

Characterization of Varnishes on Nineteenth-Century Canadian Furniture

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A project was undertaken at the Canadian Conservation Institute to identify the original varnishes on a selection of wooden furniture made in Canada in order to test assumptions about which varnishes were commonly applied to such objects and to gain a better understanding of the varnishing practices of Canadian cabinetmakers. The project focused on pieces fabricated in Ontario and New Brunswick, primarily during the nineteenth century. Varnish samples taken from twenty-one pieces of furniture were analyzed in order to determine their compositions. Objects were chosen based on evidence of the presence of an original varnish and for their strong provenance. Analysis of the varnishes was undertaken by Fourier transform infrared spectroscopy and pyrolysis–gas chromatography–mass spectrometry. Analytical results suggest that the use of fixed oil varnishes incorporating Pinaceae resin and often imported copal resins was more common than the use of shellac, and that it persisted in Canada to at least the end of the nineteenth century.

Une étude a été menée par l'Institut canadien de conservation, consistant à identifier les vernis originaux d'une sélection de meubles en bois fabriqués au Canada, dans le but de vérifier les hypothèses émises concernant la nature des vernis les plus couramment appliqués sur ce type de meuble et pour mieux comprendre les techniques de vernissage utilisées par les ébénistes canadiens. L'étude s'est particulièrement intéressée à des objets fabriqués en Ontario et au Nouveau-Brunswick, essentiellement au XIX^e siècle. L'analyse d'échantillons de vernis prélevés sur 21 meubles a permis de déterminer leur composition. Seuls des objets dont la provenance est fiable et dont le vernis avait été déterminé comme étant d'origine ont été sélectionnés. L'analyse des vernis a été effectuée par spectroscopie infrarouge à transformée de Fourier et par pyrolyse–chromatographie en phase gazeuse–spectrométrie de masse. Les résultats analytiques montrent que les vernis à l'huile siccative mélangés à de la résine de Pinaceae et, souvent, à des résines de copal importées étaient plus souvent utilisés que la gomme-laque au Canada, et ce au moins jusqu'à la fin du XIX^e siècle.

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Introduction

Conservators have long been interested in the characterization of original varnishes on furniture in Canadian collections. In the past, many furniture conservators and restorers assumed that shellac varnish was the predominant finish used during the eighteenth and nineteenth centuries in North America; however, the results of analyses undertaken at the Canadian Conservation Institute on individual Canadian pieces have often contradicted this view. Published investigations of archival documentary evidence have also cast considerable doubt on the assumption that shellac varnish was in common use in the United States during the eighteenth century.¹⁻⁴ If shellac was not commonly used in the eighteenth century in North America, the notion of its widespread use on furniture during the nineteenth century, particularly in Canada, is also called into question.

The interpretation of historical varnish recipes used on North American furniture is often difficult due to the indiscriminate use of material names and measurements. Proprietary arcana can also confound the researcher. Nevertheless, valuable information on eighteenth- and nineteenth-century varnish recipes can be found in historical cabinetmakers' and varnishers' manuals and treatises. Mussey undertook an extensive study of such manuals.¹⁻³ His study resulted in the republishing of *The Cabinet-Maker's Guide of 1827*, described as the first manual for furniture finishers published in the United States.⁴ An extensive study of paints and varnishes used in decorative and protective finishes in the

United States from 1750 to 1850 was also undertaken by Penn.⁵ Other archival sources such as account books, trade journals and newspaper advertisements have proven to be a rich source of information on the subject and likely offer a more accurate representation of local wood finishing practices.^{1,6,7} While there has been some information published on the analysis of painted finishes on early Quebec furniture,⁸ there are no known published results of the analysis of varnishes on nineteenth-century Canadian furniture. One assumes that Canadian practices were similar to those in the United States at the time, but it is reasonable to imagine that regional differences existed, based on availability of materials and access to trade routes.

A project was therefore initiated to increase knowledge of the varnish materials used on furniture in Canadian collections and to explore regional differences. The information obtained tests the accuracy of some common assumptions concerning early domestic finishes. More specifically for the objects analyzed, identification of the finish enhances the documentation of the objects and will help to guide treatment decisions. In addition, the project provided the opportunity to refine analytical strategies for furniture varnish analysis.

Historical Furniture Varnishes

A varnish is a transparent or translucent coating composed of one or more resinous materials that forms a discreet, hard film on the surface of the wood to which it is applied. Varnishes are distinct from waxes and drying oils, which generally

penetrate into the top layers of the wooden substrate and do not form a film of appreciable thickness or durability. While wax and oil finishes were used frequently on furniture fabricated before 1700, varnishes became a customary wood coating in the Western world towards the end of the seventeenth century.⁵ Early varnishes were formulated by individual craftsmen and were therefore distinctive and idiosyncratic compositions. Prepared varnishes were being manufactured in factories in Europe by 1790,⁵ and were common in shops in London by the early 1800s.⁹ Commercial varnish preparations were being produced in the United States soon afterwards, with archival records indicating limited production in New England by 1820,¹⁰ and large-scale production in New York City and Philadelphia by 1830.⁶ Customs records indicate that prepared varnish was being imported into Canada from the United States by the late 1830s.¹¹ By about 1850, commercial furniture varnishes were commonplace in North America. Even with the availability of commercial preparations, some nineteenth-century furniture coatings were prepared in the workshop by the furniture maker, particularly by those craftsmen working in rural areas.¹² Shop-made varnishes either would have corresponded to published recipes or would have been prepared according to the preferences of the maker with compositions subject to the availability of materials.

Varnishes for woodwork in use during the eighteenth and early nineteenth centuries fall into three categories: spirit varnishes, essential oil varnishes and fixed oil varnishes.^{3,5} Prior to application, each of these types of varnishes includes a natural resin component dissolved in a solvent. The most common solvents were alcohol (“spirits of wine”) or pine essential oil (known commonly as turpentine and referred to in the past as “oil of turpentine” or “spirits of turpentine”), or a vegetable oil such as linseed oil. Natural resins used for varnishes in the nineteenth century included imported varieties such as sandarac, various fresh and semi-fossilized resins known collectively as copals, and shellac, as well as both imported and domestic *Pinaceae* resins such as pine resin, also known as colophony or rosin, and commonly referred to in historical texts as “turpentine” (not to be confused with the solvent). For the conscientious cabinetmaker, choice of finish was dictated by function and environment, so moisture-sensitive finishes such as spirit varnishes were generally reserved for interior applications and household furniture, while fixed oil varnishes with more durable properties and weather resistance were common on carriages and architectural millwork as well as furniture.^{6,7}

Spirit Varnishes

Spirit varnishes were prepared by dissolving plant or animal resins, such as colophony, sandarac or shellac in alcohol. The vast majority of the varnishes presented in *The Cabinet-Maker's Guide of 1827* are spirit varnishes, and research indicates that those recipes incorporating sandarac as the main resin component were favoured during the eighteenth century.¹³ Shellac was not the main resin used in spirit varnishes in the United States during the eighteenth century, greatly due to the fact that the red dye it contained imparted

unwanted colour that could not be fully extracted until a chemical bleaching method was developed in the late eighteenth century.³ Shellac spirit varnish became common for coating furniture in the early years of the nineteenth century, especially because of its use in the popular finishing technique of French polishing, though recipes formally published in this period usually included a mixture of various resins.^{3,5} The 1827 *Cabinet-Maker's Guide* refers to French polish as “of comparatively modern date,”¹⁴ and an 1837 publication of the *Mechanic's Register* refers to French Polish as “universally employed.”¹⁵ As Penn notes, however, it is difficult to ascertain whether these sources refer to the application technique or to the shellac varnish itself.⁵

Essential Oil Varnishes

Essential oil varnishes were made by dissolving a resin or mixture of resins in turpentine or other essential oils.³ Not to be confused with triglyceride oils and fats such as linseed oil, essential oils are the volatile aromatic compounds found in plants. The main constituents of turpentine (pine essential oil) are the monoterpenes α -pinene and β -pinene.¹⁶ As such, these varnishes are better classified as spirit varnishes, but scholars continue to distinguish these varnishes as a separate classification in order to differentiate them from the better-known alcohol-based spirit varnishes. These varnishes were considered an inferior choice to alcohol-based spirit or fixed-oil varnishes because of their long drying times and inability to be polished,³ although they had more body and elasticity than spirit varnishes.⁵

The “Turpentine Varnish” presented in the *The Cabinet-Maker's Guide of 1827* is an example of this type of varnish.¹⁷ While such simple varnishes are not frequently encountered today because of their susceptibility to degradation, it is quite likely that they were in widespread use in North America during the eighteenth and nineteenth centuries, especially in rural areas.¹ Turpentine and its rosin by-product were major domestic products of the North American naval stores industry which developed in the early seventeenth century in Nova Scotia¹⁸ and continued through the eighteenth and nineteenth centuries.^{19,20} High import taxes, various trade embargos and other trade disruptions during the eighteenth century and early nineteenth century would have made the more desirable exotic resins scarce, as these were mostly of tropical origin.

Fixed Oil Varnishes

Fixed oil varnishes were a prevalent coating choice in the eighteenth and nineteenth centuries owing to their robust properties. Their durability and weather-resistance made fixed oil varnishes the preferred coating choice for architectural millwork, coaches and carriages in the nineteenth century.^{6,7} Fixed oil varnishes were prepared by dissolving one or more oil-soluble resins, such as copal, amber, dammar or sandarac, in a drying oil such as linseed oil, poppy seed oil or walnut oil.^{3,5} Most of these resins required powdering or melting in order to dissolve in the oil. Hard resins, such as copal, required heating to extremely high temperatures, referred to as “running” or “cracking” the resin, in order to encourage

dissolution.²¹ Turpentine was frequently used as a thinner. This type of varnish produced the thickest film and its partially polymerized oil-resin composition was more durable than the other types but was slow to dry unless the oil was first treated with a drier such as litharge.²² Quite often, a variety of different resins were combined in a single fixed oil varnish in order to exploit their individual properties.

Fixed oil varnishes using *Pinaceae* resins such as colophony as the resin component, sometimes referred to as “common brown varnish,” were frequently used in North America owing to the availability of materials, but they were considered an inferior product that was less durable than oil varnishes made with harder resins and were prone to darkening.¹ A recipe for this type of oil varnish was provided in *The Cabinet-Maker’s Guide of 1827*:

Take any quantity of the best linseed oil, let it boil for an hour, then to every pound of oil add a quarter of a pound of the clearest rosin in powder, stir it well till dissolved; then add for every pound of oil used, one ounce of spirits of turpentine, strain it and bottle for use.²³

This composition was described as an inexpensive varnish for use where “economy is required”²⁴ and would have been common on functional household furniture, but as with the turpentine essential oil varnish, coatings made only from softer *Pinaceae* resins that do not form polymerized films would have been less durable and more susceptible to degradation. In contrast, hard-resin fixed oil varnishes made primarily with copal, either fresh or fossilized, can withstand rigorous use. This is largely due to the durability and strength brought about through the polymerization of the labdane diterpenes as the varnish dries and ages.²¹ Though copal varnishes would likely have been the most common hard-resin fixed oil varnishes used in North America by the eighteenth century, their manufacture was expensive and required laborious and dangerous processes. For this reason, they were probably most often bought as commercial preparations and were rarely used on vernacular North American furniture.³

By far the most notable fixed oil varnish recipe was the copal and amber varnish known as *vernis Martin*, a coating developed in Paris by the Martin brothers during the late eighteenth century to imitate the highly fashionable Oriental lacquers. Though originally intended for use on the decorative coaches and carriages of the elite, the Martin brothers’ varnish was soon employed on furniture as well. As Mussey writes, “With the English publication in 1776 of the *Genuine Receipt for Making the Famous Vernis Martin*, British, and eventually American workers finally possessed the recipe for the most famous Continental varnish.”³ The published *vernis Martin* recipe calls for the combination of Chios turpentine, colophony, copal and amber with turpentine and a drying oil, either poppy seed oil, nut oil or linseed oil, with the addition of driers.²⁵ The *vernis Martin* recipe is a perfect example of the collective pursuit by varnish makers to exploit the favourable properties of several different resins in one varnish. In this case, copal and amber resins were essentially colourless, durable and provided sufficient hardness to be

polished, while the softer *Pinaceae* resins (colophony and Chios turpentine) were incorporated as plasticizers, as well as to impart additional gloss. It has also been suggested that the addition of softer resins may have been empirically found to lower the fusion temperature for the harder resins.⁶ If local *Pinaceae* resins were substituted for exotic varieties, use of a varnish composition based on the *vernis Martin* recipe would have allowed the North American varnish maker to extend his valuable supply of imported copal by combining it with cheap, local resin to create a varnish of acceptable quality. It appears that the use of such fixed oil varnishes was widespread and “the Martin’s ingredients and laborious procedures...became typical of most such hard-resin, fixed-oil varnishes of the 18th century.”³

Analysis of Furniture Varnishes

Selection of Objects

Ten pieces of Ontario furniture in the collection of the Canadian Museum of History were selected for analysis in the first phase of the project. Subsequently, eleven pieces of furniture from three New Brunswick collections (the New Brunswick Museum, the New Brunswick Provincial Collection and the Kings Landing Historical Settlement) were sampled. Objects suspected of retaining all or part of their original finish were chosen. The selection of objects was limited to those made before 1914, since it was thought that the choice of varnish may have been influenced by the introduction of synthetic coatings, such as cellulose nitrate, in the post-war period. It was important to choose well documented pieces, ideally ones for which the location where the furniture was made, the date and the cabinetmaker or workshop were recorded. The furniture items exemplified a variety of styles, from vernacular to formal, and included chairs, chests of drawers, tables, a secretary and a sofa. Most objects sampled date from the nineteenth century; however, two pieces may date from the late eighteenth century. In about half the cases, information on the individual cabinetmaker or production shop was available. Details of the type of furniture, materials, location and supposed year of construction, the cabinetmaker (if known), accession number and a description and photograph of the sample location were recorded.

Selection of Sample Locations

Since the original finishes on nineteenth-century furniture have often been worn, removed, retouched or covered, visual inspection of the pieces by experienced staff was essential to avoid sampling restored or refinished areas. Where possible, an area where only the original finish was present was selected for sampling. Certain parts of the furniture, for example the arms of chairs, were avoided since they are often refinished due to wear. Samples were taken from inconspicuous areas, such as the bottom edge of stretchers and rails, the underside of drawer faces and the top inside edges of legs. Quite often the finish was thick in some of these areas as the varnish had run and collected under the edge during application (**Figure 1**). Such areas can often be left intact even after refinishing as they are less visible and may be easily missed or ignored.

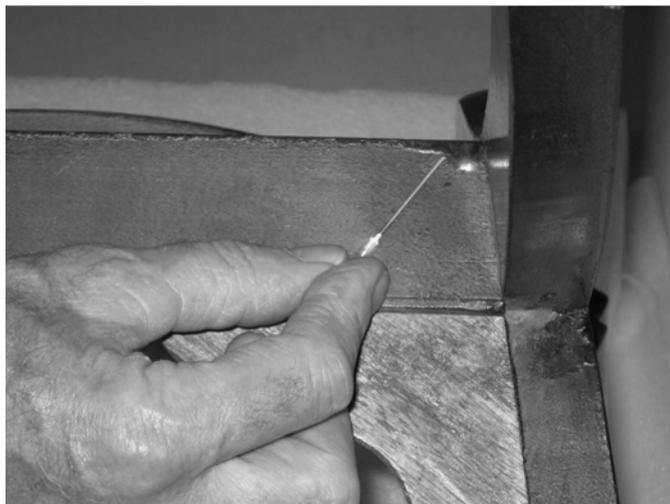


Figure 1. Sampling the underside of the rear seat rail of a chair, an example of a location on a piece of furniture where original finish may remain.

Sampling Technique

It is necessary to take a coating sample that includes the wood substrate to ensure that the original finish is obtained and orientation of the sample is unambiguous. This can be difficult since brittle, resinous coatings tend to fracture, resulting in fragments of unknown orientation. It was therefore decided not to remove the sample using a scalpel as is often done with paint samples. The sampling technique used to obtain the coating cross-sections was based on one developed by staff at Robert Mussey Associates and described by Carr, that uses commercially available hollow needle syringe tips that are then adapted to facilitate the core sampling of coatings and wooden substrates.²⁶ The sample location was photographed and a description recorded.

Analytical Methods

Two samples were taken from adjacent areas on each piece of furniture, one for the preparation of a cross-section to allow examination of the layer structure and one for analysis of the finish. Preliminary analysis was undertaken by Fourier transform infrared spectroscopy (FTIR). Detailed analysis of drying oils and resins was carried out using gas chromatography–mass spectrometry (GC-MS) and pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS), following mechanical separation of the layers, when possible. Pigmented layers in samples were also analyzed by scanning electron microscopy/energy dispersive spectrometry (SEM/EDS). Detailed instrumental methodologies are presented in the **Appendix**.

Results

A description of the pieces of furniture sampled and the analytical results are presented in **Table I**. The results of the analysis presented in this section are grouped by the type of finish identified.

Fixed Oil Varnishes

Linseed Oil and *Pinaceae* Resin

A relatively simple “common brown varnish,” prepared from the heating of a drying oil (linseed oil in most cases) with *Pinaceae* resin, was identified on three pieces of furniture from Ontario and three pieces from New Brunswick. The finish on the three Ontario pieces, including a walnut, slat-back chair (CMH D-11392) made by B. Bird of Hamilton (dated 1835-1865) and shown in **Figure 2**, consists of a single layer of the drying oil and *Pinaceae* resin varnish. The thick, non-uniform layer of finish from a run on the underside of the rear seat rail, which is shown in **Figure 1**, was sampled. The cross-section prepared from the sample is shown in **Figure 2**. Oleoresinous varnishes, such as those based on linseed oil and *Pinaceae* resin, display a green fluorescence under the experimental conditions used. A single coating of this type of finish was also present on an 1896 rod-back chair made by John Gemeinhardt of Bayfield, Ontario (CMH D-9376) and a walnut chest of drawers (CMH D-3012) fabricated in Ontario between 1880 and 1910.

A similar varnish was present as the first finish layer on a mahogany tilt-top table dating from 1790–1803, attributed to Robert Chillias of New Brunswick (NBM 2009.38.71). It was again identified in several layers on a Regency-style, mahogany side chair attributed to Alexander Mitchell of Fredericton, dating from 1827–1865 (KL 2009.29.23a). This finish was also found on a vernacular-style New Brunswick chest of drawers dated between 1830 and 1850 (KL M2004.22.1).

The identification of the drying oil component was determined by calculating the palmitic acid (P) to stearic acid (S) ratio. The P/S ratio remains relatively constant as drying oils age and, in many circumstances, this ratio can be used to determine the type of drying oil that was used. Typically, the P/S ratio for linseed oil is between 1.0 and 2.0, with the majority falling in the range of 1.3–1.8.²⁷ In many of the samples, the linseed oil was determined to have undergone heat treatment when trace peaks of cyclic C18 fatty acids (such as methyl 9-(2-propylphenyl) nonanoate), formed through the cyclization of tri-unsaturated linolenic acid upon heating, were present in the chromatograms.^{28,29} In addition to these trace markers, further evidence of heat treatment of the linseed oil was determined through the calculation of the ratio of the dicarboxylic acids suberic (Su) and azelaic acid (Az). When Su/Az ratios for linseed oil are calculated at 0.4 or higher, the oil is generally considered to have undergone heating.²⁹

The chromatogram of the varnish sample from the Gemeinhardt rod-back chair is shown in **Figure 6a**. The chromatogram is dominated by highly oxidized abietane compounds, including dehydroabietic acid, 7-oxo-dehydroabietic acid and hydroxy-dehydroabietic acids, originating from a *Pinaceae* source. The P/S calculation for this sample is 1.3, and the identification of a trace of methyl 9-(2-propylphenyl) nonanoate confirms that the drying oil is likely linseed oil that has been heated.

Linseed Oil, *Pinaceae* Resin and Copals

Copals are diterpene plant resins with macromolecular structures based on either *regular*-configured communic acid (soft copals) or *enantio*-configured labdane compounds, such as ozic acid, ozol and *enantio*-biformene (hard copals). The molecular structures of these compounds are shown in **Figure 3**.

Copal resins were identified on six furniture pieces from the Ontario collection, of which three were identified as hard copals and three were identified as soft copals. Copal resins were also identified on six furniture pieces from the New Brunswick collections.

Hard copal and *Pinaceae* are present in the fixed oil finish found on a vernacular-style, straight-front chest of drawers (CMH 978.26.1) made by William M. Garrett of Chelsey, Ontario, dated 1867–1900 (**Figure 4**). There are two applications of a hard copal, *Pinaceae* resin and linseed oil varnish finish on the slant-top desk (CMH 979.63.1), also in the vernacular style and possibly attributable to John Gore of Pelham, c.1850–1880 (**Figure 5**). The infrared spectrum of the finish on the slant top desk is shown in **Figure 7a**.

Though likely not an original finish, one interesting example of a hard copal and *Pinaceae* resin finish is that found on a mahogany balloon-back chair (CMH 986.15.6) that dates from 1865–1885 and is some-what tenuously attributed to the workshop of Thomas Campbell of Ottawa. The chair and a cross-section of the sample taken from the inside front face of the proper right, rear leg are shown in **Figure 8**. The fixed oil varnish is the second layer, displaying the green fluorescence, while the earliest layer of finish, displaying orange fluorescence, consists of shellac. While it seems unlikely that the fixed oil varnish exists as part of the original coating system since it appears as the second layer, the thickness and uniformity of both the shellac and copal varnish layers suggests the application of several coats of varnish with intermittent polishing.

Linseed oil, *Pinaceae* resin and soft copal were identified in finishes on three pieces of Ontario furniture for which the cabinetmaker is not documented: a cherry end table dating from 1840–1860 (CMH D-7113), a cherry and maple draw table dating from 1850–1890 (CMH D-7122) and a maple and walnut lamp table dating from 1840–1860 (CMH D-8839), all of the vernacular style.

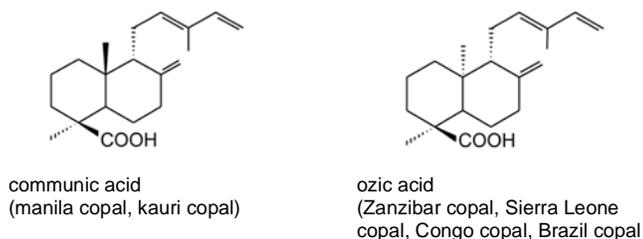


Figure 3. Molecular structures of communic acid and ozic acid monomers comprising soft and hard copals, respectively.

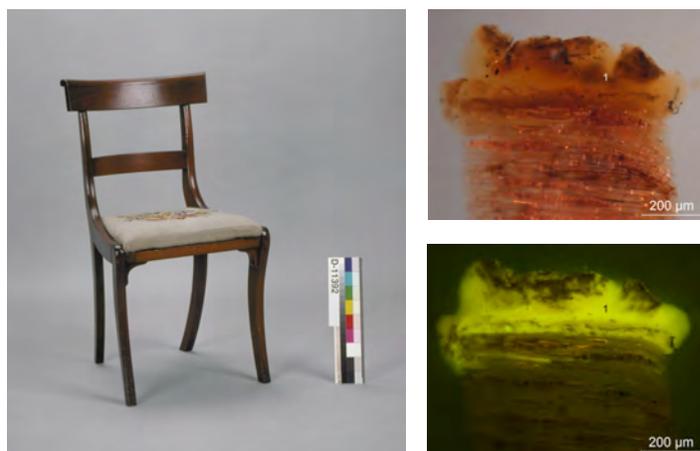


Figure 2. (a) Slat-back chair, CMH D-11392. Canadian Museum of History, Gatineau, Quebec. Images of the cross-section: (b) incident light; (c) autofluorescence.



Figure 4. (a) Straight-front chest of drawers, CMH 978.26.1. Canadian Museum of History, Gatineau, Quebec. Images of the cross-section: (b) incident light; (c) autofluorescence.



Figure 5. (a) Slant-top desk, CMH 979.63.1. Canadian Museum of History, Gatineau, Quebec. Images of the cross-section: (b) incident light; (c) autofluorescence.

Table I: Object Description, Provenance and Analytical Results.

Accession Number, ^a Object Description	Location, Cabinetmaker	Date	Sample Location	Description of Finish on Wood Substrate	Analytical Results
CMH D-3012 Eastlake-style, walnut chest of drawers with mirror	Ontario	1880- 1910	bottom edge of middle drawer on proper left side	varnish (green fluorescence)	linseed oil, ^b <i>Pinaceae</i> resin ^b
CMH D-7113 Vernacular-style, cherry end table	Ontario	1840- 1860	inside face of proper right rear leg, by proper right rear rail	varnish (green fluorescence)	linseed oil, ^b <i>Pinaceae</i> resin (pine), ^b soft copal, ^c shellac, beeswax
CMH D-7122 Vernacular-style, cherry and maple draw table	Ontario	1850- 1890	inside face of leg at interior drawer left guide	3. varnish (orange fluorescence) 1. varnish (green fluorescence)	3. shellac 1. linseed oil, ^b <i>Pinaceae</i> resin (pine), ^b soft copal, ^c beeswax
CMH D-8839 Vernacular-style, maple and walnut lamp table	Ontario	1840- 1860	underside of squared top of proper left front leg	varnish (green fluorescence)	drying oil, ^{b,d} <i>Pinaceae</i> resin, ^b soft copal ^c
CMH D-9376 Vernacular-style, rod-back chair	Bayfield, Ontario John Gemeinhardt	1896	inside proper left rear leg	varnish (green fluorescence)	linseed oil, ^b <i>Pinaceae</i> resin (pine) ^b
CMH D-11392 Regency style walnut slat-back chair	Hamilton, Ontario B. Bird	1835- 1865	proper right, underside of rear seat rail	varnish (green fluorescence)	drying oil, ^{b,d} <i>Pinaceae</i> resin ^b
CMH 978.11.1 Empire style, cherry chest of drawers	Ontario	1850- 1890	back edge of proper right side, 5 in. from the top	varnish (green fluorescence)	linseed oil-modified <i>iso</i> - phthalate alkyd
CMH 978.26.1 Vernacular-style, basswood, straight- front chest of drawers	Chesley, Ontario William M. Garrett	1867- 1900	second tier drawer, on the bottom edge of the face, under the proper left pull	varnish (green fluorescence)	linseed oil, ^b <i>Pinaceae</i> resin, ^b hard copal ^c
CMH 979.63.1 Vernacular-style, walnut and pine slant-top desk	Pelham, Ontario possibly attributed to John Gore	1850- 1880	underneath of proper right side rail at the proper front leg joint	two varnish layers (both green fluorescence)	linseed oil, ^b <i>Pinaceae</i> resin, ^b hard copal ^c
CMH 986.15.6 Mahogany balloon-back chair	Ottawa, Ontario workshop of Thomas Campbell	1865- 1885	inside front face of proper right rear leg	2. varnish (green fluorescence) 1. varnish (orange fluorescence)	2. linseed oil, ^b <i>Pinaceae</i> resin (pine), ^b hard copal, ^c beeswax 1. shellac
NB 977.309 Regency-style, mahogany-veneered sofa	New Brunswick Alexander Lawrence	c.1835	under front edge of proper right arm	5. amber varnish (orange fluorescence) 1-4. varnish (green fluorescence)	5. shellac 1-4. linseed oil, <i>Pinaceae</i> resin, soft copal, ^c hard copal, ^c shellac, beeswax
NB 983.11 Vernacular-style pine, spruce and birch secretary	New Brunswick	c.1895	under front edge of base top at proper right side	3. orange-brown varnish (green fluorescence) 2. red varnish 1. yellow paint	3. linseed oil, ^b <i>Pinaceae</i> resin, ^b soft copal ^c 2. natural resin, possibly mixed with a drying oil ^e 1. chrome yellow, iron oxide, gypsum, talc, calcium carbonate, barium sulfate, drying oil ^e

Table I: Object Description, Provenance and Analytical Results (con't).

Accession Number, ^a Object Description	Location, Cabinetmaker	Date	Sample Location	Description of Finish on Wood Substrate	Analytical Results
NB 984.4.2.b Pine, birch and unknown hardwood square-back Windsor chair	New Brunswick	c.1840	rear proper right stretcher at leg	5. red varnish (orange fluorescence) 4. thick grey paint 3. thin black varnish 2. amber varnish (green fluorescence) 1. thin black layer	5. shellac 4. calcium carbonate, barium sulfate, talc, linseed oil, ^b <i>Pinaceae</i> resin 2-3. linseed oil, ^b <i>Pinaceae</i> resin (pine), ^b hard copal, ^c , beeswax (trace) 1. not analyzed
NB 991.55.1 Eastlake-style, walnut side chair	New Brunswick John Warren Moore	1870	below proper right side seat rail at front near leg	thick amber varnish (orange fluorescence)	shellac
NBM 2003.26.1 Chippendale-style side chair, possibly maple	New Brunswick Hunter and Ross	1790	proper left side stretcher at front leg	3. amber varnish 2. thin black layer 1. brown paint	3. linseed oil, ^b <i>Pinaceae</i> resin, ^b hard copal, ^c paraffin, beeswax 2. not analyzed 1. red iron oxide, barium sulfate (barite), drying oil ^e
NBM 2004.33 Walnut, maple and pine occasional chair	Saint John, New Brunswick Alfred Lordly	1860- 1877	proper left seat rail at rear leg	varnish (green fluorescence)	linseed oil, ^a <i>Pinaceae</i> resin, ^b sandarac, paraffin (trace), beeswax
NBM 2009.25.2 Square-back Windsor chair	New Brunswick Harman Trueman	1800- 1825	under proper left side of seat	2-4. black finish (green fluorescence) 1. red paint	2-4. linseed oil, ^b <i>Pinaceae</i> resin (pine), ^b hard copal, ^c beeswax (trace), probably carbon black 1. red iron oxide, dolomite, calcium carbonate, barium sulfate (barite), quartz, linseed oil, trace <i>Pinaceae</i> resin
NBM 2009.38.71 Mahogany tilt-top table	New Brunswick Robert Chillias	1790- 1803	inside of leg opposite to catch	3. yellow varnish (orange fluorescence) 2. reddish brown varnish (green fluorescence) 1. thin black layer	3. shellac 2. linseed oil, ^b <i>Pinaceae</i> resin ^b 1. not analyzed
KL M.90.18.2 Regency-style, mahogany-veneered pine (secondary) chest of drawers	New Brunswick	1835- 1845	under edge of top on proper right front	varnish (green fluorescence)	drying oil, ^d <i>Pinaceae</i> resin, ^b soft copal, ^c collagen-type protein, beeswax (trace)
KL M2004.22.1 Vernacular-style, birch-veneered, maple and butternut chest of drawers	King's County, New Brunswick Thomas Hayes	1830- 1850	under top edge of proper right side, next to turned "column"	dark varnish (green fluorescence)	whole egg, <i>Pinaceae</i> resin (pine), ^b linseed oil, ^b beeswax (trace)
KL 2009.29.23a Regency-style, mahogany side chair	Fredericton, New Brunswick Alexander Mitchell	1827- 1865	underneath surface (finish had been stripped but remains of old or original varnish present on underside surfaces)	1-3. very thin layers of varnish	1-3. shellac, linseed oil, ^b <i>Pinaceae</i> resin, ^b beeswax

^aCMH = Canadian Museum of History; NB = New Brunswick Provincial Collection; NBM = New Brunswick Museum; KL = King's Landing

^bmolecular evidence of heat treatment

^chard copals are characterized by a polymer based on ozic acid (such as Zanzibar copal and Congo copal), whereas soft copals are characterized by a polymer based on communifolic acid (such as Manila copal and kauri resin)

^dunidentified drying oil – inconclusive P/S, possibly linseed oil or tung oil

^eFTIR analysis only

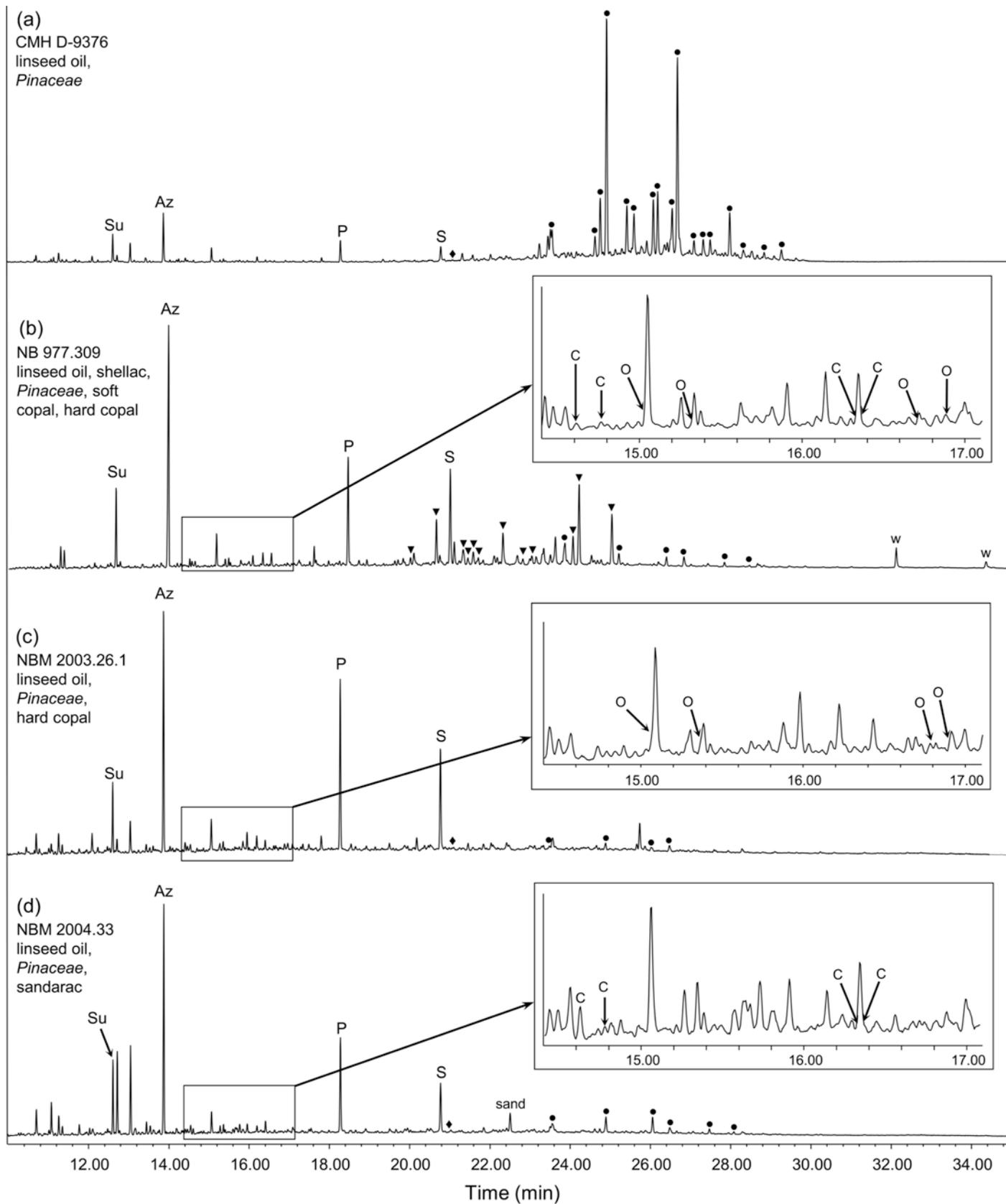


Figure 6. Total ion chromatograms of furniture finish samples: (a) rod-back chair (CMH D-9376); (b) sofa (NB 977.309); (c) side chair (NBM 2003.26.1); (d) chair (NBM 2004.33). Characteristic marker peaks for *Pinaceae* resin are labelled with circles (●), markers for shellac are labelled with triangles (▼), markers for hard copal are labelled 'O', markers for soft copal are labelled 'C', and markers for beeswax are labelled 'w'. Individual labels include suberic acid (Su), azelaic acid (Az), palmitic acid (P), stearic acid (S), sandaracopimaric acid (sand), and methyl 9-(2-propylphenyl) nonanoate (◆).

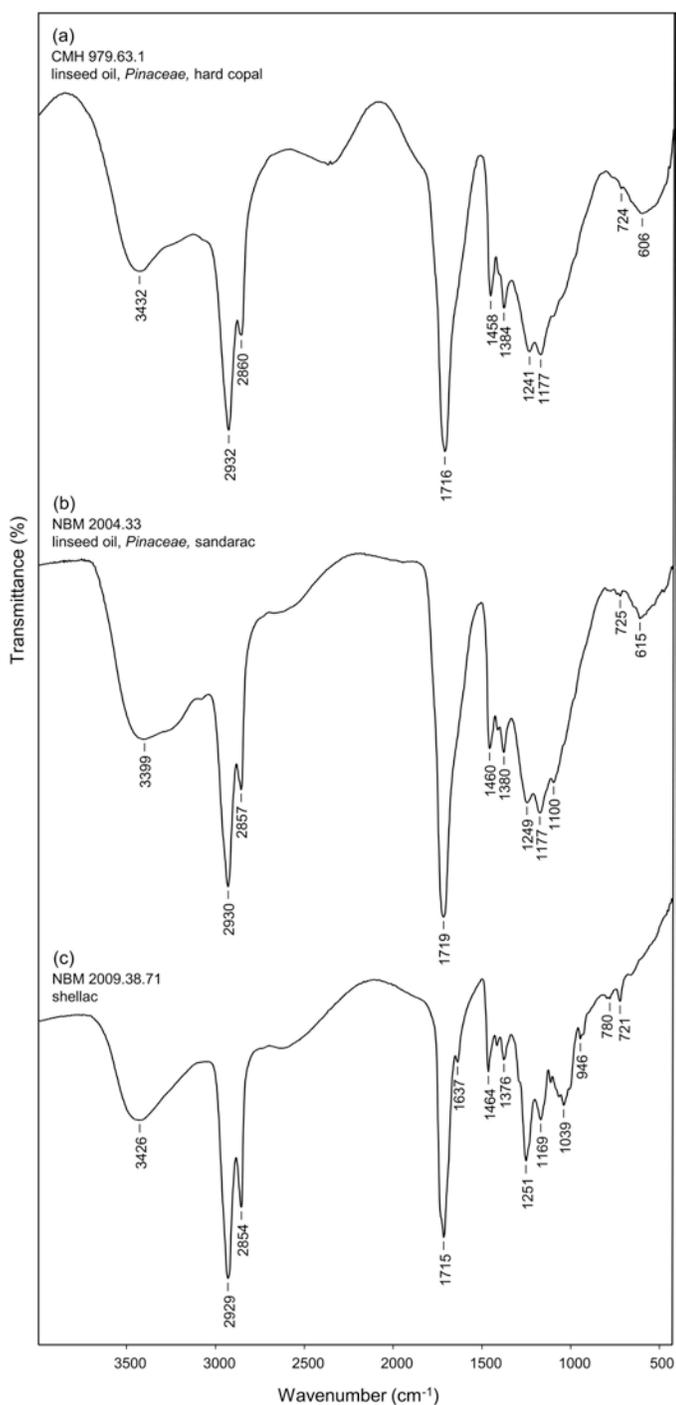


Figure 7. Infrared spectra of furniture finish samples: (a) slant top desk (CMH 979.63.1); (b) chair (NBM 2004.33); (c) tilt-top table (NBM 2009.38.71).

The mixture of linseed oil, *Pinaceae* resin and hard copal was identified on three of the New Brunswick pieces while soft copals were detected in two samples. Both soft and hard copals, in combination with linseed oil and *Pinaceae* resin, were found on one object. Several of these finishes will be discussed in detail. **Figure 9** shows the cross-section of a finish removed from a Regency-style sofa, built in New Brunswick c.1835 (NB 977.309). The finish, which separated



Figure 8. (a) Balloon-back chair, CMH 986.15.6. Canadian Museum of History, Gatineau, Quebec. Images of the cross-section: (b) incident light; (c) autofluorescence.

from the wood during manipulation of the sample, consisted of five varnish layers. A chromatogram of the finish is shown in **Figure 6b**. The layers were difficult to accurately separate and were analyzed together by Py-GC-MS. Shellac, heated linseed oil, heated *Pinaceae* resin, soft copal and hard copal were identified. The orange fluorescence of the upper layer indicates that it is composed of shellac and the lower layers displaying green fluorescence contain drying oil, *Pinaceae* resin and copal resins. In **Figure 6b**, the chromatogram is expanded to magnify the peaks originating from communic acid (marked 'C') and ozic acid (marked 'O') from the soft and hard copals, respectively. It cannot be determined whether the two types of copal are mixed together or whether they are contained in separate layers. The presence of shellac on top of the oil varnish layers likely indicates that it is a refurbishment layer.

One of the earliest pieces of New Brunswick furniture sampled was a Chippendale-style, Hunter and Ross side chair, dated 1790 (NBM 2003.26.1) and shown in **Figure 10**. The cross-section reveals that the finish consists of a lower brown paint layer and an upper, amber coloured varnish. The brown paint layer on the wood was composed of red iron oxide, barium sulfate (barite) and drying oil, and appears to have been applied as a *mahoganizing* treatment on the light-coloured, hardwood substrate. The chromatogram of the finish is shown in **Figure 6c**. Analysis identified the finish as heated linseed oil, heated *Pinaceae* resin and hard copal. The presence of traces of beeswax and paraffin wax in the chromatogram probably originates from a later application of furniture polish or paste wax. The peaks resulting from the pyrolysis of the hard copal polymer are shown in the expanded segment of the chromatogram. In this sample, the amount of heated *Pinaceae* resin is relatively less abundant than found in the other fixed oil varnishes (**Figures 6a** and **6b**).

The Hunter and Ross chair is one of three pieces from the New Brunswick collections having an opaque paint layer applied to the wood before the fixed oil varnish. Another is a square-back Windsor chair (NBM 2009.25.2) made by

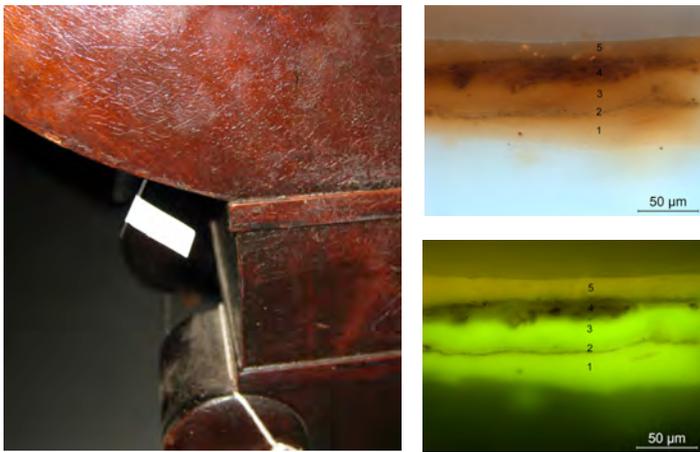


Figure 9. Sofa, NB 977.309. New Brunswick Provincial Collection. (a) Detail: sampling location. Images of the cross-section: (b) incident light; (c) autofluorescence.

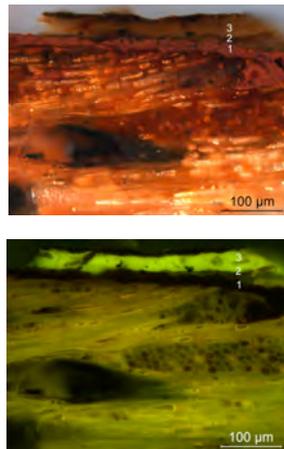


Figure 10. (a) Hunter and Ross chair, NBM 2003.26.1. New Brunswick Museum, Saint John, NB. Images of the cross-section: (b) incident light; (c) autofluorescence.

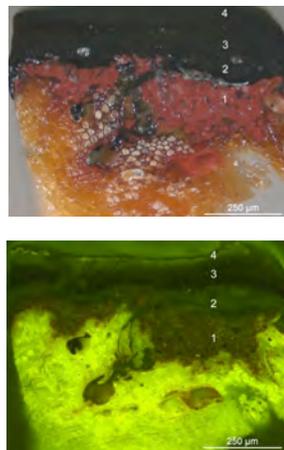


Figure 11. (a) Square-back Windsor chair, NBM 2009.25.2. New Brunswick Museum, Saint John, NB. Images of the cross-section: (b) incident light; (c) autofluorescence.

Harman Trueman during the period 1800–1825, presented in **Figure 11**. As indicated in the fluorescence image of the cross-section, there were three applications of black varnish over a red paint. The varnish consisted of heated linseed oil, *Pinaceae* resin, hard copal and probably carbon black. The red paint was composed of red iron oxide, dolomite, calcium carbonate, quartz, barium sulfate (barite) and linseed oil. This is typical of nineteenth-century Windsor chairs, since they were often painted with a first coat of red ‘filler’ paint composed of linseed oil and iron oxide, followed by a layer of black paint or varnish.³⁰

Finishes on a number of other New Brunswick pieces displayed complex stratigraphy. In the following two examples, the coatings separated from the wood on manipulation of the sample. The cross-sections are shown in **Figure 12**. Several layers of varnish were present on another square-back Windsor side chair dated c.1840 (NB 984.4.2.b). Linseed oil, *Pinaceae* resin and hard copal were present in the earliest layers and red-coloured shellac on the surface. A thin black layer remaining on the wood when the finish separated was not analyzed. A vernacular-style, New Brunswick secretary (NB 983.11), c.1895, made of pine, spruce and birch, was first coated with a yellow paint pigmented with chrome yellow and iron oxide. The subsequent coatings contained a mixture of linseed oil, *Pinaceae* resin and soft copal. The finish on a mahogany-veneered, Regency-style chest of drawers from Saint John, dated from 1835–1845 (KL M90.18.2), consisted of unidentified drying oil, *Pinaceae* resin and soft copal. Animal glue, likely a contaminant from the sampling location near a joint, was also detected.

Linseed Oil, *Pinaceae* Resin and Sandarac

Sandarac from Northern Africa is a diterpene resin based on polycommunic acid (**Figure 3**), like soft copals. The two resin types are easily differentiated, primarily by the presence of a significant abundance of sandaracopimaric acid in the former. Sandarac was only identified in one finish sample, from a New Brunswick piece. The object is a walnut, maple and pine occasional chair, built during the period 1860–1877 by Alfred Lordly of Saint John (NBM 2004.33). The sample consists of a single layer of amber-coloured varnish that displays a green auto-fluorescence (**Figure 13**). The infrared spectrum of this varnish is shown in **Figure 7b**.

Analysis of the sample using Py-GC-MS identified the sandarac component as well as heated linseed oil and heated *Pinaceae* resin. The chromatogram for the finish sample is shown in **Figure 6d**. An expanded region shows the characteristic markers for the pyrolysis of polycommunic acid (marked ‘C’), and a peak identified as sandaracopimaric acid (marked ‘sand’). As previously seen for the copal varnishes, this varnish also contains highly oxidized abietanes (marked with circles ‘●’) that indicate the presence of *Pinaceae* resin in the varnish.

Spirit Varnishes

Shellac

Shellac was detected on three of the ten Ontario pieces that were sampled: the cherry end table (CMH D-7113) where the stratigraphy of the sample was not clear, the cherry and maple draw table (CMH D-7122) where a shellac layer was present over the fixed oil varnish, and in the first layer of the mahogany balloon-back chair (CMH 986.15.6) discussed earlier and shown in **Figure 8**. As with the fixed oil varnish made with *Pinaceae* and hard copal found on top of this layer, the thickness of the shellac layer on the chair is notable. It would have been impossible to apply a single layer of shellac this thick and it is suspected that this coating may be the result of French polishing where subsequently applied layers are melded together through the application process.

Shellac was present on five New Brunswick objects. It was the surface layer of the sample from the 1835 sofa (NB977.309), shown in **Figure 9**. In **Figure 6b**, the shellac marker peaks on the chromatogram for this object are labelled with triangles (▼). Shellac was also identified in the finish on an Eastlake-style, walnut side chair from 1870, attributed to John Warren Moore (NB 991.55.1). This thick finish layer may also have been applied using the French polish technique. As indicated earlier, shellac was also detected as the surface layer of a Windsor side chair (NB 984.4.2.b) and appears to have been applied as a varnish over a grey paint layer during a later refurbishment campaign.

The sampled finish on the mahogany side chair made by Alexander Mitchell of Fredericton between 1827 and 1865 (KL 2009.29.23a) was problematic. The chair had been stripped; however, it was thought that remnants of the original varnish were still present on a concealed surface. The sample also broke during sampling or subsequent manipulation. Analysis indicated the presence of shellac, linseed oil and *Pinaceae* resin, but the stratigraphy of the sample was uncertain.

A surface layer of shellac was also detected on top of a fixed oil varnish in the finish sample from the Chillas tilt-top table (NBM 2009.38.71) and displays characteristic orange fluorescence (**Figure 14**). The infrared spectrum of the upper, shellac layer is shown in **Figure 7c**.

Modern Synthetic Varnish

The finish sample taken from a cherry chest of drawers, dated from 1850–1890, in the collection of the Canadian Museum of History (CMH 978.11.1), was found to contain a finish composed of a synthetic resin, an *iso*-phthalate alkyd. This is not an original finish since alkyds were first developed in the 1920s.³¹

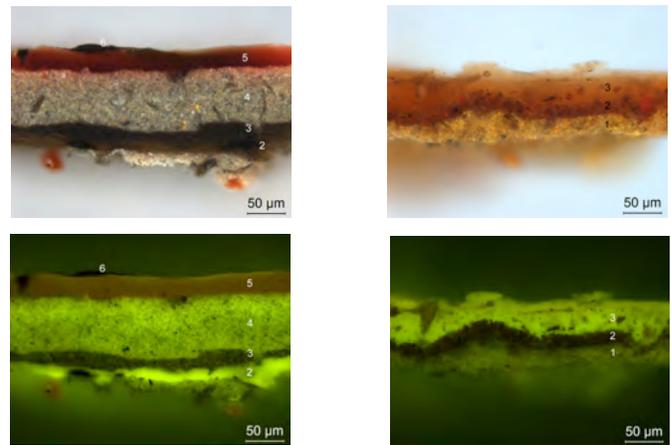


Figure 12. Incident light and autofluorescence images of the cross-sections prepared from left: the finish on the side chair (NB 984.4.2.b); and right: the finish on the secretary (NB 983.11).

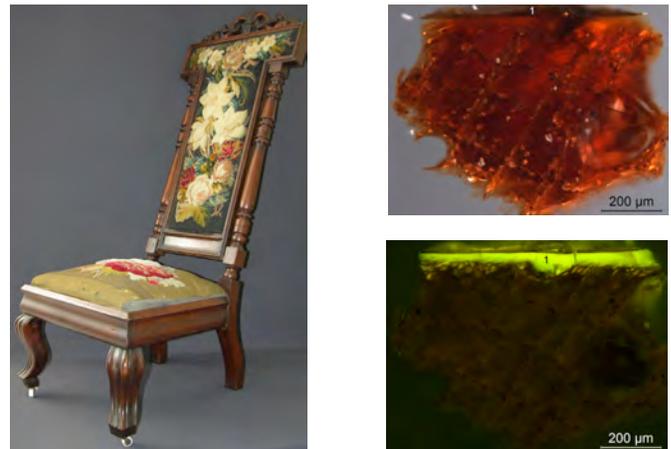


Figure 13. (a) Alfred Lordly chair, NBM 2004.33. New Brunswick Museum, Saint John, NB. Images of the cross-section: (b) incident light; (c) autofluorescence.



Figure 14. (a) Robert Chillas tilt-top table, NBM 2009.38.71. New Brunswick Museum, Saint John, NB. Images of the cross-section: (b) incident light; (c) autofluorescence.

Discussion

Sampling Methodology

The sampling technique adapted from that described by Carr proved to be a successful and efficient method of removing minute, core samples from the objects. Some difficulties arose upon ejection of the samples from the needle tip, primarily samples shattering or detaching from the wooden substrate upon ejection (see **Figures 9** and **12**). A Microfoam® plug was punched into the needle before the sample was taken to cushion the finish samples upon removal by the reamer and this seemed to help keep the samples intact. It was also found that a larger, 16 gauge needle (instead of the recommended 18 gauge needle) made removal of an intact sample easier. Care should also be taken to protect samples between collection and analysis to avoid unnecessary jostling that may cause samples to break apart.

Analytical Methodology

Examination of Cross-sections

Examination of the cross-sections of the finish samples by incident light and fluorescence microscopy was an essential first step in the analysis. Knowledge of the stratigraphy provided a useful reference for the manual separation of the various layers for analysis and the interpretation of the results. In addition, autofluorescence images provided information on the nature of the finishes, since shellac exhibited an orange fluorescence under the experimental conditions while fixed oil finishes exhibited a green fluorescence.

FTIR

Analysis of the finish layers by FTIR was a useful screening technique due to the small sample size requirement and the relative speed of the analysis. Identification of shellac and synthetic resins such as alkyds is straightforward. The infrared spectra of fixed oil varnishes are very similar to each other, even if different combinations of resins are present, as shown in **Figures 7a** and **7b**. This is due to the similarities of the natural resin spectra, particularly after aging, as well as the superimposition of the absorption bands of all the drying oil and resin components present in the varnish. In addition, certain pigments and fillers were identified in pigmented layers by the FTIR analysis.

Py-GC-MS

In the analysis of complicated natural varnish blends, the use of a technique that accurately characterizes all of the materials present is essential. Bearing this in mind, with GC-MS analysis it is important to choose a method (or multiple methods) that will allow all components to be detected. In the initial stages of the project, varnishes from the furniture objects were extracted using m-(trifluoromethyl)-phenyltrimethylammonium hydroxide (TMTFTH) and toluene, with mild heat. This popular method is useful in identifying drying oils and non-polymerized resins (such as

Pinaceae resins, shellac, mastic and dammar).³²⁻³⁶ However, it has a significant shortcoming in that it does not allow for the detection of polymerized resins (such as copals or sandarac, and many synthetic polymers) because they remain intact and cannot be extracted. In these initial analyses, the TMTFTH extraction procedure allowed for the identification of linseed oil, *Pinaceae* resin, shellac and a modern synthetic alkyd resin, however, no polymerized resins were detected. Subsequently, each of the samples was re-analyzed using Py-GC-MS with tetramethylammonium hydroxide (TMAH) reagent. The pyrolysis of the samples allowed for the polymerized resins present to be broken apart into smaller units for detection, while the derivatization allowed for the detection and identification of drying oils and non-polymerized resins. After the pyrolysis procedure, copal resins were detected in 12 of the 21 furniture objects and sandarac was identified on one other.

Interpretation of Results

With two exceptions (the shellac finish on NB 991.55.1 and the alkyd on CMH 978.11.1), every object sampled exhibited at least one layer of a fixed oil varnish, and it most often occurred as the first layer on the wood substrate. Linseed oil was identified as the drying oil whenever a specific type could be determined, which was the case for the majority of the fixed oil varnishes included in this study. Linseed oil has better drying qualities than semi-drying oils, such as poppy seed oil or walnut oil, because the triglyceride contains a relatively high concentration of linolenic acid, a tri-unsaturated fatty acid that oxidizes and polymerizes more efficiently, forming a strong medium. In the instances where linseed oil was identified, the presence of cyclic C18 marker compounds indicated that it had been heated.^{28,29} This likely occurred when the oil was heated during the varnish manufacture in order to melt and disperse the resins. Unlike tung oil, which contains a different tri-unsaturated fatty acid (eleosteric acid), linseed oil becomes bodied when heated to the temperatures required for resin dispersion, but does not gel.³⁷ For these reasons, linseed oil was likely seen as the superior choice in drying oil during the period when these furniture objects were created.

The majority of fixed oil varnishes contained copal resins and the additional presence of *Pinaceae* resin is a trend seen in all twelve copal varnish layers identified in this study, regardless of whether they contain hard or soft copal. While unrefined turpentine solvent may also contain traces of *Pinaceae* resin that could conceivably remain as a residue in a cured finish to which it has been added,^{6,7} the significant abundance of *Pinaceae* marker compounds identified in the finishes most likely indicate that the resin was purposefully added to these varnishes. In the majority of the samples, retene, a marker compound that is produced through thermal degradation of *Pinaceae*, was present in relatively moderate abundance, indicating heat treatment of the *Pinaceae* resin.³⁸ In many cases, more precise identification of the *Pinaceae* resin was not possible due to the loss of marker compounds through oxidation.^{39,40} However, in seven of the finishes, the presence of higher abundances of pimelic acid relative to

those of sandaracopimaric acid (>2) likely indicates the presence of colophony.²⁹ Venice turpentine (*Larix decidua*), another member of the *Pinaceae* family of diterpene resins, is listed among the ingredients of many superior quality varnishes in the eighteenth and nineteenth centuries.^{3,25} Chemical marker compounds for aged *Larix*³⁹ were not detected in any of these samples. This may indicate that the resin was not utilized in the finishes included in the present study, or that the markers were present in concentrations below the limit of detection for the methodology.

The abundance of samples with the distinct combination of linseed oil, copal and *Pinaceae*, similar to the *vernish Martin* recipe although simplified, supports Mussey's assertion that domestic versions of the famous varnish were in widespread use.³ The Martins used hard resins (copals and amber) in combination with softer resins (Chios turpentine, colophony and mastic), melted together and then dispersed in heated drying oil to create varnishes of unsurpassed quality and durability. The published amber varnish recipe of 1773 states that "amber can only be dissolved clear by melting it in some less glutinous gum and of an earlier dissolution."²⁵ This important statement may help to explain the presence of *Pinaceae* resin in each of the copal-containing oil varnishes identified in this study: apart from adding it as a plasticizer and gloss agent, varnish makers may have incorporated the softer *Pinaceae* resins to help dissolve the harder resins before adding drying oil and heating the mixture further.⁶ Indeed, recipes for copal varnishes used on horse drawn carriages have been shown to contain as much as 5 lb. (2.27 kg) of colophony for every 10 lb. (4.54 kg) of copal.⁷

In contrast with the frequent use of oil varnishes, shellac spirit varnishes appear to have had a more limited use as an original finish on nineteenth-century Canadian furniture. While shellac was found on eight of twenty-one objects, it always occurred as a top layer (suggesting a refurbishment layer) except in two cases (CMC 986.15.6 and NB 991.55.1) where it appears to have been applied with the French polish technique (for example, the uniform layer on the balloon-back chair in **Figure 8**). Such evidence seems to indicate that the materials and practice of French polishing may have been less established in nineteenth-century Canada. As expected, in light of their reputation for rapid degradation, essential oil varnishes were not encountered in this study.

Conclusions

The information gathered in this study of nineteenth-century furniture varnishes promotes a better understanding of the materials and formulas that were common to the domestic furniture making industry in eastern Canada in this era. While it has been a commonly held assumption that shellac spirit varnishes were the predominant finishes used on furniture during the nineteenth century, it appears that fixed oil varnishes were chosen more often by Canadian makers, particularly for vernacular furniture. Results reveal that Canadian furniture makers, even those in rural areas, were aware of, and were obtaining or attempting to replicate the fashionable fixed oil varnishes popularized in the late

eighteenth century, until at least the end of the nineteenth century. If varnishes were shop-made, it seems plausible that varnish makers, particularly those in rural areas with limited resources, would capitalize on the availability of domestically-produced *Pinaceae* resin and use it in combination with valuable imported hard resins, but without documentary evidence, this remains speculation. While no significant regional differences were observed, directions for future research might include investigations of nineteenth-century varnishes on furniture originating from other Atlantic provinces, Quebec and Western Canada. Future research on the subject should also include a thorough documentary investigation of nineteenth-century Canadian cabinetmaker and varnish maker account books, newspaper ads and customs records to determine actual purchases and practices. It is hoped that a deeper understanding of original materials and methodologies will better inform preservation and conservation treatment choices for nineteenth-century Canadian furniture.

Appendix

Analytical Methodologies

Cross-sections

Samples were mounted as cross-sections by embedding them in Bio-plastic® polyester resin and preparing them using standard grinding and polishing techniques. The cross-sections were examined by light and fluorescence microscopy using a Leica DMRX microscope. Images of the cross-sections were acquired in incident light and autofluorescence using a blue excitation filter (420–490 nm).

FTIR

Samples of selected layers were analyzed by FTIR using a Bruker Hyperion 2000 microscope equipped with a wide-band mercury cadmium telluride (MCT) detector interfaced to a Tensor 27 spectrometer. A portion of the layer of interest was positioned on a Spectra-Tech diamond microsample cell and analyzed in the transmission mode. The spectra were acquired in the 4000 to 430 cm⁻¹ range by co-adding 150 scans.

GC-MS

Selected layers of interest were mechanically separated when possible and were extracted and derivatized with Meth-Prep™ II (m-(trifluoromethyl)-phenyl trimethylammonium hydroxide, TMTFTH, 0.2 N in methanol) and toluene (1:1) and then analyzed using an Agilent 6890 gas chromatograph (GC) interfaced to an Agilent 5973 quadrupole mass spectrometer (MS). The GC oven was fitted with an Agilent HP-5MS column ((5% phenyl)-methylpolysiloxane; 30.0 m, 0.25 mm internal diameter, 0.25 µm film thickness), and for all analyses the following temperature program was used: 50°C to 200°C at a rate of 10°C/minute and then from 200°C to 300°C at a rate of 6°C/minute and a final hold time of 15 minutes; total run time of 46.67 minutes. A split-splitless injector was used in splitless mode at 250°C and the MS

interface was set at 280°C. Ultra-high purity helium carrier gas was used with a constant flow of 1.0 mL/minute. The MS was run in scan mode from 50–750 amu, with the source and quadrupole temperatures set at 230°C and 150°C respectively. The MS was operated in the electron impact positive ion mode (70 eV). Data were processed using Agilent Chemstation software, v.E.02.02 (Agilent Technologies, Inc., Santa Clara, California). In addition to elucidation of mass spectra based on molecular weight and fragmentation, mass spectral identification was also performed using the NIST 11 Mass Spectral Library and published reference data.

Py-GC-MS

For each analysis, approximately 2–20 µg of varnish was placed in a micro-vial (Agilent Technologies, part no. 5190-3187) with 1.6 µL of tetramethylammonium hydroxide (TMAH, Supelco, Bellefonte, PA) in methanol (1:25). The vial was inserted into a thermal separation probe (TSP, Agilent Technologies, Inc., Palo Alto, CA) installed in a multimode inlet on an Agilent 7890A GC interfaced to a 5975C MS. The multimode injector with TSP was operated in splitless or split mode depending on the sample size and ramped from 50°C to 450°C, at a rate of 900°C/minute to perform the pyrolysis. The final temperature was held constant for three minutes and then decreased to 250°C at a rate of 50°C/minute. For the GC separation, a Phenomenex ZB-Semivolatiles fused silica column (30 m x 0.25 mm i.d., 0.25 µm film thickness; Phenomenex Inc., Torrance, CA) was used. Ultra-high purity helium carrier gas was used with a constant flow of 1.2 mL/minute. The oven was programmed from 40°C to 200°C at 10°C/minute and 200°C to 300°C at 6°C/minute with a hold time of 20 minutes (52.67 minutes run time). The MS was operated in EI positive mode (70 eV). The MS transfer line temperature was 280°C; the MS ion source was held at 230°C and the MS quadrupole at 150°C. The MS was run in scan mode from 50–550 amu (5–25 minutes), 50–750 amu (25–30 minutes) and 50–800 amu (35–63 minutes). Data were processed using Agilent ChemStation software, v.E.02.02. In addition to elucidation of mass spectra based on molecular weight and fragmentation, mass spectral identification was also performed using the NIST 11 Mass Spectral Library and published reference data.^{39,41-43}

SEM/EDS

Pigmented layers in the cross-sections were analyzed by SEM/EDS. This analysis was performed using an Hitachi S-3500N VP scanning electron microscope integrated with an Oxford Inca X-act analytical silicon drift x-ray detector and an Inca Energy+ x-ray microanalysis system. The SEM was operated at an accelerating voltage of 20 kV in high vacuum mode using a secondary electron detector or a backscattered electron detector. Using this technique, elemental analysis of volumes down to a few cubic micrometers can be obtained for elements from boron (B) to uranium (U) in the periodic table at a level of approximately 0.1–1% or greater. These results were used to facilitate the identification of pigments and fillers by FTIR. Detailed results are not reported here.

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