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Optically Cleared Repair Tissues for the Treatment of Translucent Papers

INTRODUCTION

There are many types of translucent papers, each with its own set of conservation issues stemming from various manufacturing processes. The characteristic that makes them stand apart from other papers—transparency—can itself be at risk when there is a need for applying mending or lining tissues. This project explores the physical aspects of paper transparency and investigates the concept of optical clearing (transparentizing) of repair tissues, with the goal of achieving appropriate repairs on translucent papers without dramatically increasing the opacity of treated areas. The term "optical clearing" is borrowed from the fields of biology and medical research. It refers to the process of rendering biological tissues transparent through the application of clearing agents, which minimize the scattering of light and allow greater visibility for microscopy and imaging. This is similar to some historical processes of transparentizing paper, in which oils, waxes, and rosins were added to fill light-scattering interstices, allowing more light to travel unimpeded through the paper web. This concept is applied to conservation repair tissues, with the goal of determining a coating to serve dual functions: optical clearing agents and reactivatable adhesive.

OBJECTS TO BE TREATED

In 2016, two late-19th-/early-20th-century print portfolios bearing transparent overlays came down to the conservation lab at Northwestern University Library:

1. *Atlas Photographique de la Lune* (1896–1910) by Maurice Loewy & Pierre Henri Puiseux. A collection of 73 photogravure heliographs of the moon's surface. Each plate possesses a translucent tissue overlay with printed keys indicating the geographic characteristics depicted in the plates (fig. 1).
2. Frank Lloyd Wright's *Ausgeführte Bauten und Entwürfe* (1910–11), commonly known as the *Wasmuth Portfolio.* This two-volume work showcased Wright's architectural work to date with 100 lithograph plates, 27 of which are on translucent tissues tipped to the heavier plate with which they are associated (fig. 2).

There was significant damage to the tissues on both of these objects, with prominent tears and breaks that required mending. The translucent papers feature prominently in these two objects, and they rely both aesthetically and functionally upon the tissues' transparency: viewers are meant to see what is printed on the tissue and on the adjoining plate simultaneously. These items served as the impetus for this research project.

PAPER OPACITY

LIGHT AND PAPER

Light interacts with matter in two basic ways: scattering and absorption. Scattering involves a change in lightwave direction. *Elastic scattering* is what is typically called "reflection"; it involves the light bouncing from the material surface. *Inelastic scattering* is what is commonly called "refraction"; it is the bending of the light's path as it passes from one material to the next. This tendency to bend light is expressed as the material's refractive index (RI, or n). A bend in the path of light occurs when it passes from one material into another with a different RI; the greater the difference in RI, the larger the angle of divergence (Tilley 2011).

The interaction of light with paper is complicated by paper's disordered physical structure. Paper, at its simplest, is made of a web of cellulose fibers, which are themselves constructed of networks of macro- and microfibrils. Paper is far from a "pure" substance; it is anisotropic, stochastic, and heterogeneous.

Pure cellulose itself is a translucent material, absorbing only in the UV (Hubbe, Pawlak, and Koukoulas 2008). It has an RI between 1.46 and 1.56, depending on its origin (Saarela, et al. 2008). But between the cellulose fibers in paper are pockets of air, which has an RI of 1.0; 50% or more of the volume of a typical sheet of paper is occupied by air (Hubbe, Pawlak and Koukoulas 2008). When a wave of light attempts to pass through paper, it has to transition back and

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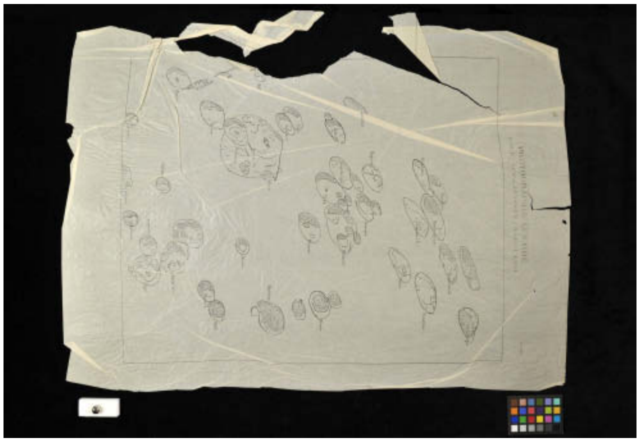


Fig. 1. A damaged translucent overlay from *Atlas Photographique de la Lune*.

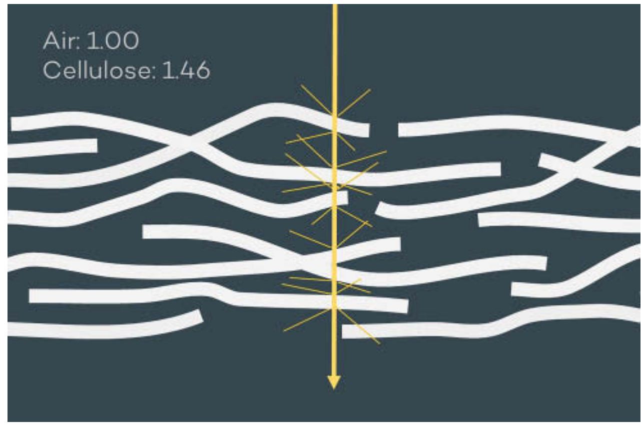


Fig. 3. A beam of light encounters many scattering surfaces as it attempts to transmit through a disordered medium like paper.

forth between air and cellulose a large number of times. (This is complicated even more by nonuniformities within the fibers, which present more transitions.) Each transition presents the potential for scattering. When confronted with dozens of layers of fibers, there is little chance for each wave of light to make its way through a sheet of paper (fig. 3). A beam of light that hits paper gradually diminishes in intensity as it penetrates the layers in a process called "attenuation" (Tilley 2011).

HISTORICAL PRODUCTION OF TRANSLUCENT PAPERS

In the vast majority of its use, opacity is a desirable quality in paper. Printers need to be able to place text on both sides of a leaf without it showing through to the other side. But for use as tracing paper or overlay, papermakers have found means of making paper more transparent. "Translucent paper" is used here as an umbrella term for any paper that has had its opacity reduced through in-production means. Detailed explanations of these processes, as well as means of categorization and identification, are available in several other articles (Bachmann 1983; Homburger and Korbel 1999; Laroque 2000). The four primary historical methods of transparentizing are as follows:

Fig. 2. A damaged translucent plate from the *Wasmuth Portfolio*.

1. Impregnating: Following formation of the sheet, the paper is coated with oil, resin, or wax that fills the light-scattering interstices between the fibers. This was the earliest method widely used (Bachmann 1983).
2. Acid treatment: An acid bath (typically sulfuric acid) causes a colloidal cellulose layer to coat the fiber web and fill the light-scattering interstices. This was a mid-19th-century development (Homburger and Korbel 1999).
3. Overbeating: The pulp is beaten for a longer period than normal. The fibers in the formed sheet are more fibrillated (interconnected), and, with this higher Relative Bonded Area (RBA), there are fewer light-scattering interstices present. This method came about in the late 19th century (Homburger and Korbel 1999).
4. Calendering (or supercalendering): This is done in combination with other processes; it encourages greater interconnectivity of the fibers and tends to give the paper a glossy surface (Laroque 2000).

The overarching theme of these methods is the formation of a more cohesive, interconnected sheet. In a sense, the goal is to bring the sheet from the typical "web" structure of paper towards more of a homogeneous "film" to avoid the scattering of light.

TREATMENT OF TRANSLUCENT PAPERS

As a result of these production methods, translucent papers possess several unique sensitivities, which can vary wildly by category. Some are highly hygroscopic and sensitive to polar solvents and may expand and warp dramatically in their presence (Van der Reyden, Hofmann, and Baker 1993). Others may resist the absorption of water due to their film-like quality or due to the presence of impregnating agents (Page 1997). Impregnating agents can also be disturbed by solvents, making those papers susceptible to loss of transparency (Van der Reyden, Hofmann, and Baker 1993).

An extensive literature review of the treatment of translucent papers was published in 2000 by Claude Laroque in *Studies in Conservation* Volume 45 (International Institute for Conservation of Historic and Artistic Works). This project will not present its own literature review of translucent paper treatment to avoid repetition. Needless to say, a very wide range of treatments have been explored in the past, from standard "wet" linings with wheat starch paste to reactivated precoated tissues (reactivated with either solvent or heat). The adhesives and carriers used by conservators have ranged from the more traditional (starch pastes, proteinaceous glues; Japanese tissues) to the modern (polyvinyl acetates, acrylic-based adhesives; nonwoven nylon). Maintenance of transparency is an aspect of treatment that has mostly been treated in qualitative terms. This is likely due to availability of equipment and a reliable testing method. One previous article included quantified opacity measurements of modern tracing papers, and characterized changes in opacity in response to various solvents (Van der Reyden, Hofmann, and Baker 1993). But increases in opacity due to the application of repair tissues have not been the focus of these studies.

Adding material to translucent papers, as in mending or lining, will inevitably increase the opacity of the treated area. This issue has previously been approached through the use of extremely lightweight Japanese tissues. The great length and strength of kozo fibers allows for a sheet with very low mass with relatively high durability. The low mass of the paper means there is less material for light to penetrate in transmitting through the paper. This follows basic logic: the lower the mass of the repair tissue, the smaller the increase in opacity.

Recent developments in the production of nanocellulose have led to the introduction of nanocellulose papers into the conservation field, which have been proposed for the treatment of translucent papers. The nanofibrils or nanocrystals that compose these papers are of such small size (10–20 nm in diameter, 2 μm in length) that interstices between the fibers are reduced enough to avoid the scattering of light (Dufresne 2012; Hu et al. 2013). Papers made from a combination of Japanese fibers and nanocellulose are also available, as in Bacterial Cellulose (BC) paper made by Gangolf Ulbricht.

OPTICAL CLEARING

This project seeks to establish another means of achieving low opacity in repair tissues, and borrows the concept of *optical clearing* from the fields of biology and medical research. Optical clearing (also called refractive index matching) refers to the process of rendering biological tissues translucent through the application of *clearing agents*, which minimize the scattering of light and allow greater visibility for microscopy and imaging (Tunchin 2007). Much like paper, biological tissues are disordered media made up of networks of polymeric fibers. The ideal clearing agent has an RI similar to that of the fibers; the agent replaces the air between the fibers and serves as a "bridge" of easier transition for the light (fig. 4). The closer the refractive indices of the fiber and clearing agent, the less chance for scattering (Saarela et al., 2008). The historical transparentizing method of impregnation is itself an optical clearing process.

Fig. 4. A clearing agent provides a bridge of easier transition between the fibers of a disordered medium.

Though the term may be unfamiliar, optical clearing is something that conservators encounter on a regular basis. The tendency of repair tissues to become transparent when wet with paste is an optical clearing process, with water serving as the primary clearing agent. This project seeks to explore the possibility of a more permanently and efficiently cleared state. The ideal coating would serve dual functions: reactivatable adhesive and optical clearing agent.

TESTING

OPACITY MEASUREMENT

Opacity readings for this study were taken using an X-Rite i1Basic Pro 2 spectrophotometer, in conjunction with Color Translator & Analyzer (CT&A) software by BabelColor. The system uses a Contrast Ratio Opacity (OP) measurement, as defined by ISO 2471. Measurements are taken via two consecutive readings: first, with the sample placed over a white (highly reflective) backing; second, with the sample placed over a black (highly absorbent) backing. The spectrophotometer measures the brightness of each, and performs the following function:

$$\text{Opacity (Y)} = \frac{Y\ (black)}{Y\ (white)} \times 100.$$

This function provides the opacity measurement, expressed as percentage opacity (e.g., a fully opaque material would have an opacity of 100%).

A white/black backing was fashioned in-house for the opacity measurements in this project. Teflon film, which provides 99% reflection across the visible spectrum, was used for the white backing. A black cavity, as described by ISO 2471, was made for the black backing; this was constructed out of thick mat board, painted black, with a hole the size of the spectrophotometer lens cut into it, adhered to a piece of board coated with Avian Black-S Coating by Avian Technologies, LLC (fig. 5). This provides a near 0% reflection across the visible spectrum.

A Note on Percentage Opacity vs. Percentage Change

Some figures in this project are expressed as percentage opacity, and others as percentage change in opacity. These can be confusing. A repair tissue with a starting opacity of 20% can be optically cleared to an opacity of 2%; this means a reduction of 18% opacity, which is a decrease of 90% of its original opacity (or a "percentage change" of –90%).

Fig. 5. The white/black backing fashioned for the Contrast Ratio Opacity measurements.

Similarly, a substrate with a starting opacity of 50% can be increased to 55% following the application of a mend; this is a 5% opacity increase, and a percentage change of +10%. When it comes to affecting the visual appearance of a substrate, it is percentage change in opacity that really matters. A substrate with a starting opacity of 20% is far more affected by a 5% increase than a substrate with a starting opacity of 75%; the first would have a percentage change of +25%, the second a change of +8.3%.

TEST 1: OPTICAL CLEARING WITH CONSERVATION ADHESIVES AND COATINGS

The first test conducted was designed to measure the optical clearing efficacy of a variety of adhesives and coatings commonly used and trusted in book and paper conservation. The test also sought to determine what conservation repair papers are most effectively cleared.

Methodology

Seven tissues were included in this test. Five relatively lightweight Japanese repair tissues were selected that exhibit an array of qualities: a lightweight white kozo paper (Tengujo 5g); a colored kozo paper (Somegami 5g); a medium-weight white kozo paper (Uso Mino 12g); a lightweight gampi paper (Usuyo 11g); and a medium-weight gampi paper (C-Gampi 16g). Also included were two papers that incorporate nanocellulose materials. A film made purely of nanofibrillated cellulose was acquired from Innovatech (henceforth referred to as MFC, short for microfibrillated cellulose). The seventh paper tested was BC Tissue by Gangolf Ulbricht, a paper made from a combination of bacterial nanocellulose and kozo/mitsumata fibers. This paper is specifically marketed for the treatment of transparent papers (Seger and Kochendörfer 2015).

Samples were cut at 3 cm^2 and divided into groups: three samples of each tissue for every adhesive to be tested. All samples were measured for opacity using the contrast-ratio method. The samples were then coated with their corresponding adhesives,[1] allowed to dry, and then measured for opacity a second time (figs. 6 and 7).

Results

The two most successful optical clearing agents tested were Plextol B500 (fig. 8) and Avanse MV-100, the two adhesives described for preparing heat-set tissue by conservators at the National Archives and Records Administration (NARA) in their article on that subject (Varga, Herrmann, and Ludwig 2015). Plextol caused an average percentage change of –65%. The very lowest reading in all the samples occurred in the BC Tissue coated in Plextol at a mere 1.5% opacity (fig. 9).

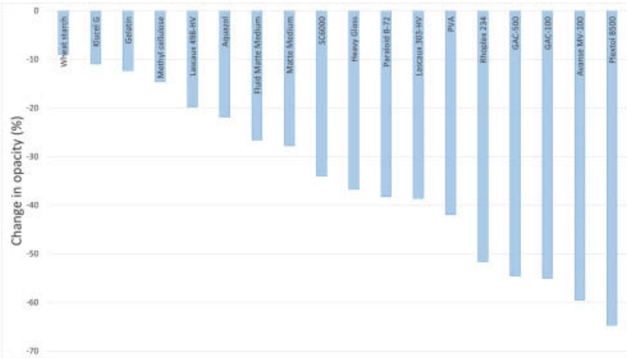


Fig. 6. The results from Test 1, condensed in terms of average percentage change in opacity by coating, in order of least effective to most effective.

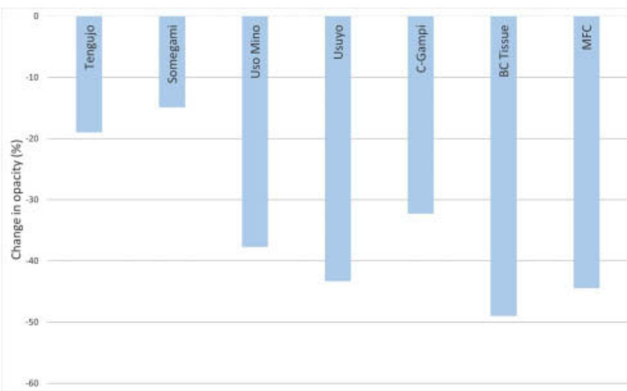


Fig. 7. The results from Test 1, condensed in terms of average percentage change by paper type.

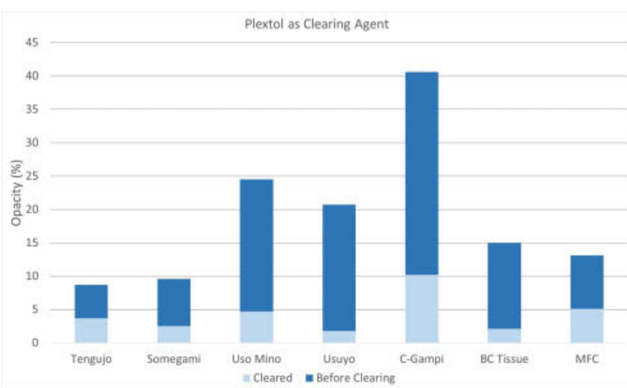


Fig. 8. The results of the most effective clearing agent, Plextol B500. The darker segments of the bars are the papers' original opacities, and the lighter segments are the optically cleared opacities.

The two papers that incorporate nanocellulose exhibited the greatest flexibility in opacity. Where the solution-based adhesives (e.g., methyl cellulose) caused little change in the traditional papers, they successfully cleared the nanocellulose papers. BC Tissue performed the best overall, with an average drop of nearly 50% across all adhesives. The largest individual decrease in opacity occurred in the Usuyo gampi paper coated with Plextol, which dropped by over 90% of its original opacity (fig. 10).

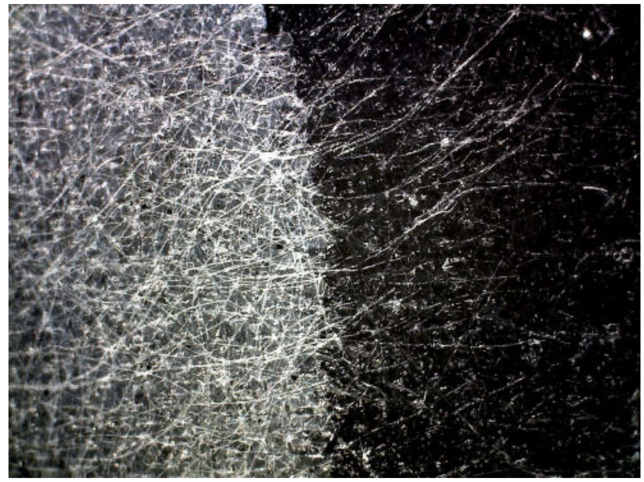


Fig. 9. A sample of BC Tissue over a black background (140× magnification). The left side is uncoated, and the right side has been optically cleared with Plextol B500.

Plextol and Avanse were followed by GAC-500, GAC-100, and Rhoplex AC-234, all of which are acrylic dispersions. Acrylic-based adhesives proved to be the most effective in lowering the opacity of repair tissues. Acrylic dispersions have fantastic film-formation properties, meaning their drying process results in very cohesive, even films, free of voids and irregularities (Chorng-Shyan 2008; Lovell and El-Asser 1997).

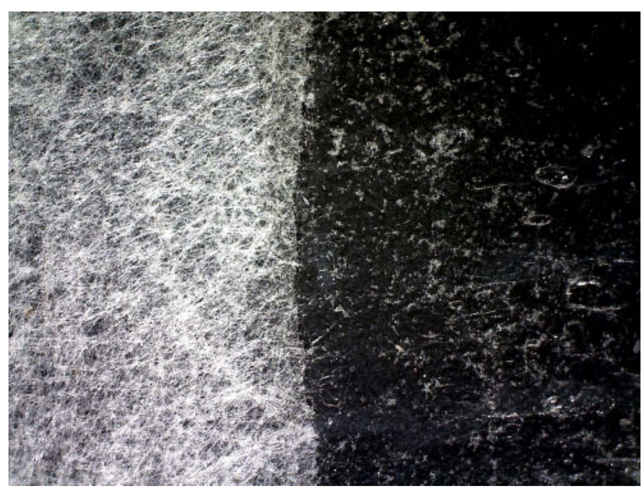


Fig. 10. A sample of Usuyo gampi over a black background (140× magnification). The left side is uncoated, and the right side has been optically cleared with Plextol B500.

This is ideal for the optical clearing process, where the goal is to disperse all air from the paper web. The RIs of all acrylic components fall within a very close range of the cellulose RI,[2] so an effective match is achieved for smoother transitions between fibers. Acrylic polymer chains are highly irregular, with bulky branches and side groups. Because they cannot be packed into crystalline formations, they form isotropic and 100% amorphous films, making them ideal for light transmission, with no crystalline areas to cause scattering (Seymour and Carraher 1984; Chorng-Shyan 2008).

Of the traditional repair papers, the gampi tissues showed a much greater flexibility in opacity. For example, whereas Tengujo had a starting opacity (average 9%) significantly lower than the Usuyo (average 20%), the Usuyo opacity consistently dropped below that of Tengujo after coating. Gampi tissues exhibit a higher RBA—their fibers are more interconnected with smaller interstices, and the fibers are much smaller than the highly visible kozo fibers.

The opacity of the nanocellulose papers proved to be more flexible than the traditional papers and reacted differently to some of the coatings. Where the nonacrylic adhesives did little to reduce opacity in the Japanese tissues, there was success in clearing the BC tissue with Aquazol (–61.6%). Similarly, the MFC was successfully cleared with gelatin (–49.13%) and Aquazol (–63.4%).

It was assumed that the MFC would clear the most successfully and achieve the lowest opacities, but this was not the case across all adhesives. Whereas the MFC achieved the lowest readings in the solution-based adhesives (wheat starch paste, methylcellulose, Aquazol, Klucel G), it cleared less with dispersion-based adhesives (Jade 403, acrylics). This may be due to the size of the particles in polymer emulsions, which may be too large to effectively penetrate the microscopic interstices between the MFC's microfibrils.

Only one of the adhesives dramatically *increased* sample opacities: Rhoplex AC-73 (average +62.1%). This is certainly due to the minimum film-formation temperature (MFT) of this acrylic dispersion, which is 37°C (98.6°F). All coatings were applied at room temperature (72°F), and the AC-73 subsequently dried to a brittle, opaque crust. When applied to the Usuyo gampi tissue over a hot plate set to 80°C, the Rhoplex AC-73 did successfully lower the opacity of several samples to a degree visually comparable to some of the other acrylic dispersions.

Lascaux 498-HV, which is perhaps the most commonly used acrylic adhesive in book and paper conservation, did not perform well in comparison to other acrylic dispersions, resulting in an average 20% decrease in opacity across all papers. It was outperformed even by the matte mediums, which contain light-scattering agents. Following the success of the heated Rhoplex AC-73 application, a similar test was performed with Lascaux 498-HV. With its MFT at 5°C (41°F), a film-formation temperature higher than room conditions may help with the adhesive's clearing efficacy. A small amount of diluted 498-HV was heated to 80°C and applied to samples of the Usuyo gampi tissue, which were also kept warm over a hot plate. The clearing was improved from a mere –10% at room temperature to –55%.

TEST 2: DILUTION AND OPACITY

It is standard practice to apply precoating adhesives to repair tissues in highly diluted states. This is done to obtain a coating that is as thin as possible upon drying while still achieving appropriate adhesive ability. A coating that is too thick can cause unwanted aesthetic effects (gloss) as well as tackiness and excessive adhesive penetration into the treated substrate. In Test 1, all adhesives were applied in relatively thick states to avoid variables and to observe the greatest potential for clearing. All of the acrylic adhesives, for example, were applied entirely undiluted.

The Avanse/Plextol recipe laid out by Varga, Herrmann, and Ludwig calls for a 4:1:1 mixture, with four parts water diluting one part Avanse MV-100 and one part Plextol B500. At the time, their study found this to provide the ideal coating to avoid tack and sheen while still achieving adequate adhesion (Varga, Herrmann, and Ludwig 2015) on most papers.

Methodology

A simple test was devised to observe the effects of dilution on the optical clearing capabilities of the top-performing clearing agents, Avanse MV-100 and Plextol B500. Six ratios of the Avanse/Plextol mixture were made: a 1:1 undiluted mixture, followed by five increasingly diluted mixtures (1:1:1, 2:1:1, 3:1:1, 4:1:1 and 5:1:1). Each ratio was applied to five samples of the Usuyo gampi tissue (this tissue showed the greatest percentage change in opacity for both Avanse and Plextol). The adhesive mixtures were applied by brush to both sides of one half of each 3 cm × 3 cm^2 sample. These were allowed to dry on a silicone baking sheet for 2 hours at room conditions (72°F, 40%RH). Two opacity measurements were then taken on each sample using the Contrast Ratio Opacity method. One reading was taken in the center of the coated area, and one reading was taken from the edge of the coated area; this was done to capture the variation in coating that occurred across the surface of the samples—the more dilute mixtures dried to uneven coatings.

Results

As expected, there was an obvious trend in the results, with a direct relationship between coating thickness and optical clearing efficacy (fig. 11). However, the decrease in clearing capability was less dramatic than expected within the first few levels of dilution; even at the 3:1:1 mixture, the Avanse/Plextol recipe was able to clear the Usuyo by 75% of its original

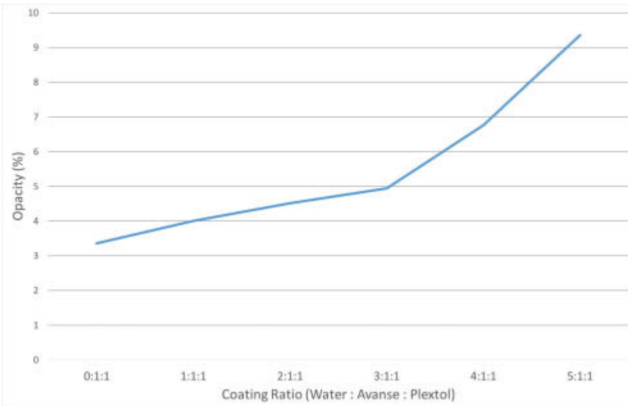


Fig. 11. The results from Test 2, showing a direct relationship between coating thickness and optical clearing efficacy.

opacity. Beyond this level of dilution, though, there is a definite upswing in opacity. When diluted beyond a certain degree, the dispersed polymer particles are interrupted by too much water and are unable to coalesce. Instead of a continuous film, a speckled pattern is formed within the cellulose web (fig. 12).

TEST 3: GLOSS AND OPACITY

There is a direct relationship between the efficacy of clearing agents and the resulting gloss of the cleared tissue. All of the most successful clearing agents in Test 1 also caused a significantly glossy surface. Acrylic dispersions form coherent films with very smooth surface topography; this extreme smoothness encourages both transmission and specular reflection of light (Tilley 2011).

Some acrylic media are designed to produce a relatively matte finish with the addition of a light-scattering substance (often a silica dust). Two matte mediums made by Golden Artist Colors were included in Test 1: Matte Medium and Fluid Matte Medium. These proved to be moderately effective clearing agents (both performed better than Lascaux 498-HV, for example).

Methodology

A test was devised to establish the relationship between gloss and transparency across varying mixtures of acrylic adhesive and acrylic matte medium. The test followed a similar procedure to the dilution/opacity test (Test 2): eight mixtures of matte/adhesive medium were made with an increasing ratio of matte acrylic medium to glossy acrylic adhesive (0:1, 1:4, 1:2, 1:1, 3:2, 2:1, 4:1, 1:0). Each mixture was applied by brush to both sides of five 3 cm × 3 cm[2] samples of the Usuyo gampi tissue. These were allowed to dry on a silicone baking sheet for two hours at room conditions (72°F, 40%RH). Two opacity measurements were then taken on each sample using the Contrast Ratio Opacity method. One reading was taken in the center of the coated area, and one reading was taken from the edge of the coated area (fig. 13).

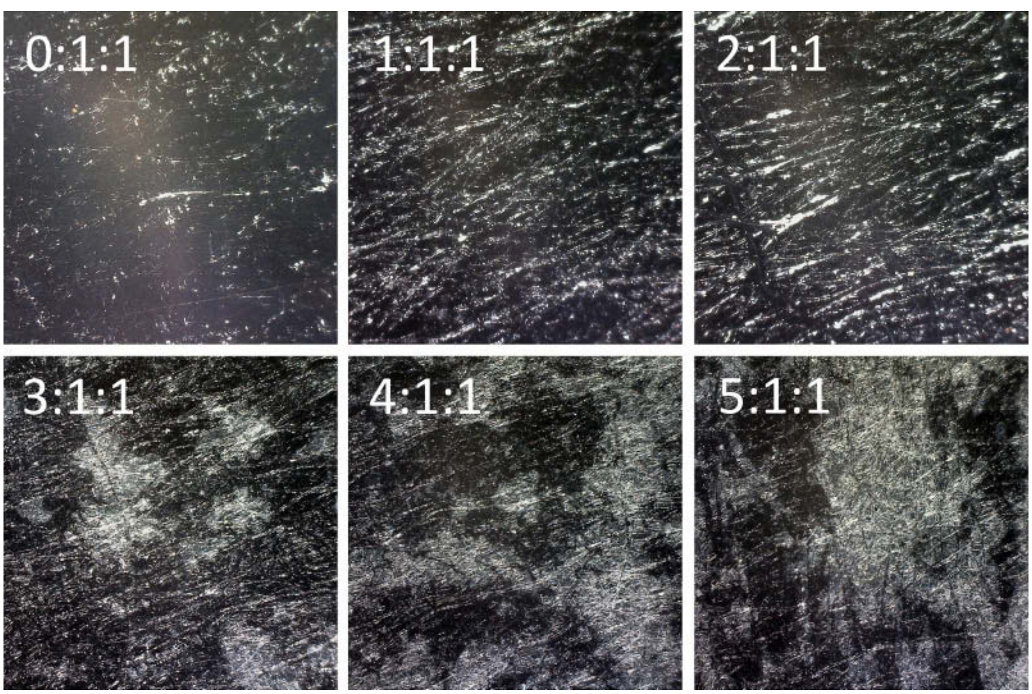


Fig. 12. Samples from Test 2 (140× magnification). A speckled pattern of uncoated fibers forms on the diluted samples.

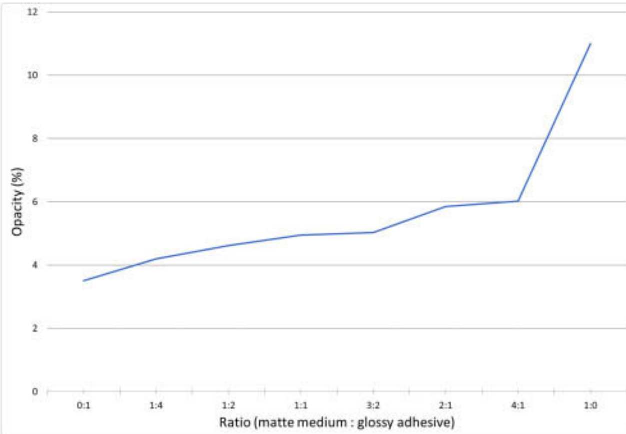


Fig. 13. The results from Test 3, showing a direct relationship between coating gloss and optical clearing efficacy.

Following the readings, the samples were photographed in raking light to capture a qualitative assessment of their glossiness (fig. 14).

Results

The resulting upward trend in opacity was less pronounced than expected—even the 4:1 mixture, with four times as much matte medium than glossy adhesive, remained at a relatively low opacity (6%, compared to the Usuyo tissue's original 20% opacity). The opacity nearly doubled between the 4:1 (6%) and 1:0 (11%) samples.

TEST 4: LIGHT-AGING AND OPACITY

The tendency of acrylic media to yellow over time, especially when stored in dark environments, is well documented (Whitmore and Colaluca 1995; Whitmore, Colaluca, and Morris 2002; Jablonksi, et al. 2003). Increases in turbidity have also been documented in acrylics. This may be caused either by the formation of crystallized particles within the acrylic film or by the migration of surfactants to the film's surface (Whitmore, Colaluca, and Farrell 1996; Hayes, Golden, and Smith 2006). Though many of the acrylic adhesives used in this study have been extensively tested and proven to have acceptable aging characteristics, it was determined necessary to observe the longevity of the clearing effects of these materials in relation to yellowing and turbidity.

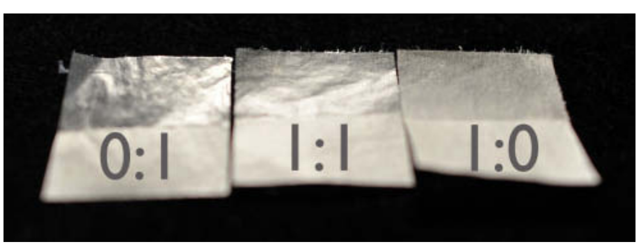


Fig. 14. Three samples from Test 3, showing the increase in gloss as the ratio of matte medium increases.

Methodology

Thirty samples of 3 cm^2 were cut from the Usuyo gampi paper. Fifteen samples were assigned to each of the two adhesives/coatings selected for aging: Plextol B-500 and Avanse MV-100. The samples were coated and divided into three groups: five of each adhesive to be dark-aged, five of each to be aged in sunlight, and five of each to be aged under fluorescent light. All samples were measured for opacity using BabelColor CT&A and for color profiling using X-Rite i1Profiler. Fifteen of the samples were also measured in their uncoated areas to obtain color-change information for the Usuyo tissue itself.

Three aging supports were cut from archival board and labeled. A sheet of silicone-coated polyester film, cut to the same size, was adhered to the board on the two vertical edges with double-sided tape. V-shaped slits were cut into the polyester film to serve as holding notches, so that each sample could be held in place without being adhered or covered. Opacity and color measurements (L⋆a⋆b⋆) were taken of all samples prior to aging. One aging support was placed in an archival box and stored in a cabinet (dark aging), one was placed under a fluorescent light in 24/7 operation (fluorescent aging), and one was placed in a southeast facing glass window (daylight aging). Each aging support was accompanied by a blue wool standard (BWS). Color profiling measurements were taken of each BWS prior to aging.

Each sample was measured for opacity (BabelColor CT&A) and color profile (X-Rite i1Profiler) every 30 days. Exposed (uncoated) areas of the Usuyo tissue were also measured for color profile to factor in any changes occurring within the paper itself. To obtain color-change information, the profiling information for each month's readings were compared to that of the 0-day readings using the i1Profiler data analysis software, which generates a L⋆a⋆b⋆ delta E⋆ ($\Delta E^\star$) figure for each sample. (It is typically said that a distinguishable change in color begins at $\Delta E^\star$ 1.0, though a 2.0 indicates readily noticeable color change).

Results

In terms of color change, the Avanse MV-100 performed very well; none of the color changes in any of the three exposures reached $\Delta E^\star$ 1.0 (fig. 15). Plextol B500 exhibited a small amount of color change; the samples exposed to daylight reached $\Delta E^\star$ 2.0 at 120 days and then stabilized (fig. 16). These changes occurred as a *decrease* in yellow tones. This change was exhibited even more strongly in the light-exposed Usuyo; both the fluorescent and daylight samples surpassed

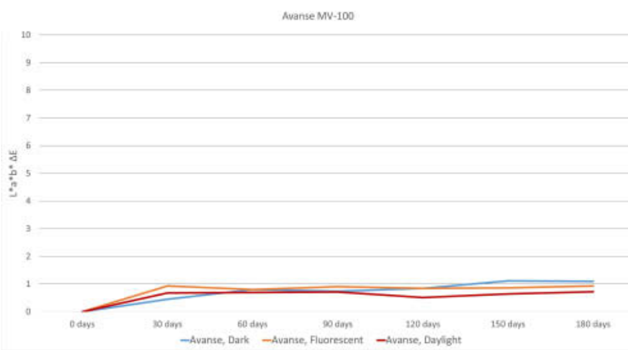


Fig. 15. Color change observed in the Avanse samples, in terms of $\Delta E^\star$.

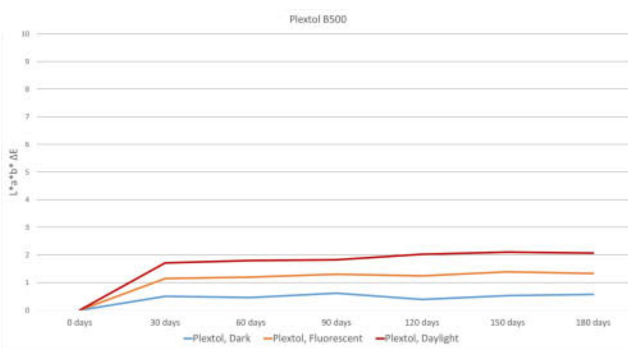


Fig. 16. Color change observed in the Plextol samples, in terms of $\Delta E^\star$.

$\Delta E^\star$ 2.0 after 60 days, indicating light-bleaching. It is possible, then, that any color change observed in the coated samples was occurring in the paper itself, rather than in the coating.

In terms of opacity, Avanse exhibited more change, with a slight increase in opacity observed in the light-exposed samples. The daylight-exposed samples increased from an average of 2.26% to 6.04% over 180 days (fig. 17). This change was noticeable to the naked eye; there was a clear turbidity increase in the light-aged Avanse samples (fig. 18). This haziness could be caused by the migration of emulsifiers to

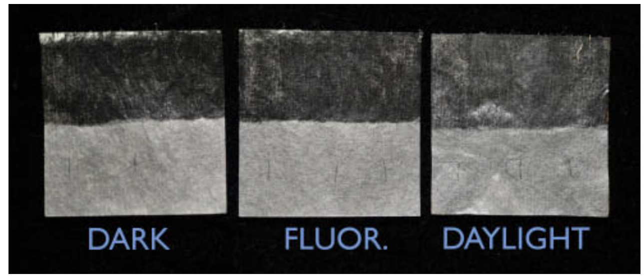


Fig. 18. Avanse samples, seen after 120 days of aging.

the film's surface, or by oxidation and scission of the polymer chains, causing the formation of micropores (Jablonski et al. 2003; Hayes, Golden, and Smith 2006). It should be noted, however, that this decreased opacity is still far lower than the 20% average for the uncleared Usuyo. The dark-aged samples exhibited a negligible amount of change.

The Plextol samples proved far more stable in terms of opacity (fig. 19). Though there was a very small increase in average opacity in the daylight-aged samples (1.48% to 2.51%), all of the readings taken were within the normal range of a newly coated sample.

TEST 5: APPLICATION METHOD AND OPACITY

As demonstrated by Test 1, conservation adhesives can be used to dramatically decrease the opacity of repair tissues. The last test series was designed to illustrate the effectiveness of optical clearing in the context of application to translucent substrates. The goal was to compare the effect of using optically cleared tissues to some other common repair application methods.

Methodology

Two modern transparent papers were selected: an interleaving tissue with a matte surface and a glassine with a glossy surface. These were cut to 10″ × 10″ and divided with pencil

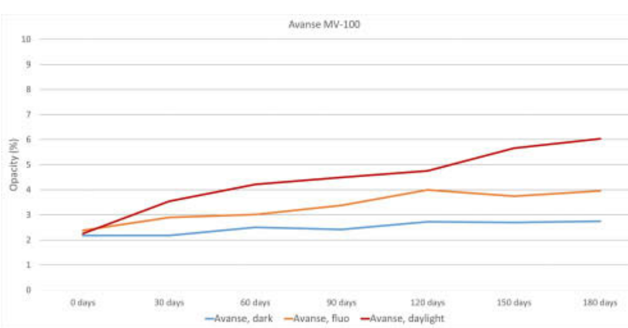


Fig. 17. Opacity change observed in the Avanse samples.

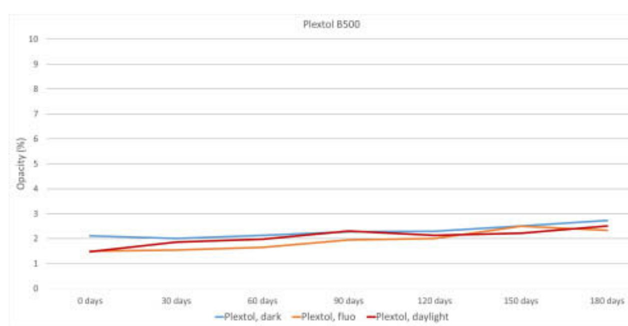


Fig. 19. Opacity change observed in the Plextol samples.

into 25 boxes—five columns of five boxes each. Five treatment methods were selected for testing:

1. Wet application with wheat starch paste, using the 10% recipe of standard use in the Northwestern laboratory, dried under weight with blotter and Hollytex.
2. Tissue precoated with a 50/50 wheat starch paste/methyl cellulose mixture, reactivated with gellan gum and dried under weight with blotter and Hollytex.
3. Tissue pre-coated with Klucel G (1%), reactivated with a 50/50 ethanol/acetone spray over a suction table (as described by Susan Page in her 1997 BPG *Annual* article).
4. Tissue pre-coated with a 4:1:1 mixture of water/Plextol B500/Avanse MV-100 (as described by Varga, Herrmann and Ludwig in their 2015 BPG *Annual* article), reactivated with a tacking iron.
5. Tissue precoated and optically cleared with a 1:1:1 mixture of water/Plextol B500/Avanse MV-100, reactivated with a tacking iron.

Prior to treatment application, opacity readings were taken of the transparent papers in the areas to be treated. The interleaving tissue and glassine had average opacities of 28% and 30.6%, respectively.

All five of the treatments were executed using BC tissue by Gangolf Ulbricht, as this tissue achieved the lowest opacity readings in the optical clearing test. All treatments were applied with samples of BC tissue cut to 1” × 1”. Following treatment, two opacity measurements were taken of each treated area: one in the center and one at the sample edge (fig. 20).

Results

There were consistent differences in the final opacities of the treated areas, which could be clearly seen with the naked eye (fig. 21). The tissues precoated with Klucel G and applied over the suction table resulted in the greatest increase in opacity, adding over 8% opacity to both the interleaving tissue

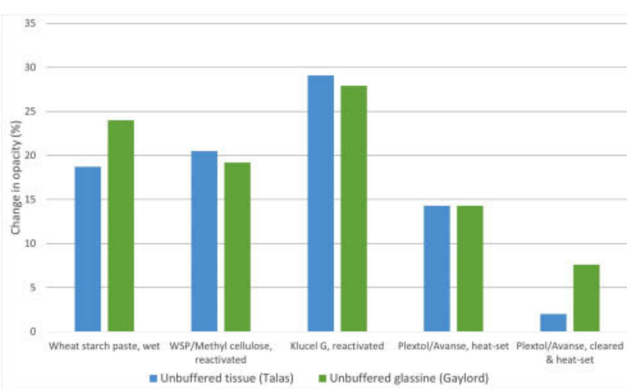
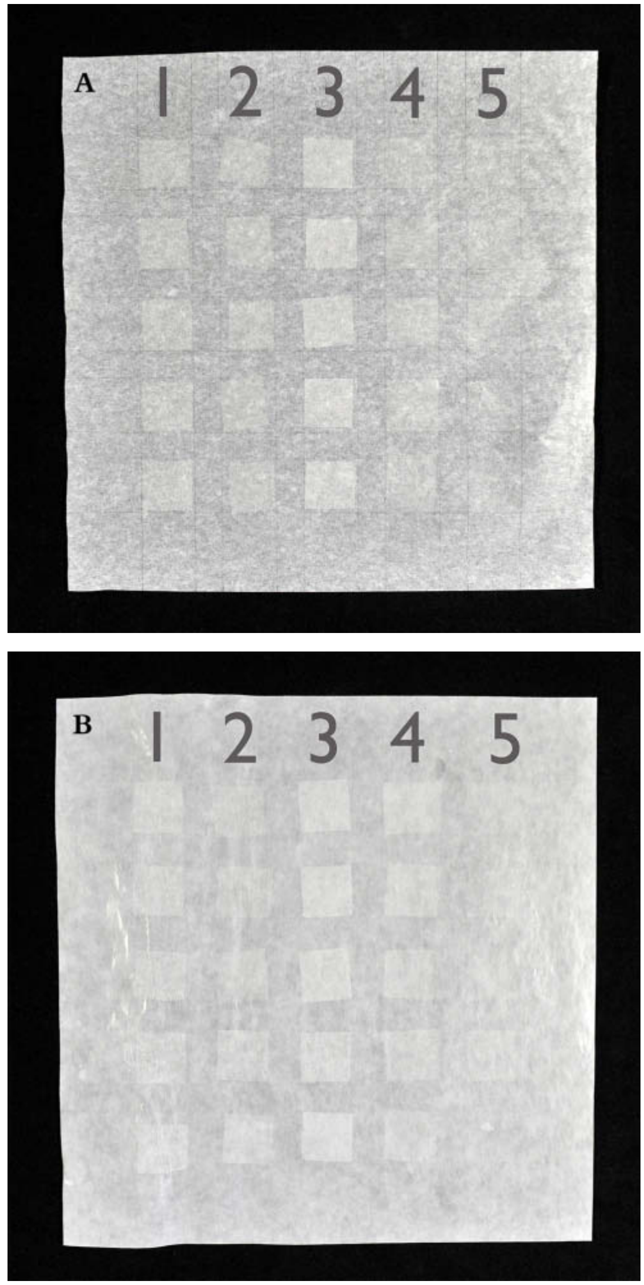


Fig. 20. Results from Test 5, viewed in terms of percentage change in opacity.



Figs. 21a and 21b. The BC Tissue samples from Test 5, applied to their respective substrates with a variety of methods. There are obvious differences in the resulting opacities. The rightmost columns (#5) are the optically cleared samples.

and glassine (percentage change of +29% and +28%, respectively). The optically cleared tissue resulted in the smallest increase in opacity, adding 2.3% to the glassine and a mere 0.6% to the interleaving tissue (percentage change of +7.6% and +2%, respectively). An abbreviated sample was made to demonstrate the dramatic effects of optical clearing. Two small rectangles of Usuyo gampi tissue were applied to a piece of glassine. The first was adhered with wet wheat starch paste

(10%) and dried under weight. The second was optically cleared with Plextol B500 and adhered with a tacking iron. The mend applied with wheat starch paste caused an increase in opacity of 18%, while the optically cleared mend caused an increase of only 2.5% (fig. 22).

PRACTICAL APPLICATION

MAKING AND APPLYING OPTICALLY CLEARED TISSUE

It is fortunate that the two adhesives proving to be the most successful clearing agents in Test 1—Plextol B500 and Avanse MV-100—are also the two acrylic adhesives described for heat-set tissue by conservators at NARA, published in a 2015 article in the *Book and Paper Group Annual*. At the time, their research found the Plextol/Avanse recipe to function well in terms of adhesion, visual cohesion, off-gassing, reversibility, and aging (Varga, Herrmann, and Ludwig 2015).

Their recommended instructions for making the pre-coated tissue involve placing the repair tissue (a lens tissue or kozo paper) over a silicone-coated polyester film, and using a screen to squeegee the adhesive mixture (4:1:1 water/Plextol/Avanse) onto the tissue. The coated tissue is then allowed to dry adhesive side up on the polyester film.

A different process was used to make the optically cleared tissues in this project. A less dilute mixture of the adhesives is used, as the dilution test (Test 2) showed that a highly dilute mixture loses its clearing efficacy. A 2:1:1 mixture was found to be ideal for this project. The lens/kozo tissue is replaced with Gangolf Ulbricht's BC Tissue for its superior clearing ability and relative handling strength.

Typically, the goal in making precoated tissues is to apply the adhesive only to the surface of one side of the repair tissue

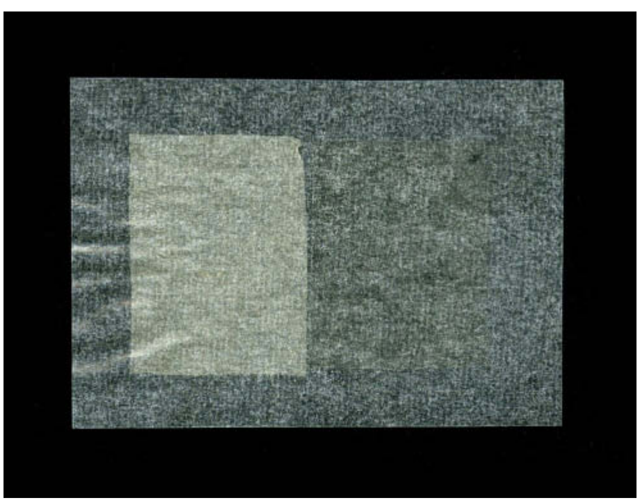


Fig. 22. The abbreviated method application test. On the left side, the Usuyo gampi tissue was applied with wet wheat starch paste. On the right side, the Usuyo gampi tissue was optically cleared with Plextol and applied with heat.

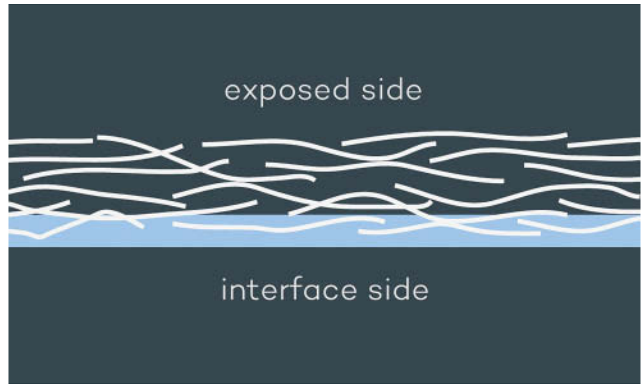


Fig. 23. The cross-section of a typical precoated tissue, with the adhesive restricted to the interface side.

(fig. 23). This avoids having any exposed adhesive following application. For optically cleared tissue, however, the adhesive needs to penetrate the paper web in order to diminish light-scattering interstices. The ideal optically cleared tissue would have the adhesive coating one side of the tissue (the repair-interface side), penetrating the remainder of the tissue, but not coating the opposite side of the tissue (the outward-facing side). The ideal coating would be very thin, but nonetheless forming a cohesive film within the cellulose web (fig. 24). To achieve these qualities, the following "mini-*hikkake*" method was used for this project, mimicking the traditional Japanese technique for applying paper linings with a drop-stick:

1. The tissue is cut into small, easily handled strips (roughly 15cm × 6cm).
2. The tissue is placed onto silicone-coated polyester, which is itself placed over a dark surface. The dark surface allows greater working visibility.
3. A bamboo skewer is placed under one short end of the tissue strip. This will function as the mini-*hikkake* (or drop-stick).
4. Using a flat brush, the adhesive mixture is brushed onto the tissue, starting at the *hikkake* and moving outward.

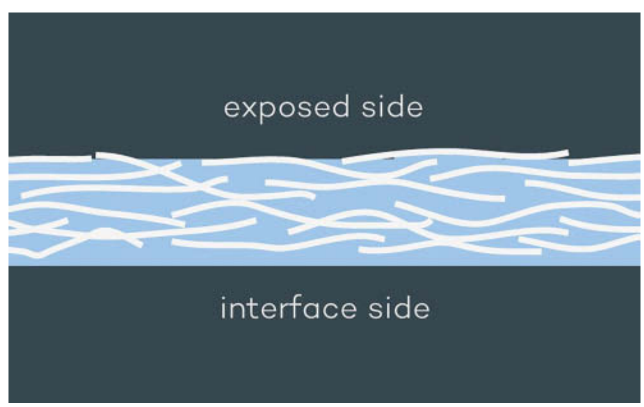


Fig. 24. The cross-section of an optically cleared tissue, with the adhesive fully penetrating the fiber web.

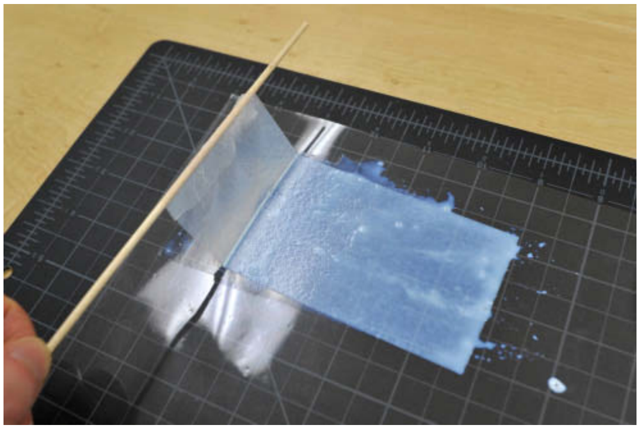


Fig. 25. Using the "mini-hikkake" to flip the coated tissue.

The small size of the tissue strip allows adhesive application without prior humidification, which can disturb the acrylic film-formation.

5. Using the mini-*hikkake*, the tissue is lifted, flipped, and placed adhesive-side down onto the silicone-coated polyester (fig. 25).
6. A dry brush is used to smooth wrinkles and disperse air bubbles.
7. *Optional:* When partially dry (roughly 3 minutes after flipping), a Teflon folder is used to burnish the tissue to redistribute and flatten the adhesive, or to remove excess adhesive if necessary.

With this coating method, the adhesive side of the tissue dries against the polyester film. The opposite side (the outward-facing side) has no directly applied adhesive, and dries to a more matte surface.

The coated tissue can remain on the silicone-coated polyester until usage. The tissue is strong, easily adhered, and easily handled, so very thin strips (2–3 mm) function well (fig. 26). A tacking iron is used at a temperature of 100–150C° for application between sheets of silicone-coated release paper, and adhesion requires only about 5 seconds of heat application. The somewhat rough surface of the release paper helps to diminish the sheen of the mend.

TREATMENT

Optically cleared, heat-set tissues were applied to both of the objects introduced at the beginning of the article.

1. *Atlas Photographique de la Lune*: BC Tissue coated with 2:1:1 water/Plextol/Avanse, reactivated with a tacking iron (100 ºC) between silicone-coated release paper.
2. "Wasmuth Portfolio": Somegami 5g coated with 2:1:1 water/Plextol/Avanse, reactivated with a tacking iron (100 ºC) between silicone-coated release paper.

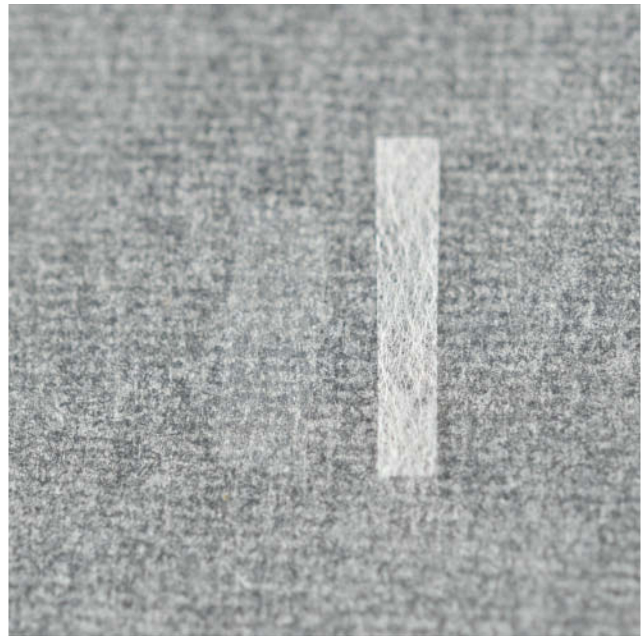


Fig. 26. A small strip of optically cleared tissue (left), adhered to a modern glassine. The sample is shown next to a strip of Tengujo of a similar size (right).

The cleared tissues are extremely easy to handle and quick to apply. The strength of the tissue/acrylic combination means that repair strips can be as narrow as 2 mm. This means that a little goes a long way: only one sheet (11.8″ × 16.5″) of the BC Tissue was used to mend all 25 of the tissues from *Atlas Photographique de la Lune* treated in this project.

The optically cleared mends are nearly invisible when viewed from a 90º angle (fig. 27), and, depending on the original opacity of the paper being treated, cause very little decrease in transparency.

REVERSIBILITY

As explored in the Varga, Herrmann, and Ludwig article, the Plextol/Avanse mixture can be reactivated with ethanol or acetone (Varga, Herrmann, and Ludwig 2015). These solvents can be applied passively with a vapor chamber.

The coated tissues were also found to be reversible using gellan gum as a poultice. In fact, this proved to be a much easier removal method. Though acrylic media is not soluble in water, films made from acrylic dispersions can be swelled with water. This may be due to the presence of surfactants that remain in the polymer film after drying. Surfactants possess both hydrophobic and hydrophilic ends (Chorng-Shyan 2008); their presence would allow water particles to soften the polymer network, enough for it to loosen its grip on the substrate fibers.

Optically cleared repairs that had been applied to interleaving tissue in Test 2 were removed with gellan gum

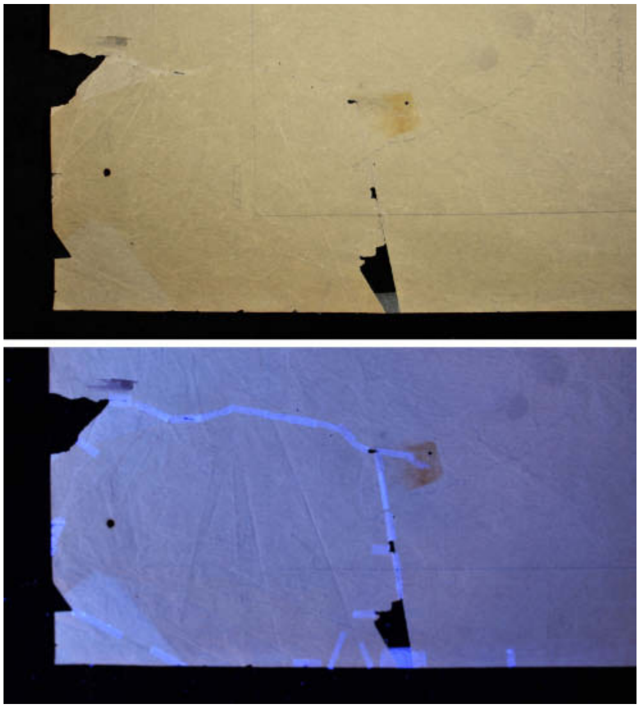


Fig. 27. A translucent overlay from *Atlas Photographique de la Lune*, viewed under visible light (top) and UV (bottom).

following 2 months of aging. The gellan gum was cut to the same shape of the repairs and applied directly for 30 seconds, and the repairs came up cleanly. The hydrophobic nature of the film prevented any of the gellan's moisture to penetrate the substrate. Images taken under ultraviolet lighting before and after the removal showed no remaining residue on the substrate (fig. 28). Avanse MV-100 fluoresces under UV (Varga, Herrmann, and Ludwig 2015) and the repairs showed brightly before removal.

Because the thermoplastic adhesives in these repairs soften and conform to the surface of the substrate surface, rather than penetrating the substrate surface as in a wet application, the "reversibility" of heat-reactivated repairs may be considered superior to that of repairs applied wet, or even of precoated tissues reactivated with solvents. Scanning electron microscopy images were taken of repairs in cross-section. The adhesive was shown to conform to and "grip" the paper fibers, without significant penetration (fig. 29).

Further testing is required to determine whether this hydrophilic swellability is a temporary condition. Over time, cross-linking in the polymer network may prevent softening with water. The migration of surfactants to the acrylic film's surface may also decrease its swellability.

ALTERNATE RECIPES

Though the mini-*hikkake* coating method creates a less glossy tissue, conservators may find that they require an even more

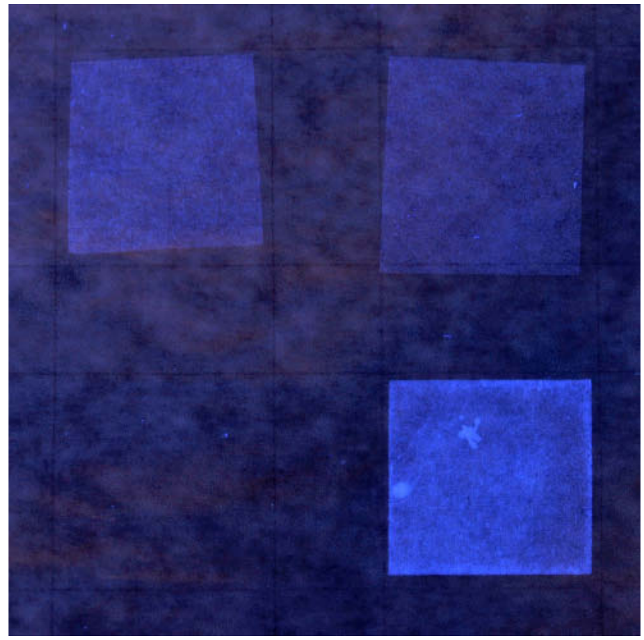


Fig. 28. Samples from the reversibility test, shown under UV. The lower left corner shows the area where an optically cleared repair was removed with gellan gum, leaving behind no residue.

matte repair tissue—transparent papers vary in their own glossiness, so methods and recipes may need to change on a case-by-case basis for an aesthetic match. As observed in the gloss/opacity test (Test 4), matte acrylic mediums can be added to the acrylic adhesives to achieve a less glossy surface without greatly diminishing their clearing efficacy. They are also less tacky, so high-ratio mixtures may have a higher glass

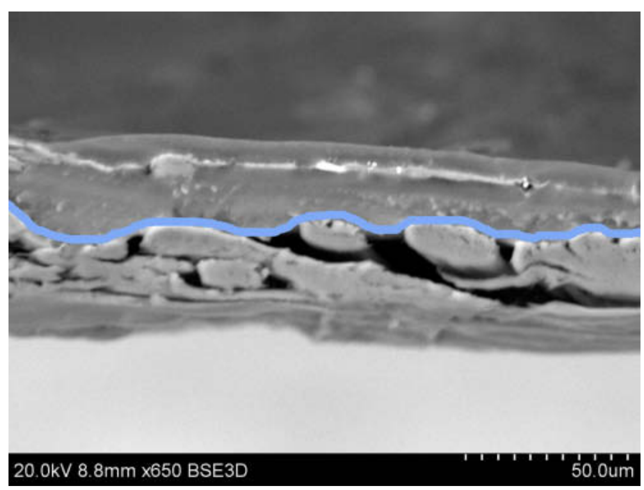


Fig. 29. A scanning electron microscope image of the cross-section of an optically cleared repair tissue (top) adhered to a modern interleaving tissue (bottom). The blue line shows the border of the acrylic adhesive, which lightly grips the fibers of the substrate without penetrating them.

transition temperature and require longer or higher heat application.

Though the acrylic dispersions proved the most effective clearing agents in general, other adhesives can make sufficient clearing agents, especially when applied to papers made with nanocellulose. MFC, which is a pure nanocellulose film, is extremely sensitive to moisture, and it can distort and break in the presence of water-based adhesives like acrylic emulsions. Aquazol proved to be the most efficient clearing agent for MFC. Because Aquazol is soluble in alcohols and is a thermoplastic, it could be used in conjunction with MFC for an effective optically cleared tissue.

A NOTE ON THE AGING PROPERTIES OF AVANSE AND PLEXTOL

Since the publication of their article on the subject, conservators at the National Archives and Records Administration (NARA) have observed some concerning aging qualities of their Avanse-Plextol Tissue (APT) recipe, including mends that have darkened in color over the years and inconsistent adhesion across various substrates.

In response to these observations, conservators and scientists at NARA and the Library of Congress are currently conducting research into the aging properties of APT alongside pre-coated tissues made with several other adhesives.

CONCLUSIONS

A number of conclusions can be drawn from the testing conducted in this project: Mending application method has a definite effect on treatment opacity. Optical clearing can effectively lower the opacity of repair tissues prior to application. Acrylic dispersions are generally the most effective clearing agents among conservation adhesives. High-density tissues (gampi, nanocellulose) are most effectively cleared.

Clearing agents can be lightly diluted, but thicker coatings are more effective. Matte acrylic media can be added to clearing agents to reduce gloss but maintain transparency.

The transparency of acrylic coatings has acceptable longevity. Optically cleared tissues made with acrylics exhibit high reversibility in the short-term, though further testing is needed.

A DEFINITION FOR OPTICALLY CLEARED REPAIR TISSUE

An optically cleared repair tissue is any precoated conservation tissue in which the adhesive coating serves the secondary function of optical clearing agent, reducing the scattering of light and encouraging transmission.

ACKNOWLEDGMENTS

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NOTES

1. The adhesives and coatings in Test 1 were applied generously to both sides of the samples. For the adhesives that required mixing, relatively high-density solutions were made (wheat starch paste: 10%; methyl cellulose: 5%; gelatin: 10%; Klucel G: 10%; Aquazol: 20%; Paraloid B-72: 10%). The environment in which the coating took place had a temperature range of 72–74°F and a humidity range of 35–40%.
2. The refractive indices of acrylic components:
Poly (methyl methacrylate): 1.491
Poly (ethyl methacrylate): 1.498
Poly (butyl methacrylate): 1.483
Poly (methyl acrylate): 1.476
Poly (ethyl acrylate): 1.467
Poly (butyl acrylate): 1.465
These fall within close range of the RI of cellulose: 1.469–1.55

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SOURCES OF MATERIALS

Avanse MV-100, Plextol B500, C-Gampi Paper 16 g/m2, Tengujo 5 g/m2, Usuyo Gampi-white 11 g/m2
Talas

Japanese Somegami 15.3 Kozo Conservation Tissue, 5 g
Japanese Paper Place

BC Tissue 4 g/m2 and Uso-Gami Thinnest 9 g/m2
Hiromi Paper, Inc.

Microfibrillated Cellulose (MFC)
Innovatech Engineering

Avian Black-S
Avian Technologies, LLC

Teflon RELIC WRAP film
Gaylord Archival

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