AN UPDATE ON TAPE AGING AND REMOVABILITY STUDIES

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The goal of today's conservator is to prolong the life of our cultural heritage materials. Success in this endeavor involves understanding of the physics, mechanics, and chemistry of the materials and techniques of artworks, archaeological artifacts, industrial heritage objects and ethnographic materials. In essence, any material that contributes to our history, produced by a human or by nature, is within the realm of modern conservation study. To describe the task completely is beyond the scope of this paper, however, for those conservators who specialize in paper based objects, one can see that pressure sensitive tapes fall under our broad mandate. The interaction of PSA's with paper has a long history of study by conservators. The removability of tapes, as well as their long term chemical and physical effects on paper is a major issue in the treatment of permanently valuable paper objects. Some recent studies have added greatly to our understanding of aging and removability of tapes, as well as contributing to the empirical models we use to deconstruct tape/paper interactions.

At the center of the issue lies the fact that tapes have made their way onto important objects since they were invented. The individual who applied the tape was making a genuine attempt to prevent further deterioration, or to keep essential parts together, to label an artifact or to stabilize it in the field. A great amount of faith was invested in the tape to solve complicated preservation problems. The success of the action can only be discussed in relative terms, retroactively, and it is helpful to view negative outcomes (damage caused by tape) as part of the history of the object.

Of critical importance is the cooperation between the tape industry and conservation. There are clearly beneficial rewards to cross disciplinary efforts. In 2006, the American Institute for Conservation of Historic and Artistic Works[i] presented the first Special Recognition for Allied Professionals Award to John Johnston, celebrating a long standing relationship between our two fields. In the recent past, tape manufacturers have aided in the conservation study of important original manuscripts of Ernst Jűnger held at the German Literature Archives, Marbach[ii], and in support of the treatment of sketches by Paul Cezanne in the Philadelphia Museum of Art[iii]. In both of these projects, the benefit to the object far exceeded the good that could have been accomplished by the conservators alone.

With such a rich history of cooperation, and in order to foster this relationship, I would like to report some recent studies on tape aging and removability. These studies enhance our knowledge of the long range changes that happen with tape, and illuminate the complicated interactions that take place in compound objects. Looking at the years-out behavior of tapes is seldom part of the R&D function of a producer, and the study of off-label application is not a chore for the manufacturer. It is however, the mandate of conservation, and in many cultural institutions with conservation science departments, significant work is being done.

STUDY ONE: Suitability of tape products for use in preservation

By far the largest project is being conducted by the Canadian Conservation Institute (CCI) in Ottawa[iv]. CCI has a long record of investigating the properties of adhesives, and has the facilities and expertise to perform natural and accelerated aging protocols. Begun in 2001 as a cooperative initiative of the National Archives of Canada, the goal was to identify tapes or classes of pressure sensitive products that could safely be used in the museum/archives environment. The important distinction to be made here is that the experiment was looking at tapes for non-contact use--- not for use directly on objects. The products should not, in confined long term storage or in under exhibition conditions, contribute to the local environment in a negative way. Their main use is in the assembly of housings (boxes and mats) and in the construction of shipping crates.

CCI began by conducting a survey to identify tape products in common use in museums and archives worldwide. A short list of undesirable physical and chemical properties in tapes was assembled, and after screening the initial list of products (146) using analysis and information provided by the manufacturers, the final group, 22 pressure sensitive products, was set for the study.

The criteria for selection included:

- Products with wood rosin tackifiers, natural or synthetic rubbers, or PVC were eliminated
- Products that tested outside an acceptable pH range of 6.0 to 8.0 were eliminated
- Products with pigments or colorants including optical brighteners were eliminated
- No silicones would be included
- A few tapes with non-desirable properties would be included for comparative data

Analysis of the accepted products was done using FTIR; both the carrier and adhesive materials were identified. ASTM methods were used for determination of pH. Colorimetry data was also collected (L*a*b*). The Photo Activity Test [v] (a pass/fail test) was also conducted to determine potential interaction between the product and silver based photographic systems. By 2005, the analysis data was complete, and the samples were prepared for natural and artificial aging protocols.

The tape products were each applied to two papers and to one photographic print paper. The papers were chosen based on fiber content and the type of sizing. The first, a late 19th century journal paper, was acid processed wood based pulp. The other paper was a recently manufactured alum rosin sized sulfite pulp. The photographic paper was a resin coated (RC) printing paper, processed in the 1970's. It was included at the request of photographic materials conservators. With a low porosity surface, and a bright white appearance it was optimal for showing slight shifts in color. The test products were applied to the verso of the RC paper and to random sides of the two plain papers with a roll down machine. Several sets were made in anticipation of recurring evaluations. The first set of samples were aged for 28 days at 80°C and 65% relative humidity (ISO 5630/3 1986). The second set was naturally dark aged at 22°C and 45% relative humidity. At somewhat regular intervals, sets were removed from the aging room for evaluation. Color change was measured, pH was recorded, and a team of conservators performed removability tests. For the removability assessment, the samples were placed in a solvent bath for a brief period, removed, and then manipulated with swabs or micro-spatulas, in a way that simulated actual removal techniques. Behavior of the tapes in a range of organic solvents, including water and alkalized water, were scored by each conservator. The removability results were discussed by the group in order to sort out anomalies and come to a consensus on rating the difficulty on a subjective scale. In total three removability sessions of the naturally aged samples were conducted at intervals between 2005 and 2011, and an interim report with the analysis, color data, pH and PAT results was published in 2006[vi]. In 2011 the project was presented with updated data and interim conclusions[vii].

Figure 1. A conservator applies an organic solvent to a test sample

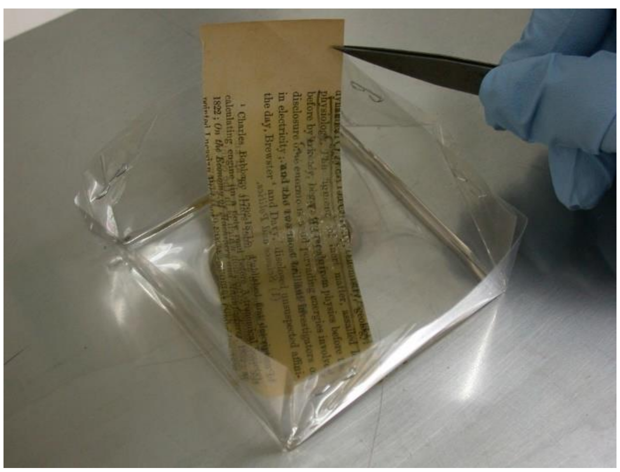

Figure 2. The sample is immersed in a solvent bath

To date the CCI project is the largest study of commercial tapes undertaken in the field of conservation. Such a long project produced questions, provided hard data, and suggested some trends that need further study. The main goal was accomplished by providing a source of information that conservators can use to make decisions about the 22 tapes and their suitability for use. The data was summarized into a numerical rating system that facilitates the evaluation of the tapes in relationship to one another. This presentation of data shows when one product might be more suitable than another in a given situation. For example, a tape that fails the PAT test might be acceptable for use in proximity to non-metallic objects, or a tape with pH on the low end of the range (6.0) might be acceptable with textile collections. The outliers (those with the lowest score) are tapes in common use, and the study was not meant to exclude these tapes from the preservation toolkit, but suggest that they are not universally suitable.

Where budgetary concerns are at play, the rating system may show suitable options with different price points.

One analytical method that was not included (due to time and resource constraints) was determination and identification of any volatiles generated in the controls and on aging. As an ongoing research project, the samples continue to age at the CCI facility, and hopefully in the future, some instrumental analysis can be done in this regard. The fact that only two of the tapes in the study passed the photo activity test is one result that suggests further investigation.

STUDY TWO: The production of acids in paper

A second notable project, one that focusses on the aging of paper rather than the aging of tapes, was conducted by the Preservation Directorate of the Library of Congress (LoC)[viii]. The study[ix] was designed to identify and to quantify volatile products of paper degradation. The test was based on an artificial aging design that varied from the standard approach. The study hoped to augment information on products of paper deterioration that had long been proposed but not confirmed. The rate of the production of acids generated by alpha cellulose and hemicelluloses was a particular focus of the research. The experimental design optimized the capture of evolving compounds by conducting aging of the samples in sealed glass tubes or in aluminized envelopes. Rather than hanging loose sheets in the aging oven, placing smaller samples in sealed enclosures proved effective in capturing transitory volatiles that are lost in "open" oven aging protocols.

The papers used were manufactured for the ASTM Institute for Standards Research in 1996. Other papers from the US Forest Products Laboratory were tested in order to collect comparative data in the "open" oven test. After conditioning at 23°C and 55% RH, the samples were placed into the containers and sealed. The containers were placed in the oven and subjected to a variety of temperatures and times. The interior atmosphere of the tubes was then extracted and analyzed for volatile components using capillary electrophoresis.

The analysis identified several acids: formic, acetic; oxalic, lactic, and glycolic acids; in the lignin containing samples vanillic, furoic, and ferulic acids were identified as well as phenolic ketones and aldehydes. These results were not unanticipated, however, analysis revealed quantities of these acids that had not been previously detected. Even under ambient storage conditions, new papers generated high concentrations of these acids, particularly formic acid, within just a few weeks in the enclosures. The most stable paper, a 100% long fibered cotton pulp filled with 5% calcium carbonate formed significant amounts of nine different carboxylic acids in just 5 months. Production of acids in this paper confirmed that that alpha and hemi celluloses undergo these chemical mechanisms at ambient and even near-freezing temperatures.

This study has contributed to our understanding of how degradation of paper may promote the degradation of tapes, especially natural rubber based types. On evaluation the data suggests a livelier interaction between paper and tape components than was previously modelled. Now that data has been produced on acid species, quantities formed, and rates, we have a better picture of the dynamics involved in changes that take place over the life of our cultural heritage objects. Keep in mind that pressure sensitive tapes, in and of themselves, are cultural heritage objects!

Study Three: A practical tape removal conundrum

A third study, which is more a collection of observations than a structured inquiry, is based on a common paper conservation treatment. The washing of paper objects has long been a practice undertaken to reduce staining in damaged papers, and as a way to apply bleaching or alkalizing substances. The process can be done on paper that is physically stable enough to bear wet handling, and, of course, with media that are water stable. The paper is tested prior to washing, as are any media; good candidates for washing include those objects that have overall damage from contact with poor quality materials (such as wood) or those that have been damaged by water. Poor quality papers often benefit from washing in alkalized water that promotes the clearing of water soluble acids and the re-formation of hydrogen bonding.

When a paper object has degraded tape on it, treatment can also involve immersion in organic solvents to mitigate the tape adhesive and staining. If large quantities of tape and overall damage of the paper has occurred, immersion treatments are economical and effective. In this example, a 20th century etching executed on a cotton fibered paper, the damage from contact with the wooden backing in a frame is evident. There is rubber based masking tape around the perimeter that has deteriorated and in some cases fallen off. The residual adhesive is rubber based and has penetrated the paper to a degree. The etching ink is safe to wash, and based on previous experience, a good outcome is to be expected.

Figure 3. This 20thC etching was taped into the display mat with a rubber based masking tape

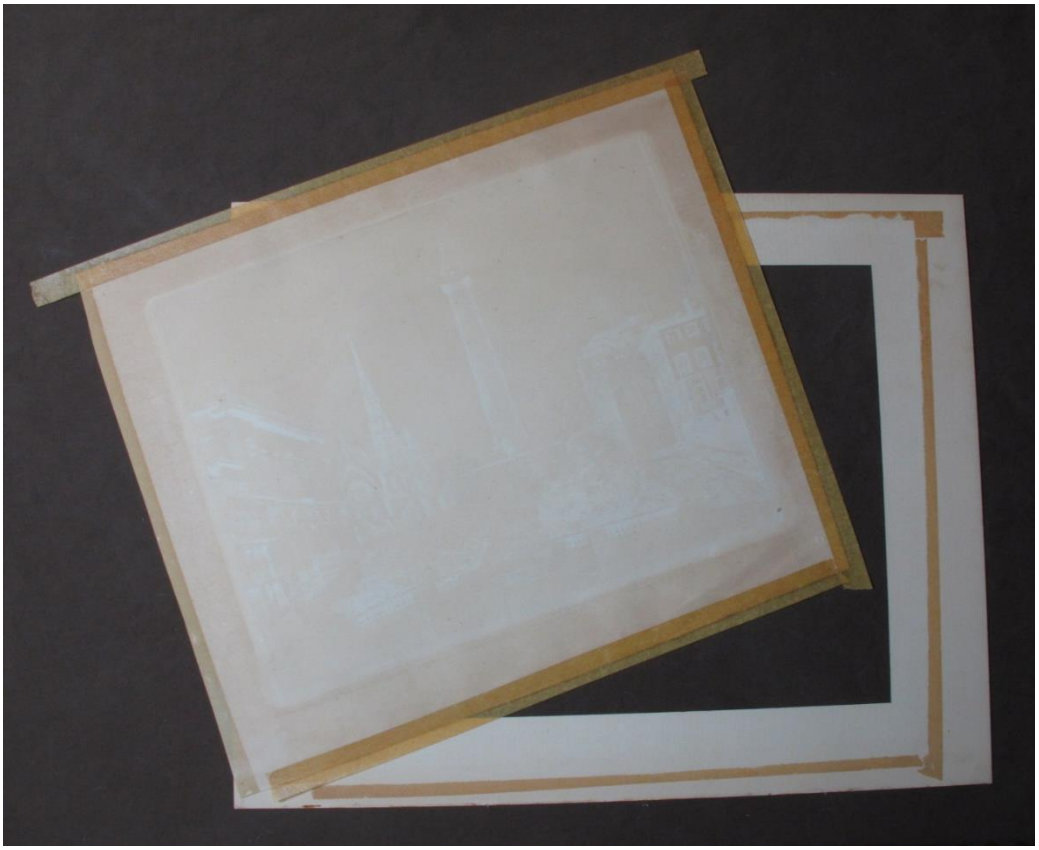

Figure 4. The staining from prolonged contact with a poor quality backing is evident on the print verso

Figure 5. Detail of the lower left: the arrow points to staining from the cut edge of the poor quality mat

Testing the tape residue is done with a variety of paper friendly solvents[x] in order to find a single solvent or mixture of solvents that will remove the adhesive. The successful solvent(s) are then tested on the paper and on the etching ink. Having done due diligence and confirmed that aqueous washing and solvent bathing will be effective, one vital question arises: in what order should the immersions be done?

This "wash first/solvent first" question arose because in the field, depending on where conservators are trained, conflicting opinions exist as to which protocol is preferred. Some argued that the paper would expand in the water bath and that any water soluble components of tape degradation would be washed away. The resulting loss of deterioration products was thought to create a less occluded fiber network and thus aid in the penetration of the organic solvent in the subsequent step.

Conversely, performing the solvent bath first was thought to be more efficient because it removed the hydrophobic adhesive components that have penetrated the paper. Washing after solvent would be more thorough if the adhesive residue was removed first. This group also was concerned that the differential stresses placed on the adhesive-blocked paper could cause mechanical damage at the tape/paper interface upon expansion in water.

The opinions of the two groups were so strongly held that a series of wash first/solvent first experiments were done as part of a five day professional development class that I teach to intermediate and senior level conservators. After many nebulous results, it became clear that we needed to create working models for each protocol – no small task. The factors and considerations are complex; both the paper and the tape contribute to the conditions that promote optimized solubility.

Progress on the models has been slow, given the need to study each material and its potential for interaction. At this writing development of the models is stuck on obtaining a better understanding of the water soluble products of rubber based tape deterioration. Also brought to the table are the results from the Library of Congress study. We now see a more active role of the paper in the generation of problematic compounds.

Clearly there is a lot of interesting and challenging work to be done. Gratifying discoveries and advances in this field of research will continue to take place, and this author promises periodic reporting of our cooperative efforts. The field of conservation needs the support of the pressure sensitive tape industry and, as this paper has shown, the undertaking of cross disciplinary projects in support of our cultural heritage is a very worthy and noble goal.

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[i] The American Institute for Conservation of Historic and Artistic Works, 1156 15th St Suite 320 Washington DC 20005.

[ii] Kamzelak R, and Reichow-Rauchle, M, "Conserving Pressure-Sensitive Tapes: Interim Report on a Project at the German Literature Archive in Marbach Supported by tesa SE, Hamburg*", Restaurator, Vol.31 Issue 2 Jan. 2010 pp106-122; ISSN online 1865-8431*

[iii] Zeiske, Faith, "The Conservation of Two Sketchbooks by Paul Cezanne", *Proceedings of the 1992 Manchester Meeting. Institute for Paper Conservation 1992. Worcester, UK pp 54-60 Fairbrass, S ed. ISBN 0950726834*

[iv] Canadian Conservation Institute, 1030 Innes Road, Ottawa ON, K1A 0M5 CANADA.

[v] Photo Activity Test (ISO 8916) developed by the Image Permanence Institute, Rochester Institute of Technology 70 Lomb Memorial Drive Rochester, NY 14623-5604.

[vi] Down, Jane and Williams, Scott "The CCI Tapes and Heat-Set Tissues Project", *Papier Restaurierung, Vol 7 No 1 2006, pp13-17.*

[vii] Down, Jane et al. 'Update on the CCI Adhesives, Tape and Heat-set Tissues Project*", Proceedings of Symposium 2011: Adhesives and Consolidants for Conservation. Ottawa 2011.*

[viii] Library of Congress Preservation Directorate 101 Independence Avenue SE Wash. DC 20540-4530.

[ix] Shahani, C and Harrison, G, "Spontaneous Formation of Acids in the Natural Aging of Paper", Studies in Conservation, 47 Supplement 3, pp 182-192. *Institute for International Conservation Conference Proceedings, Baltimore MD 2002.*

[x] Although a large number of organic solvents exist that are effective for dissolving psa's, the long range effect they have on paper has only been studied in a few instances. Solvent immersions are done under ambient conditions, typically 72°F and 50% RH. Chlorinated solvents are not used due to their potential bleaching effects, and overly hazardous solvents are avoided. The commonly used solvents are: acetone, toluene, petroleum benzine, heptane, ethyl alcohol, isopropyl alcohol, methyl ethyl ketone, ethyl acetate, amyl acetate, and combinations of the above. The solubility parameters of mixtures are determined by

the use of Hansen solubility parameters and calculations figured by percentage contribution. Occasionally alkalizing agents are added such as calcium carbonate.

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