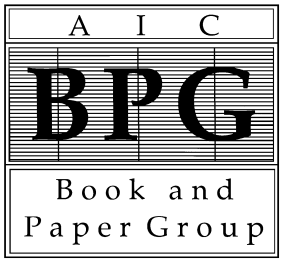

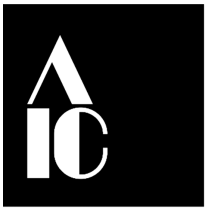

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Analysis and Assessment of the Degradative Properties of Strawboard as a Secondary Support

INTRODUCTION

The earliest paperboards were originally made by laminating layers of paper together using a variety of papers and glues, including starches, gelatin, and varnishes (Bower 2002, 18). These early boards were often made by artists and craftsmen but rarely by paper mills. Boards were used for a variety of things, including boxes, binders' boards for books, and artists' drawing boards. By the late 19th century, pasteless boards for artists began to be made by mills where several pieces of paper were couched one on top of the other to create a single board. Millboard was a product of the paper industry, as it did not use any glue but rather a deep deckle to hold the pulp and extreme compression to form the board. The multi-vat process was similar to pasteless boards and used the cylinder mould machine to move a sheet from vat to vat, adding to the previously couched sheet. This allowed for varied thickness as well as varied fiber content layers (Bower 2002).

The shift from handmade to machine-made paper began with the introduction of the Fourdrinier paper machine in 1806 and led to increased paper production as well as demand for fibers (Joint Textbook Committee of the Paper Industry 1983, 155). Prior to the 1800s, paper was made almost exclusively from rags, but rags alone could not meet the demand for fiber, so experimentation with other fibers increased. One of the new fiber types derived from various forms of straw including barley, rye, wheat, and oat (Bevan and Cross 1888, 58). Paperboards, including strawboard, have traditionally been used as secondary support for artworks; this research will focus on the degradative properties of strawboard and whether it is a safe material to be in contact with artwork.

Papers presented during the Book and Paper Group Poster Short-format Session, AIC's 52nd Annual Meeting, May 20–24, 2024, Salt Lake City, Utah

HISTORY AND MANUFACTURE OF STRAWBOARD

Strawboard was originally introduced in Holland during the 19th century. The boards were made using pure straw pulp on a multi-vat board machine (Bower 2002). Strawboard made in the United States for paperboard was unbleached (American Society for Testing Materials 1963, 75), and typically about 80% to 100% of the fiber furnish was straw, with the remainder being wastepaper (Joint Textbook Committee of the Paper Industry 1983, 173), likely made from rag fibers or other new materials such as esparto, wood pulp, and bagasse. Straw was used widely in the United States and other countries for making paper and paperboard during the 19th century, beginning around 1829 in the United States. The introduction of wood pulping in the 1840s quickly dominated papermaking, and its use was relatively short lived, lasting only until the 1890s (Joint Textbook Committee of the Paper Industry 1983, 155). By the 20th century, straw had been largely replaced by wood for use in papermaking, but its use in other products continued, especially in corrugated boards for packaging; the last mill using straw closed in the 1960s.

A patent from 1929 for making corrugated strawboard suggests that the production of both a strong and flexible material is particularly difficult due to the nature of the fiber (Weston and Clark 1929). The processing of the fibers influences the properties of the board: caustic cooked straw produces a fine fiber that creates a strong sheet; however, it requires the machine to run much slower and has a higher cost due to the chemicals used. Lime-cooked straw produces a sheet that can be run quickly through the machine but creates a shorter and coarser fiber, leading to brittleness (Weston and Clark 1929). The expense of strawboard production and the introduction of the more cost-effective wood pulping process likely contributed to the decline of straw paper and strawboard. A reference in *Pulp and Paper Manufacture* (Joint Textbook Committee of the Paper Industry 1983, 155) notes that straw was easily pulped by using inexpensive lime, which contributed to its early success. This likely led to a brittle

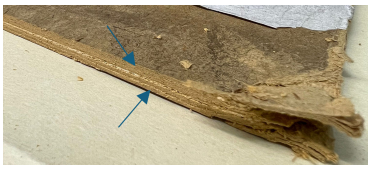
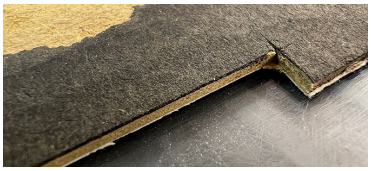
 Board A1 (primary board material)	Sample Source: Backing board for a mid-19th century etching,* adhered to perimeter Fiber Distribution: Relatively small and even Color: Yellow/tan Texture/Structure: Fluffy, paper-like, flexible Thickness: 4 mm overall (2 × 2 mm layers) **The etching paper was stark white.*
 Board A2 (central layer)	Sample Source: Backing board for a mid-19th century etching,* adhered to perimeter Fiber Distribution: Larger size variations with clear pieces of straw visible Color: Pale yellow Texture/Structure: Stiff, brittle, rough Thickness: Approximately 0.5 mm **The etching paper was stark white.*
 Board B	Sample Source: Backing board for a late-19th century print, adhered overall Fiber Distribution: Small, even distribution, some larger pieces Color: Pale tan Texture/Structure: Compact, relatively flexible, one layer, faced with paper* on both sides Thickness: 2 mm **Facing papers were removed for testing.*

Table 1. Board Sample Descriptions

material that would not be very durable and, in the case of art, did not provide adequate support.

SAMPLES

For this study, two samples of strawboard were compared (table 1). The first sample (Board A) was a mid- to late 19th-century board used as a backing for an 1850s etching depicting Niagara Falls. The board was extremely brittle, with a tendency to easily fragment, crumble, and separate (fig. 1), but the print paper was pristine white, which raised the question of whether the board was adversely affecting the print. Contact with poor-quality materials can often lead to the formation of degradation products resulting in staining, which was not present in this case. Fiber samples were taken from the exposed margins of the board. When cutting an approximately 0.5 × 6 cm sample, the board layers separated naturally through their thickness along a middle layer

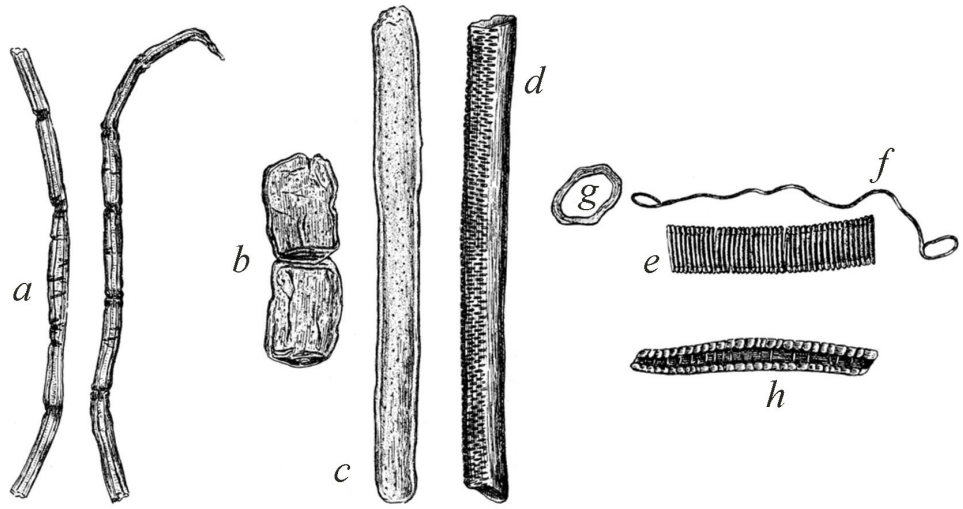


Fig. 1. Characteristic features of straw fibers: Bast fibers (a); thin-walled parenchyma, short (b) and long (c); pitted vessel elements (d) with tightly packed pores; spiral vessels fully intact (e), unraveled (f), and as individual annular wall thickenings (g); and sclerenchyma elements (h). From Herzberg 1902, 77–78.

of different composition from the primary board material. This suggests that the board was made in the multi-vat process. The primary board material was darker in color and had an almost fluffy composition. The central layer was thinner, much lighter yellow, and more brittle. In testing, Board A1 refers to the primary board material, and Board A2 refers to the lighter central layer.

The second sample (Board B) was a backing board attached to a late 19th century print. In contrast to Board A, this board was faced with paper on the recto and verso, and the core was a single layer of compressed fibers. The use of facing paper on strawboard is common, as it tends to be brittle and requires additional support (Etherington and Roberts 1982). The furnish of the board had large distinct pieces of straw fibers visible and was quite compact. When a sample was taken similar in size to Board A, the board held together firmly.

MATERIALS AND METHODS

Several analytical techniques were used to investigate the properties and materials comprising the strawboard samples. Polarized light microscopy (PLM) and scanning electron microscopy (SEM) were used to characterize the fibers and surface structure of the samples. PLM is commonly used in fiber identification, and SEM has been used to identify different structural elements of straw (Liu, Yu, and Huang 2005). Fiber staining (Herzberg) enhanced the visible morphology and aided in confirming specific fibers based on the colors observed. Attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy has been used in other paper fiber research (Kostadinovska, Spirovska, and Taylor 2016) and helped identify possible adhesives and binders present. The pH of the samples was determined by a cold extraction method (TAPPI 509). This method is used in the paper industry but is not typically viable for conservation due to the large sample size required. It was possible here based on the experimental design and size of the sample boards used in this study.

PLM and Fiber Staining

A Leica DM750P polarized light microscope equipped with an ICC50W camera was used to identify and photograph the fiber components of the strawboards. Fiber samples from each of the two boards were taken for observation: the primary board component of the Niagara sample (A1), the center layer of the Niagara sample (A2), and the board material of the second sample (B, facing papers removed). Each sample was dyed using Herzberg stain following the TAPPI/ANSI T 401 om-15 standard for fiber analysis of paper and paperboard (TAPPI 2015b).

Scanning Electron Microscopy

Secondary electron and backscatter electron images were obtained using a Tescan Vega3 XMU tungsten variable pressure scanning electron. Samples were analyzed under high vacuum at an accelerating voltage of 5.0 kV. They were prepared by adhering them to a stub covered with carbon tape and coating them with platinum/gold to reduce charging and improve image quality. PELCO Colloidal Graphite was used to help hold the fragile samples together and aid in reducing charging.

ATR-FTIR Spectroscopy

FTIR analysis was used to identify sizing and adhesives in the strawboard samples. Infrared spectra were collected using a Nicolet 6700 FTIR spectrometer (Thermo Scientific) with a Thermo Scientific Smart iTR ATR accessory. Samples were analyzed by pressing them against the Diamond ATR crystal. The spectra are the average of 32 scans at 4 cm^{-1} spectral resolution. An ATR correction routine was applied to compensate for variations in penetration depth with wavenumber. Sample identification was aided by searching a spectral library of common conservation and artists' materials (Infrared and Raman Users Group, http://www.irug.org) and other available spectral databases using Omnic software (Thermo Scientific).

Hydrogen Ion Concentration (pH) of Paper Extracts (Cold Extraction Method)

The hydrogen ion concentration (pH) of three samples was obtained following the TAPPI 509 om-15 standard (TAPPI 2015a): the primary board component of the Niagara sample (A1), the center layer of the Niagara sample (A2), and the board material of the second sample (B, facing papers removed). Samples were cut from the interior of the boards to reduce contaminants found along exposed edges. Each sample (1 +/− 0.1 g) was macerated and soaked for 1 hour in a covered beaker of deionized water, brought to a total volume of 70 mL. The solution was tested at ambient room temperature of 22.7°C using a Horiba B-713 LAQUAtwin Compact pH Meter equipped with a glass electrode with temperature compensation and accuracy within ±0.1 pH. Each sample was tested twice, with the average pH rounded to the nearest 0.1 pH unit. Proprietary buffer solutions were used for a two-point calibration (4.01 and 7.00). Some modifications were made to the standard due to the availability of materials: reagent grade water was replaced with deionized water, and a Mylar cover was placed on the surface of the water while waiting rather than passing pure nitrogen or CO_2-free air through the sample.

Material Suitability Testing

Oddy testing was performed on a sample of the Niagara strawboard (Board A). The strawboard was tested using the British Museum version of the Oddy test. Borosilicate test tubes (50 mL) were rinsed with deionized water, followed by a low-water acetone wash. The tubes were placed in a 60°C oven for approximately 30 minutes to dry. Coupons of 0.004

Fig. 2. a. Board A1, Herzberg stain, long fiber bundle; b. Board A1, Herzberg stain, serrated epidermal cells over a fiber bundle; c. Board B, Herzberg stain, serrated epidermal cells over fibers

in thick pure copper, lead, and silver were cut into approximately 1 × 3.5 cm pieces. Each coupon was sanded using 1800 grit MicroMesh, being careful to handle the surface as little as possible. To prepare the platinum-cured silicone stoppers, they were first rinsed in deionized water and patted dry with Kimwipes. Three 1 cm wide parallel slits were cut into the underside of each stopper to hold the coupons. To assemble the package, a 2 g sample of material was placed in the bottom of the test tube. A small borosilicate culture tube containing approximately 0.65 mL of deionized water was added next to the sample. The metal coupons were rinsed with low-water acetone, patted dry with a Kimwipe, and fitted into the slots in the stopper using tweezers. The coupons were adjusted so that they were firmly in place in the stopper and would also not be in contact with other coupons or the side of the test tube once assembled. The stopper was added and sealed with several pieces of Parafilm M, followed by Teflon tape wrapped around the top of the tube and up over the stopper. This was done to prevent built-up pressure inside the tube from dislodging the stopper while in the oven. A control test tube was prepared in the same way without adding any sample material. After the tubes were sealed, they were placed in a 60°C oven for 29 days. The tubes were removed from the oven, the stoppers removed, and the coupons imaged. Samples were compared to Buffalo State University Lab Oddy Test Coupon Grading Guides to determine appropriate ratings.

RESULTS AND DISCUSSION

PLM and Fiber Staining Analysis

There are many different elements of straw that can be observed using PLM, and several look quite similar to hardwood elements. The drawings provided in *Papierprüfung: Eine Anleitung zum Untersuchen von Papier* by Herzberg (1902, 76–79) were essential to identifying key elements of straw fibers (see fig. 1). Throughout all three samples, long bundles of fibers were observed (fig. 2a). Serrated epidermal cells, a diagnostic feature of straw, were a common occurrence in all samples with cells appearing interlocked on top of the long fibers (see figs. 2b, 2c) and also individually. These types of cells exhibit a wavy or serrated edge with their width-to-length ratio ranging anywhere from 1:1 to 1:10. Figure 3a shows a bast cell with evenly spaced nodes that are similar to esparto; however, they curve rather than bend at the nodes (Brückle, n.d., Western Papermaking). Board A and Board B have rings that are part of the cell wall (see fig. 3b) and a few pitted vessel elements, which are abundant in hardwood but not as commonly seen in straw. A good example is found in the main material of Board A (fig. 4, see fig. 3c). Both long and short parenchyma are seen throughout, which are a cell type not seen in esparto (Herzburg 1902, 78). Some of the longer parenchyma are very ribbon-like and appear like twisting cotton fibers (see fig. 4); however, the length and rounded ends are characteristic of the longer parenchyma found in straw.

Overall, the composition appears to be primarily straw in both boards, although this is based on limited sampling from each. The center layer has no discernable difference in composition based on the photomicrographs; however, the composition is visually much more varied in size, with rough pieces of straw visible to the naked eye. There may be esparto in Board A2 and Board B (fig. 5), with the purple stain suggesting esparto in both samples and a possible comma-shaped hair indicative of esparto in Board B; fibers also tend to be much shorter in esparto samples, as is seen in figure 5. The overall yellow staining of most fibers is in line with an unbleached pulp. There was no blue, which would indicate a chemical pulp (TAPPI 2015b).

SEM Analysis

Four samples of Board A and one sample from Board B were taken and prepared for analysis: front of A1; back of A1, A2, and B; and cross section of A. The samples taken represented different areas of the board as well as different structural aspects (fig. 6). Due to the varied surface of the samples, initial imaging using carbon coating resulted in heavy amounts of charging from uneven coating, which prevented acquiring usable images. A second set of samples was made and

Fig. 3. Fiber elements. a. Board A1, straw bast cell; b. Board B, cell wall annular thickenings; c. Board A1, pitted vessel element; d. Board A2, sclerenchyma cell.

coated, this time with a conductive coating of platinum/gold. Charging was still an issue, and a second coating was necessary for resolving information and preventing the charging of the surface. The cross section proved particularly difficult to image without charging due to the texture and was unable to be captured. However, it was observed that there were five distinct layers in Board A, two even layers on the top and bottom (A1), and one thinner central layer (A2).

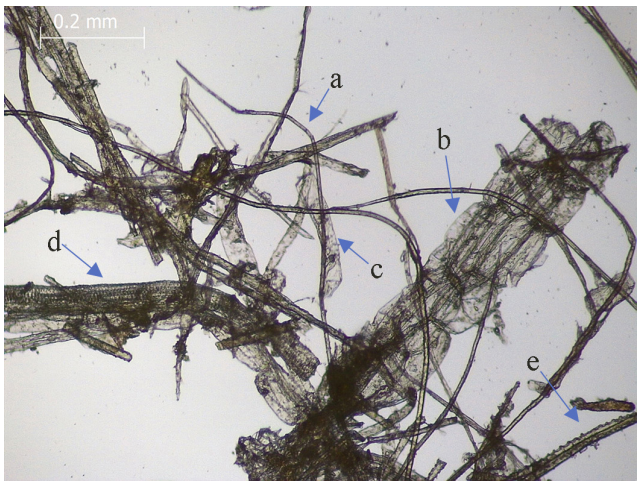


Fig. 4. a. Board A2, bast fiber; b. Short parenchyma; c. Long parenchyma; d. Pitted vessel element; e. Serrated epidermal cells.

Board A1 (see fig. 6a) appears more uniform than Board B (see fig. 6d) with a mat of large bundles and individual fibers throughout. Images of both A and B samples show the distinct serrated epidermal cell features with the teeth interlocking (see fig. 6b). Some elements of straw can resemble hardwood, such as the pitted vessel element shown in figure 6c; however, the pitting in straw is closer together and round or slit-like (Herzberg 1902, 78).

ATR-FTIR Spectroscopy Analysis

ATR-FTIR was helpful in identifying potential adhesives and binders used in the production of the boards. When analyzing Board A, it was interesting to find that the only sample with a possible resin was the exterior of the board, which had a carbonyl peak (fig. 7a). There was no sign of proteinaceous material, resin, or oil detected in the interior of the board. Sample Board A1 was split into two layers to analyze the join between the material (Board A interior). This lack of material

Fig. 5. Possible esparto. a. Board A2, purple Herzberg stain, serrated epidermal cells over fibers; b. Board B, Herzberg stain, serrated epidermal cell, bast cell, and long parenchyma. Possible comma-shaped hair (arrow) and purple stain associated with esparto.

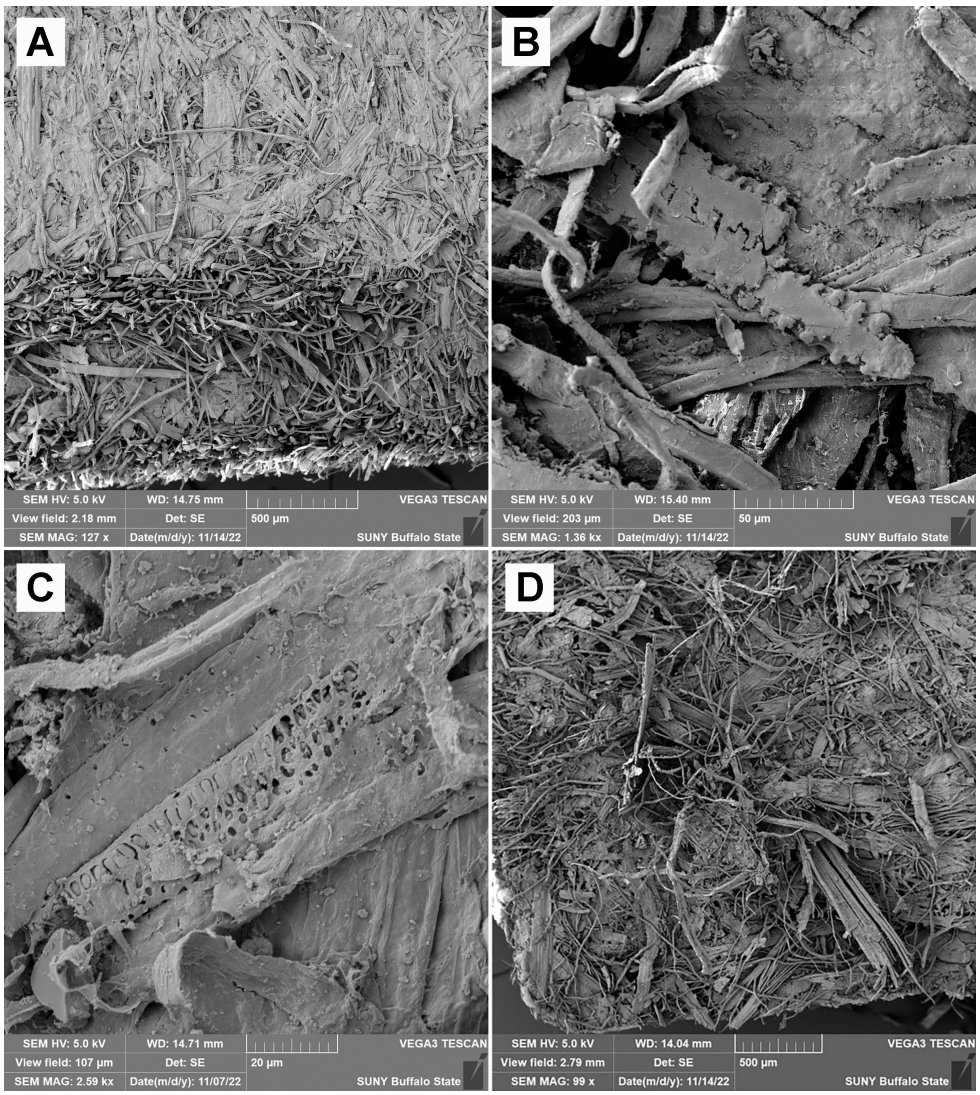


Fig. 6. SEM images. a. Board A1, recto; b. Board A1, verso, detail of interlocking serration; c. Board A2, center layer; d. Board B showing fiber bundles.

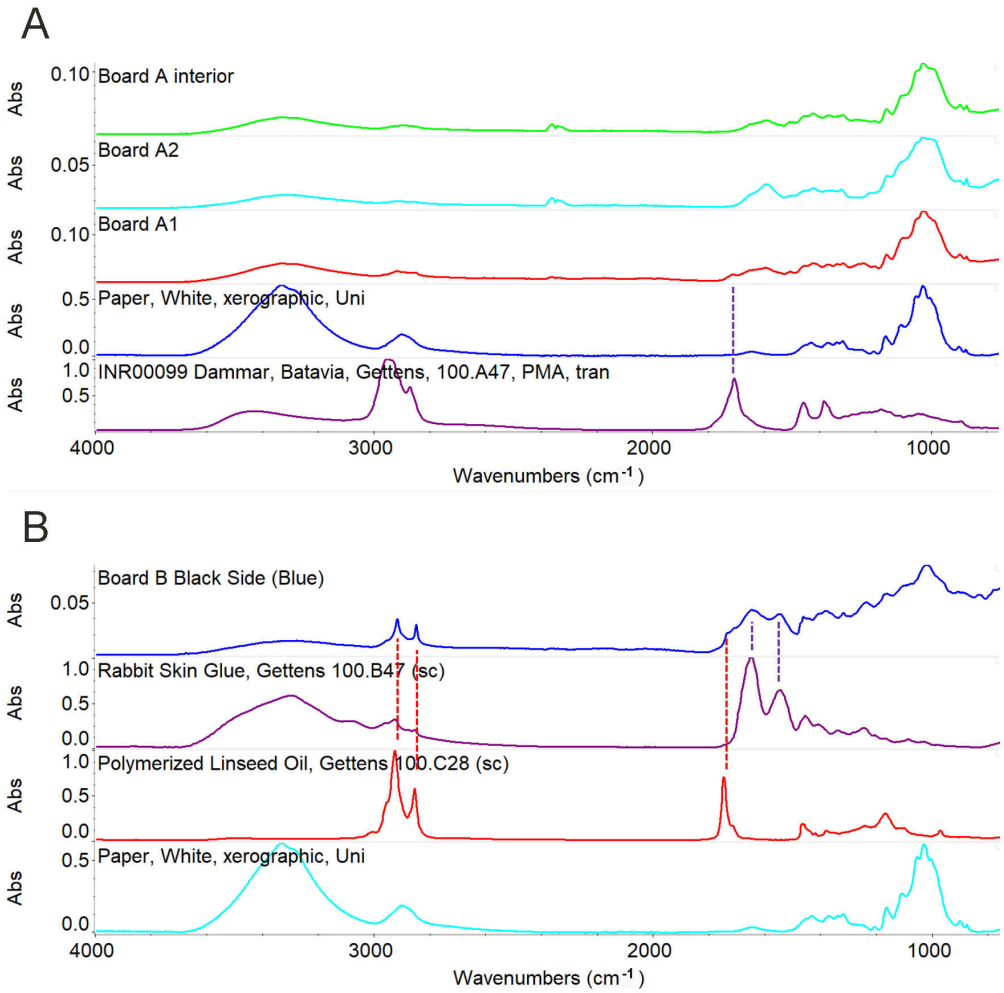


Fig. 7. ATR-FTIR spectra. a. Board A1 (exterior) shows potential evidence of an oil or resin, whereas the interior sample of the board does not; b. Board B, facing paper, artwork side. Possible proteinaceous material and an oil or resin.

on the interior supports the literature reference to strawboard being made on a multi-vat cylinder mould machine that would couch together the wet sheets, moving from one vat to the next without the use of adhesive. This would also explain how the central layer (Board A2) was incorporated as a different composition.

Both sides of Board B had papers adhered: on one side was a mounted print, and on the other side was black facing paper. Facing papers were removed for testing. The spectrum for the artwork side shows a possible match to a proteinaceous material, such as an animal glue used to attach the artwork, and also an oil or resin, which may be from the binding medium in the printing ink (see fig. 7b).

TAPPI 509 Analysis

The pH of both boards was taken (Table 2). A 1.0 g sample of Board A1 (the primary component) was cut into approximately 5 × 5 mm pieces and soaked for 1 hour before testing the pH. Upon addition of the sample to deionized water, discoloration immediately began to leach out into the solution. Over the course of an hour, the color of the solution did not change markedly from the initial 10 minutes of soaking. Before acquiring the pH, the solution was stirred and a small amount decanted for the pH reading. The meter was

Sample	Average pH	Observations
Board A1 (primary board material)	8.0	Produced the most discoloration
Board A2 (central layer)	8.9	Significantly higher pH, possibly from interior location and fiber processing
Board B (facing papers removed)	7.6	Slowest to wet up

Table 2. Average pH From the Cold Extraction Method

Fig. 8. Control coupon (left) and Board A strawboard coupons (right) after 29 days. Copper (left), lead (center), and silver (right).

calibrated with two-point calibration using pH 4.01 and 7.00 proprietary buffer solutions. The sample was measured twice with a pH of 8.0 both times. The remaining samples were prepared in the same way and measured twice with resulting pH of 8.8 and 8.9 for Board A2 (central layer), and 7.6 and 7.6 for Board B samples. During sample preparations, observations were made that Board B did not absorb water as readily as Board A samples. This may be due to the adhesive on Board B, which could inhibit the water from easily penetrating the sample. The lower pH of Board B may also be attributed to the presence of the proteinaceous material and oil or resin identified by FTIR, which has likely degraded and subsequently lowered the overall pH of the board.

Unlike wood fibers, straw is a naturally alkaline material with a pH above 7 and buffering capabilities (Halvarsson, Norgren, and Edlund 2010). The alkaline pH reading also supports the historic use of either caustic soda or lime cooking processes, which would impart an alkaline reserve in the strawboard material. The significant difference between Board A1 and Board A2 may be related to the processing method used. The central layer is extremely rough and brittle, which is in line with the description of the lime pulping process described in the 1929 patent (Weston and Clark 1929). The primary board material may have been made with caustic soda pulping, which would produce a finer furnish and less brittle board. Another contributing factor for the difference in pH between Board A1 and Board A2 is that the central layer (Board A2) is not exposed to the environment and therefore would degrade at a slower rate than the exposed outer layers.

Material Suitability Testing

Material suitability testing, such as the Oddy test, can be used to determine if destructive components of a material will off-gas and cause damage to an object. Samples are compared to a control and based on visual observations are given a rating of permanent, temporary, or unsuitable (fig. 8). When the test tube was opened, it smelled strongly of fermented plant material, and the culture tube was nearly empty of water, the board having likely absorbed it. The sealed test tube was weighed before aging and recorded as having a weight of 51.5 g; after aging, it weighed 51.4 g. This suggests a strong seal and an anaerobic environment that would result in decomposition, much like a sealed bag of leaves being turned into compost. Possible volatile organic compounds (VOCs) created during this decomposition process of plant material include hydrogen sulfide, mercaptans, organic acids, ammonia, methane, and carbon dioxide (Texas AgriLife Extension Service 2009).

The copper coupon showed no signs of corrosion and was rated as permanent. Both the lead and silver coupons were rated as temporary. The lead coupon had an overall white discoloration and a concentration of dense yellow corrosion located on the portion of the coupon that was inserted into the stopper. It was rated as temporary due to the bulk of the corrosion occurring on the part of the coupon inserted into the stopper. It is possible that the stopper may have been contaminated inside. The silver had a thin white hazy swatch on both sides. The relatively good results could be attributed to the age of the sample, with the bulk of any possible VOCs having already been off-gassed. Based on the results, this sample should be considered temporary.

FUTURE WORK

This research would benefit from the use of a much larger sample pool. This would help with gaining a better understanding of the typical composition of strawboard. Comparison of boards with and without facing papers would help determine whether there is a correlation in pH as was seen in this study. Additionally, studying the artwork associated with the boards could further the understanding of the interaction between the two materials. Because material suitability testing was only run on one sample and is a subjective test, it could be helpful to use additional tests. For example, microchemical tests and direct isothermal desorption gas chromatography mass spectrometry (DID-GC-MS) could be used to identify specific VOCs harmful to the works on paper. Finally, differentiating between the sources of straw (barley, wheat, rye, and oats) would require an extensive collection of fiber element measurements, as the ranges for the different types tend to overlap. Better separation and staining of the fiber samples, possibly using additional staining techniques such as Graff C, could help identify these different fiber elements and types of straw.

CONCLUSIONS

Based on the fiber elements seen using PLM and SEM analysis of the two samples, the composition of both boards appears to be predominantly straw with some other fiber inclusions. FTIR suggests that the interior of the boards does not contain adhesive, which is consistent with a multi-vat cylinder mould production process associated with strawboard. The carbonyl peak associated with a resin found on the surface of Board A is likely a contaminant rather than something introduced during the production of the board. The addition of facing papers was common due to the brittle nature of strawboard, and FTIR was able to detect both a proteinaceous and possible oil or resin material suggesting an adhesive and binding medium. While facing papers may add structural support that the board lacks, they can introduce acidic degradation products into the artwork through contact with the poor-quality facing papers and the adhesive used to attach them. The difference in pH between the two board samples, one with facing papers and one without, supports the idea that the materials associated with the facing papers could lower the board's pH. Straw is naturally more alkaline than wood pulp, and both possible processing methods involve alkaline chemicals. The stark white of the artwork attached to Board A prompted this research and can reasonably be attributed, in part, to the alkaline nature of the bare strawboard on which it was mounted. As a secondary support, strawboard without facing papers does not appear to present a threat to artwork in the form of chemical degradation through acidic hydrolysis and the production of degradation products; however, it cannot adequately provide the structural support that the artwork requires and could cause staining if it comes into contact with moisture.

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