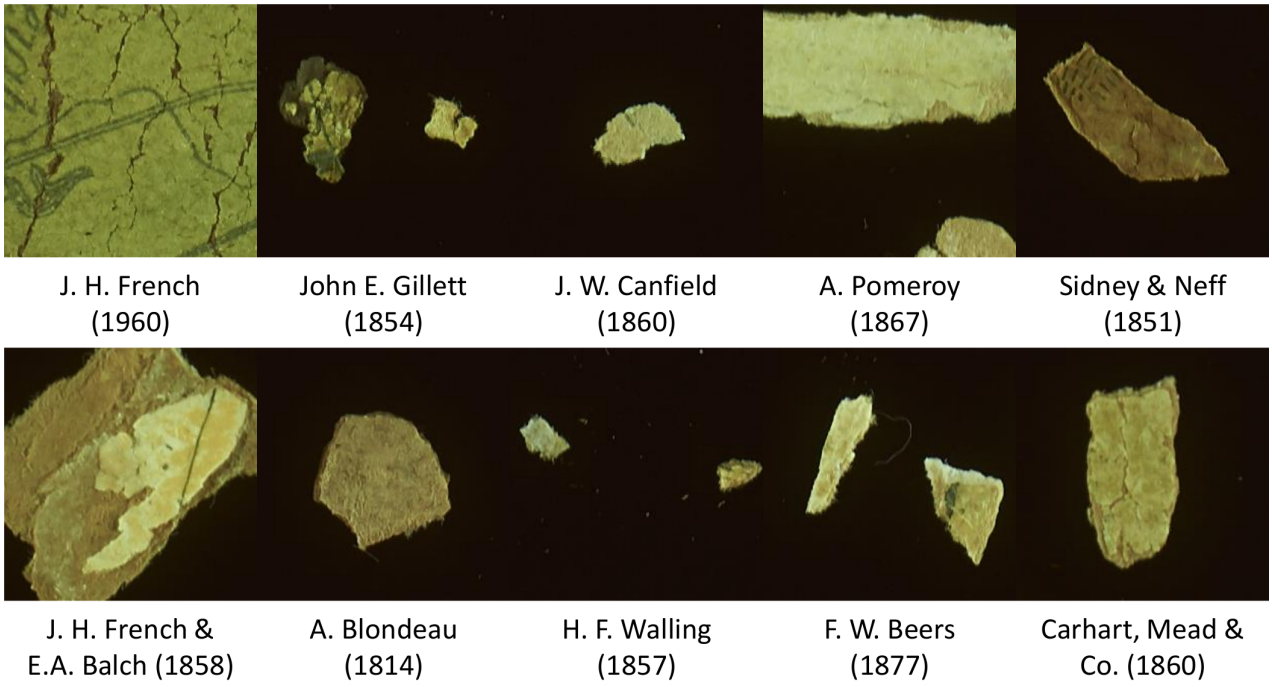

Fig. 2. UVA-visible fluorescence photographs of unknown samples. The historical varnishes generally fluoresce a very yellow color compared to the new, known samples but are also too small to meaningfully evaluate visually.

samples range from nearly nonfluorescent and dark to light orange in fluorescence under UVA.

ATR-FTIR

The FTIR spectra of the known standard samples prepared on paper both sized and unsized displayed very similar spectra, which was thus in distinguishable from each other under our experimental conditions. These samples were intended to be used as standards for comparison with the historical sample spectra; however, due to time constraints, we focused on comparison of the unknown historical samples with spectra obtained from previous studies and from the IRUG database (De la Rie 1989; Russo and Avino 2012; Azémard, Vieillescazes, and Ménager 2014; Price, Pretzel, and Lomax 2014; Cortea, Christache, and Sandu 2016; Martín-Ramos et al. 2018).

We surmise that the following peaks are most notable for natural resins:

- A broad band can be found in the 3500 cm^{-1} region due to the stretching of O-H groups.
- Methylic (-CH_3) and methylenic (-CH_2) give sharp, strong peaks in the ranges of 2960–2930 cm^{-1}, 2875–2865 cm^{-1}, and around 2844 cm^{-1} (C-H stretching).
- Bands between 1467–1448 cm^{-1} and 1387–1382 cm^{-1} are present due to the C-H bending.
- Bands at 1644 cm^{-1}, 1315 cm^{-1}, 3050–2990 cm^{-1}, and 1230–1270 cm^{-1} can indicate C=C stretching.
- Signals in the fingerprint region (below 1000 cm^{-1}) can be a good source of information for distinguishing among the resins. However, it will depend on the signal-to-noise ratio and FTIR conditions and setup.
- A weaker signal may be found at 1240 cm^{-1} due to C-O groups.
- A strong signal was noted between 1715 and 1690 cm^{-1} due to the absorption of C=O groups.
- Aged drying oils have characteristic bands at 3400, 2930, 2855, 1780, 1735, 1713, 1459, and 1418 cm^{-1} (strong); 1245 and 1178 cm^{-1} (medium); and 1097, 980, and 725 cm^{-1} (weak).

Some differences can exist between the spectra for aged and nonaged varnish films, although these differences can be better picked up with other methods, such as Raman spectroscopy (Dietemann et al. 2009; Nevin et al. 2009).

All unknown (historical) samples displayed typical terpenoid signatures for resins—methylene bands circa 1450 cm^{-1} and a doublet between 2900 and 2800 cm^{-1}, along with carbonyl bands between 1710 and 1650 cm^{-1}—but do not distinguish the particular resin or resin mixture present. In addition, J. H. French (1860), Gillette, and F. W. Beers show broader carbonyl peaks spanning from 1770 to 1700 cm^{-1} (Gillette and F. W. Beers) and from 1750 to 1690 (for J. H. French), suggesting that drying oils were mixed with the resins to make the varnishes in these maps. The low signal-to-noise ratio of some spectra is attributed to the smaller size of these map samples, which did not cover the measurement area completely. However, even in these cases, it is possible to discern the key bands for their assignment as natural resins (figs. 3, 4).

Solubility Testing

Ethanol and isopropanol were the most effective cleaning solvents for all varnishes except dammar. In some applications of ethanol and isopropanol, 100% solvent load was more than necessary and some solvent ran from the application area (fig. 5). In all effective cleaning tests, the varnish was visibly absorbed by the Evolon within seconds of application, and 60 seconds may have been a longer application than necessary for reducing the varnish.

In some applications of acetone, the solvent evaporated from the Evolon before the application was complete and the blotter stuck to the surface, so the evaluation of acetone for cleaning these resins is incomplete. The sample papers swelled locally where xylene was applied. The dammar sample blanched immediately in the cleaning area when ethanol and isopropanol were used. Xylene was not an effective solvent for most of the samples but did remove some varnish from the dammar sample without blanching.

DISCUSSION

This study was limited in scope. We were not able to obtain all of the resins that were mentioned in historical recipes, most notably Canada balsam. This study does not account for how the structure of the varnished map (media, paper composition, application method) may affect treatment. We only used gum arabic sizing, although others were mentioned in historical literature, such as gelatin, albumen, isinglass, and parchment size, all of which may affect the FTIR spectra, fluorescence, and solubility of the varnishes differently. We did not use any of the historical varnish solvents, such as turpentine, instead using pure ethanol.

The FTIR spectra for the historical (unknown) samples gave signatures for terpenoid resins, and three of them also suggested the presence of drying oils. We had a limited number of historical samples, some of which were quite small and gave low absorbance signals and a low signal-to-noise ratio, most likely because the diamond cell was not completely covered by the sample. The standard known samples we prepared were run at a later time, showed a low signal-to-noise ratio, and were not suitable for comparison. Due to time constraints, we were not able to repeat these measurements and instead used information from the literature that allowed us to distinguish the presence of terpenoids and terpenoid/drying oil mixtures in the historical samples. However, we expect to remeasure these samples at a later

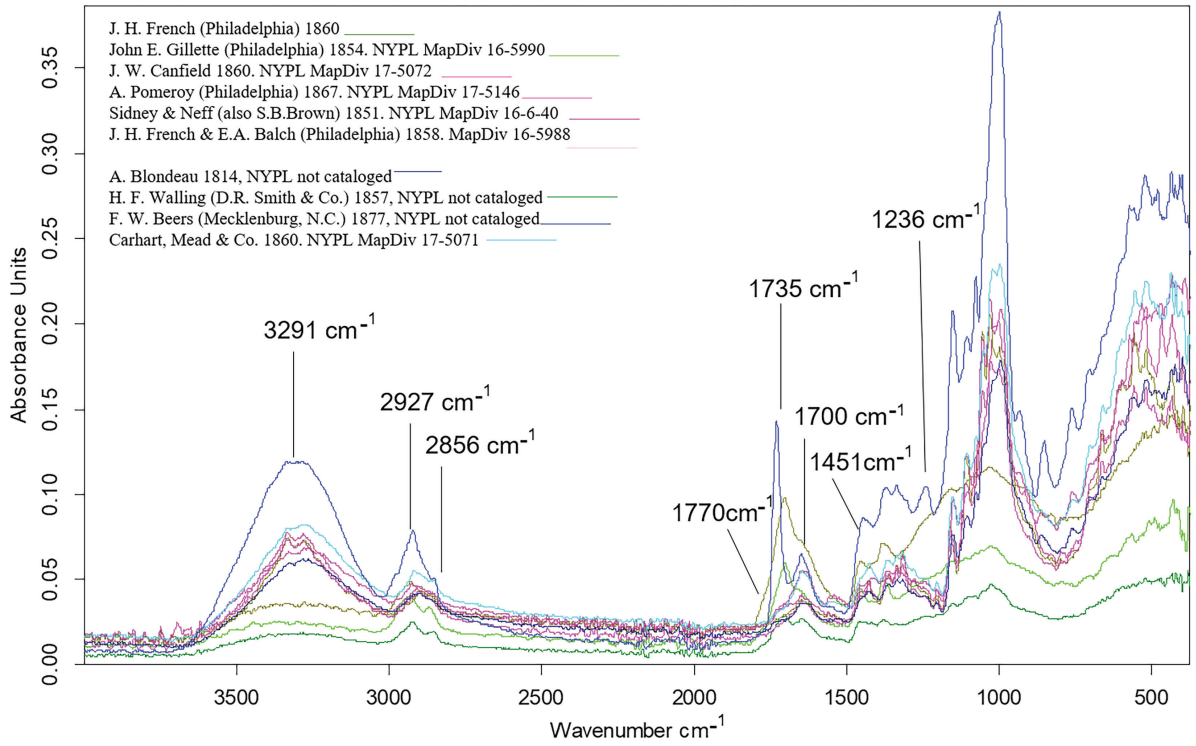

Fig. 3. Overlay of FTIR spectra collected from historical samples.

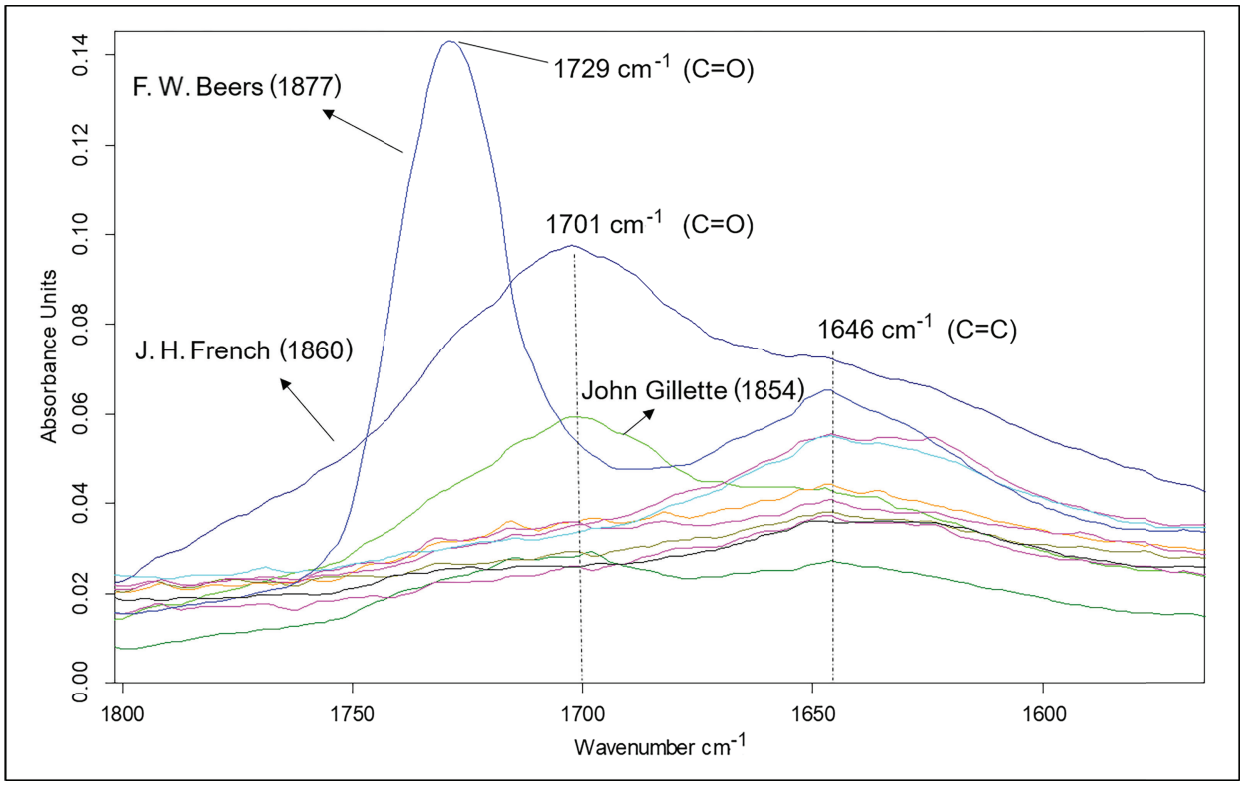

Fig. 4. Major peaks between 1800 and 1500 cm^{-1}.

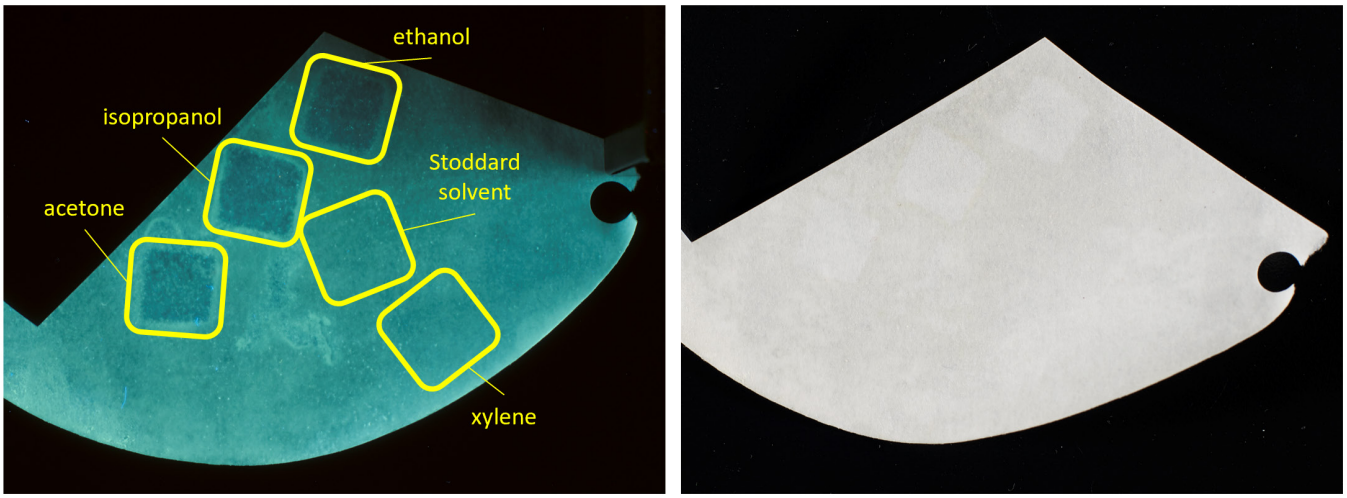

Fig. 5. Manila copal sample after cleaning tests under UVA illumination (left) and normal light (right). The isopropanol ran from the application area, resulting in some solubilized varnish accumulating in the center of the sample.

time to determine whether it is possible to distinguish among the resins using prepared samples with this instrument.

This preliminary study leaves room for future work with several possible directions for identifying resins on varnished wall maps. This could include repeating the FTIR analysis of our known samples, recreating the known samples with quantified aging, and comparing FTIR data of cleaned and uncleaned areas of the samples. External reflectance FTIR could also be useful for analyzing larger samples of maps in situ. Other analytical methods may prove advantageous over FTIR, including Raman spectroscopy, gas chromatography-mass spectroscopy, and NMR-MOUSE stratigraphy. Cross-section microscopy of historic samples could provide new insights into the structures of varnished maps. Once a testing method is optimized, testing may be expanded to a larger sample set of historical maps. In treatment cases, solvent testing can also be systematically performed on historical maps.

CONCLUSIONS

Cleaning tests confirm that ethanol was an effective solvent for all of the samples except when a drying oil is added to the varnish recipe. Ethanol did, however, cause some blanching of the dammar sample. Xylene was generally not an effective solvent and caused paper swelling.

UVA examination produces ambiguous results for varnishes on paper, but a trained eye might be able to distinguish shellac, especially if it has been dark aged.

The FTIR spectra for the historical samples found that they were made of varnishes containing terpene resins with and without a drying oil. Our data was unable to distinguish which specific resins were used.

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NOTE

1. NYPL has maps by mapmaker John E. Gillette with his name spelled "Gillet," "Gillett," and "Gillette." The name on this particular map is spelled John E. Gillett."

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SOURCES OF MATERIALS

2-propanol (purified grade), Filter paper (qualitative P2, 15-cm diameter; catalog number 09-803-5F), Stoddard solvent (Acros Organics)
Thermo Fisher Scientific Inc.
https:/www.thermofisher.com

Congo copal (crystalline form; product #6016); Dammar varnish, glossy (product #79301; 1:2 dissolved in double-rectified turpentine, not UV stabilized); Manila copal (product #60150); Mastic varnish for Claude Yvel gel (product #79351); Sandarac (product #602–historic number); Shellac polish transparent (pre-prepared; product #60453); Venetian turpentine (product #62010)
Kremer Pigments Inc.
https://kremerpigments.com

Ethanol (200-proof, anhydrous USP; CAS 64-17-5)
Decon Labs Inc.
https://deconlabs.com

Evolon CR (product #TNW002002), Gum arabic
TALAS
https://www.talasonline.com

Gamblin refined linseed oil (product #00456-1604)
Blick Art Materials
https://www.dickblick.com

Kodak #2E pale yellow optical Wratten 2 filter
B&H Photo
https://www.bhphotovideo.com

PECA 918 IR cut camera filter
Image Science Associates
https://imagescienceassociates.com

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