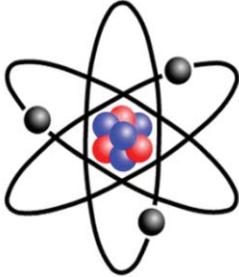


# RATS



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**RESEARCH AND TECHNICAL STUDIES**

## Research and Technical Studies Specialty Group Postprints

From the 41<sup>st</sup> Annual Meeting  
Indianapolis, IN  
May 29 – June 1, 2013

Volume 4  
2013



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Volume 4  
2013



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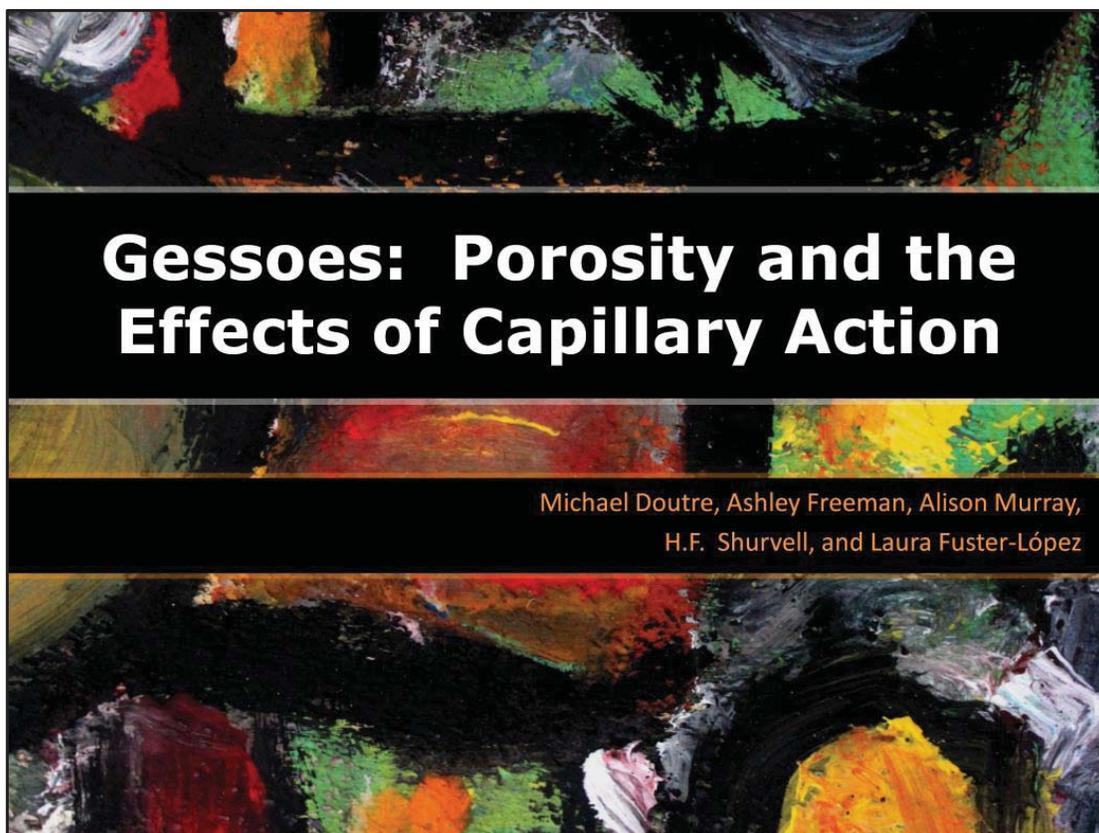
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# Gessos: Porosity and the Effects of Capillary Action

Michael Doutre, Ashley Freeman, Alison Murray,  
H.F. Shurvell, and Laura Fuster-López

Michael Doutre<sup>1</sup>, Ashley Freeman<sup>2</sup>, Alison Murray<sup>3</sup>, H. F. Shurvell<sup>4</sup>, and Laura Fuster-López<sup>5</sup>

<sup>1</sup> Research Technologist, Art Conservation Program, Queen's University

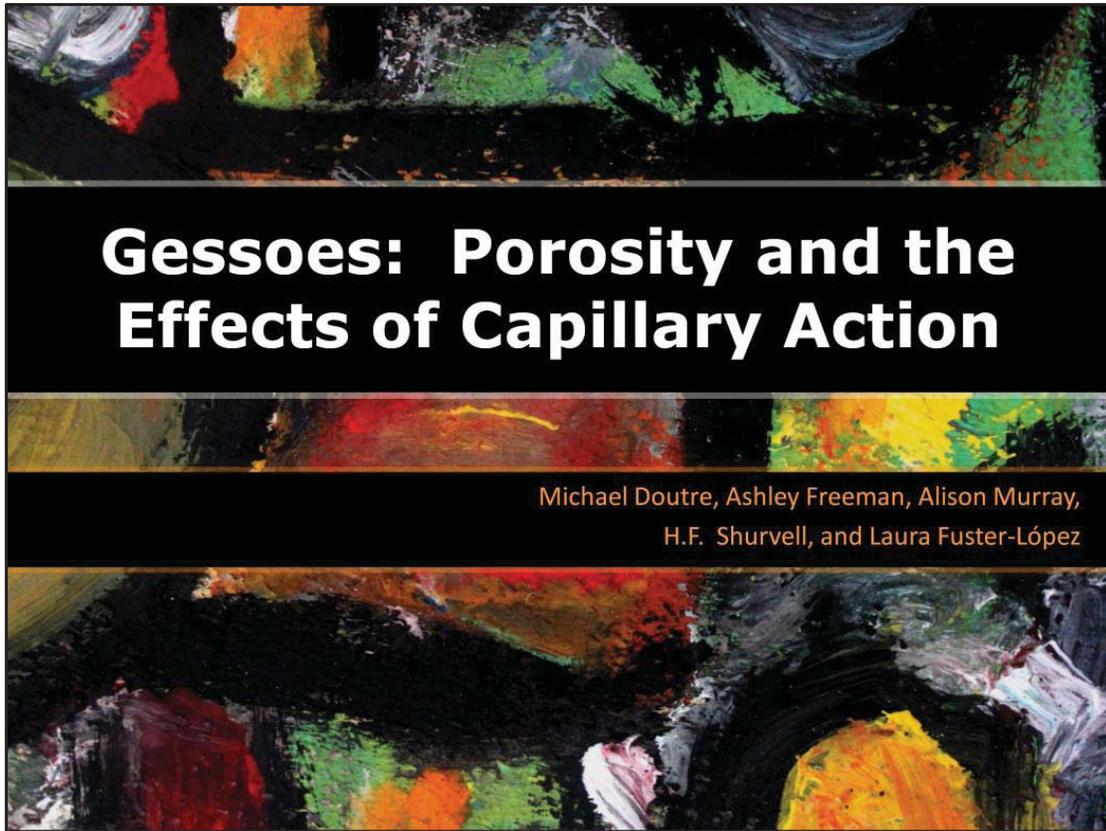
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Presented at the Paintings/RATS joint session  
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The American Institute for Conservation of Historic and Artistic Works (AIC)  
Indianapolis, In, May 29-June 1, 2013



## Acknowledgments

Research collaboration with



With support from

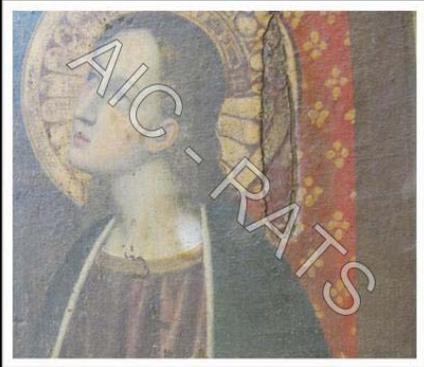


And many thanks to all those who supported this project and in particular Dr. Brad Diak and Charlie Cooney at Queen's University for their continued support.



## Gessos as Fills

- Reversible and retreatable
- Chemically stable
- Match the physical behaviour of the original work
- Stable across a range of conditions



*Annunciation (Before Treatment, Unknown, Scandicci)*



-We have been investigating materials used for losses in easel paintings.

-In particular we are interest in materials for filling losses, which interrupt the ground layer and distract from the pictorial plane.

## Gessoes as Fills

- Act as a preparatory layer for inpainting
- Act as a barrier between additional materials applied in treatment and the original materials

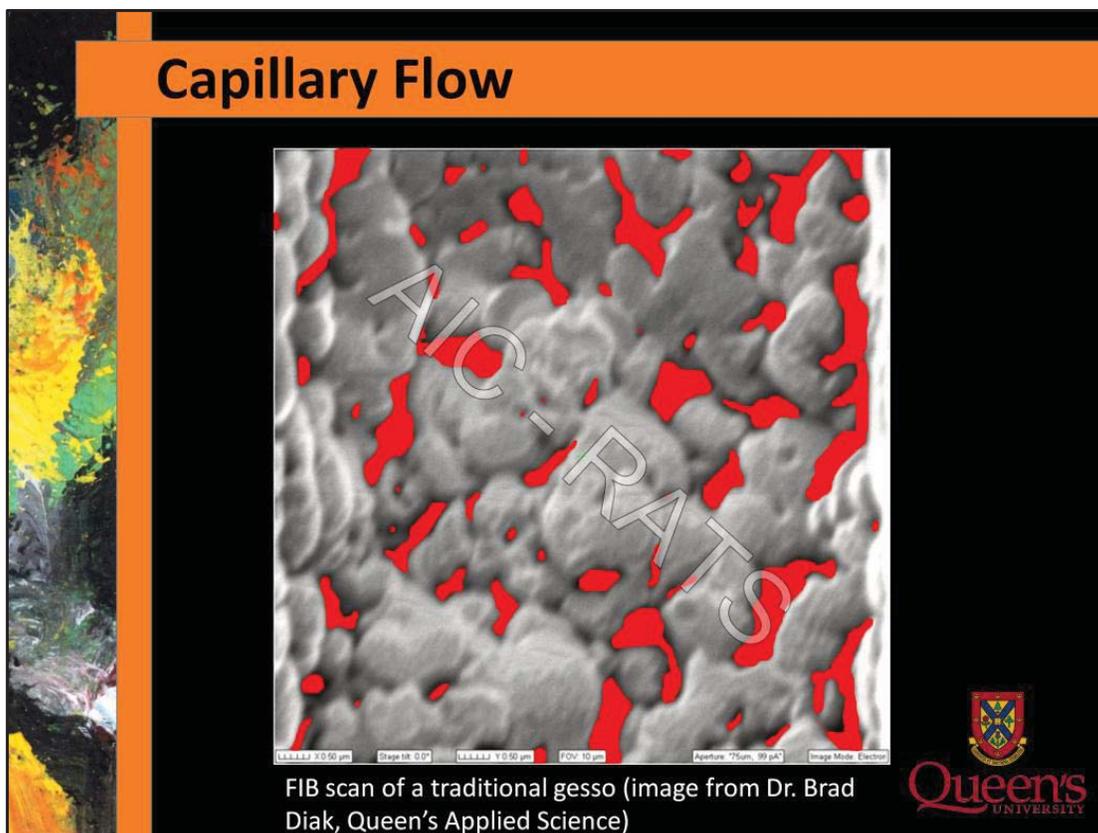


*Annunciation (During Treatment, Unknown, Scandicci)*



-By their nature, gessoes facilitate the diffusion of fluids by capillary action.

-The diffusion characteristics of a material can affect many properties including longevity, removal, and handling. Such properties may also influence specific treatments, for example inpainting.



-Marked in red are fine porous structures we believe to drive the bulk of fluid movement within the paint film by capillary action.

-This image is a Focused Ion Beam scan of a "traditional" rabbit skin glue and calcium carbonate gesso.

## Wet Treatments



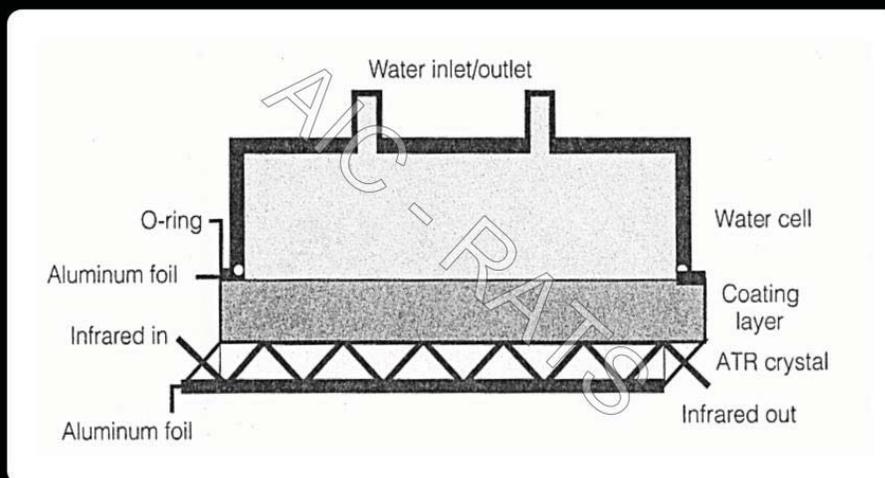
- Inpainting
- Cleaning



-When used as an infill material for a painted work, a gesso will be exposed to inpainting and cleaning solutions.

-As these are fluids, how they interact with the gesso will be strongly affected by diffusive capillary action.

## Previous Work- Whitmore *et al.*

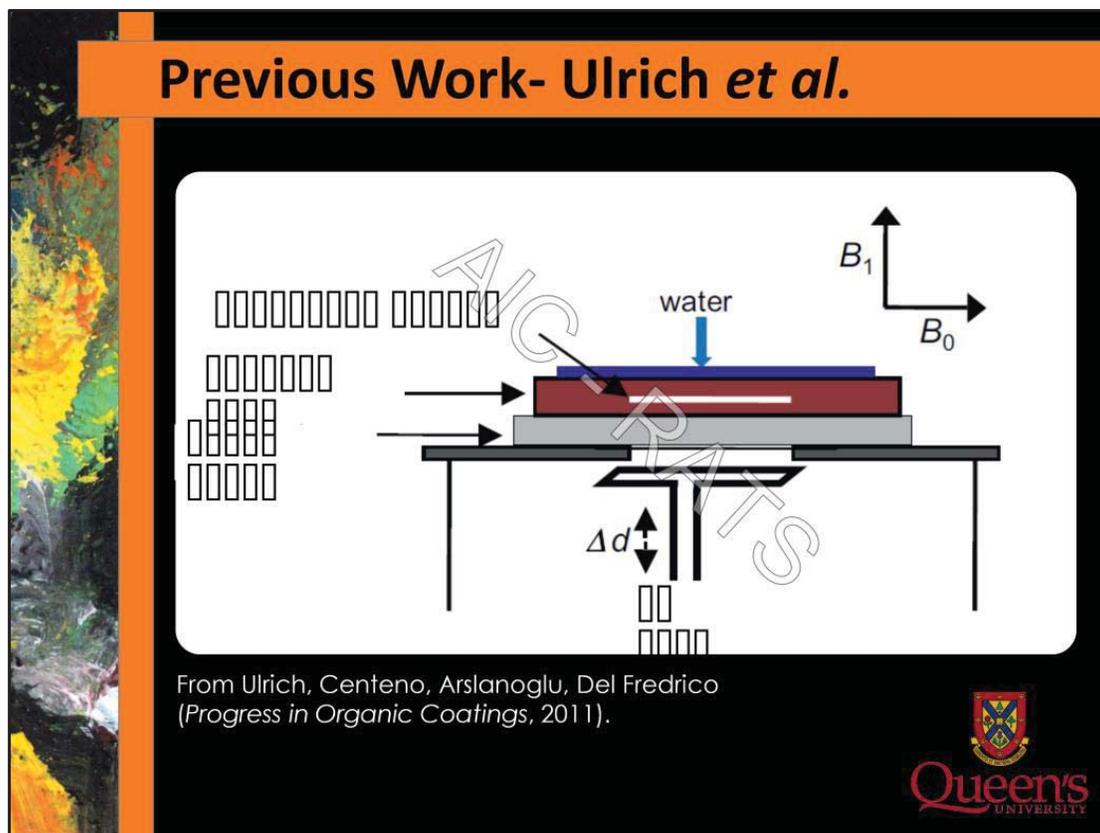


From Whitmore, Morris, and Colaluca  
(Proceedings: *Modern Paints Uncovered*, 2006).



-This work is based upon previous work on the diffusion of water in a paint film by:

Whitmore, P., H. Morris, and V. Colaluca. 2007. Penetration of Liquid Water through Waterborne Acrylic Coatings. *Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium*. 217-223.



-This work also takes aspects from:

Ulrich, K., S. Centeno, J. Arslanoglu, and E. Del Federico. 2011. Absorption and diffusion measurements of water in acrylic paint films by single-sided NMR. *Progress in Organic Coatings* 71: 283–289.

Specifically, a droplet of solution was placed on a film mounted on the instrument in place of a flow cell.

## Characterizing Diffusion

From Washburn's equation,

$$\text{Diffusion Coefficient} = \frac{\text{Film Thickness}^2}{6 \times \text{Breakthrough Time}}$$


-Diffusive behavior is characterized by the Diffusion Coefficient.

-This coefficient is a product of the thickness of the material and the “breakthrough time”, which is the time it takes for a volume of fluid placed on one side to reach the other.

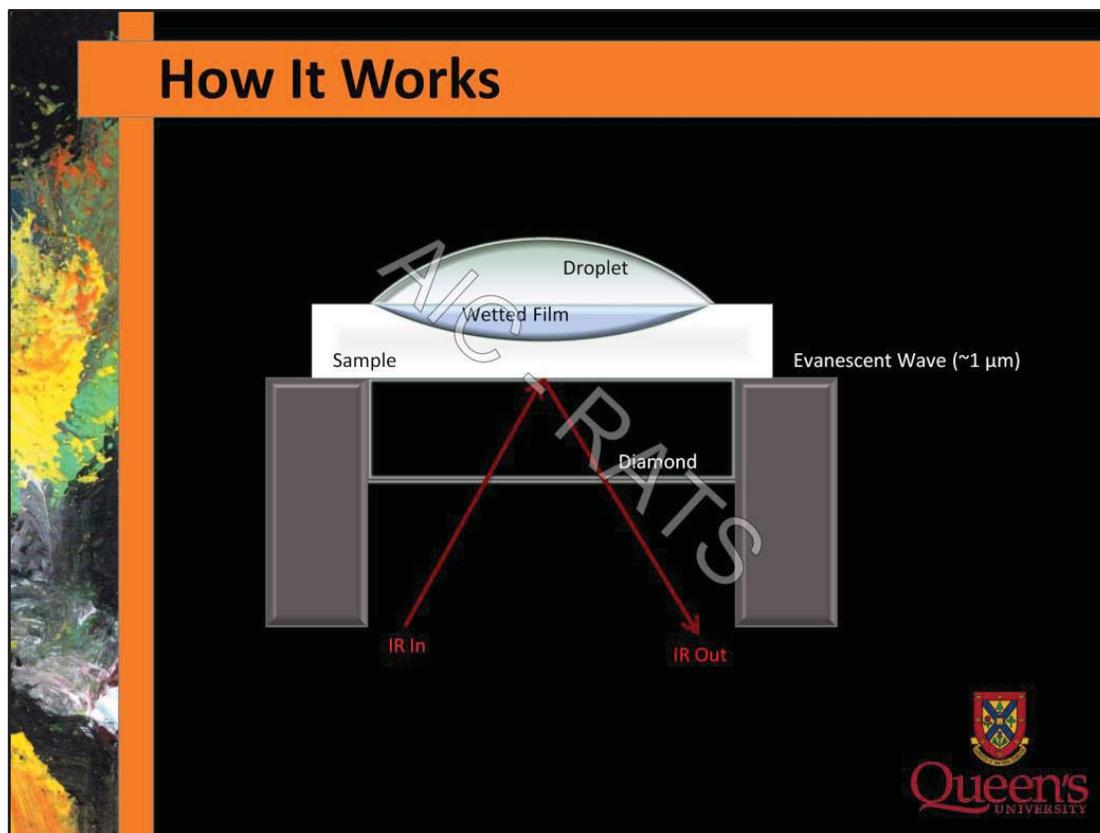
-So given that distances are easily measured with accuracy, diffusion characterizations depend on an accurate measurement of the breakthrough time.



-For our measurement of the breakthrough time, we used a Nicolet Avatar™ 320 FT-IR spectrometer equipped with a Nicolet SMART™ Golden Gate attenuated total reflectance (ATR) accessory (Thermo Instruments, Canada).

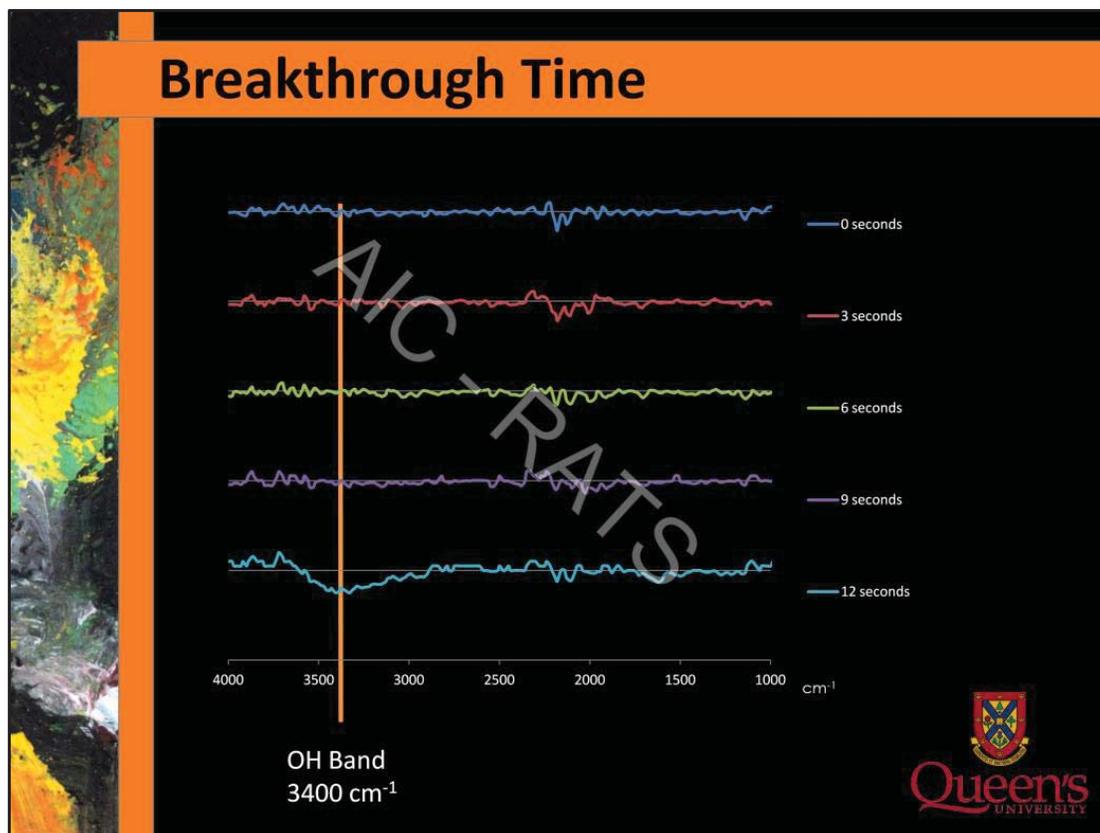
-Due to how our films were prepared, they self adhered to the ATR crystal.

-A droplet of solution was then placed on the film, over the ATR crystal, to supply the needed volume of fluid for unhindered diffusion.

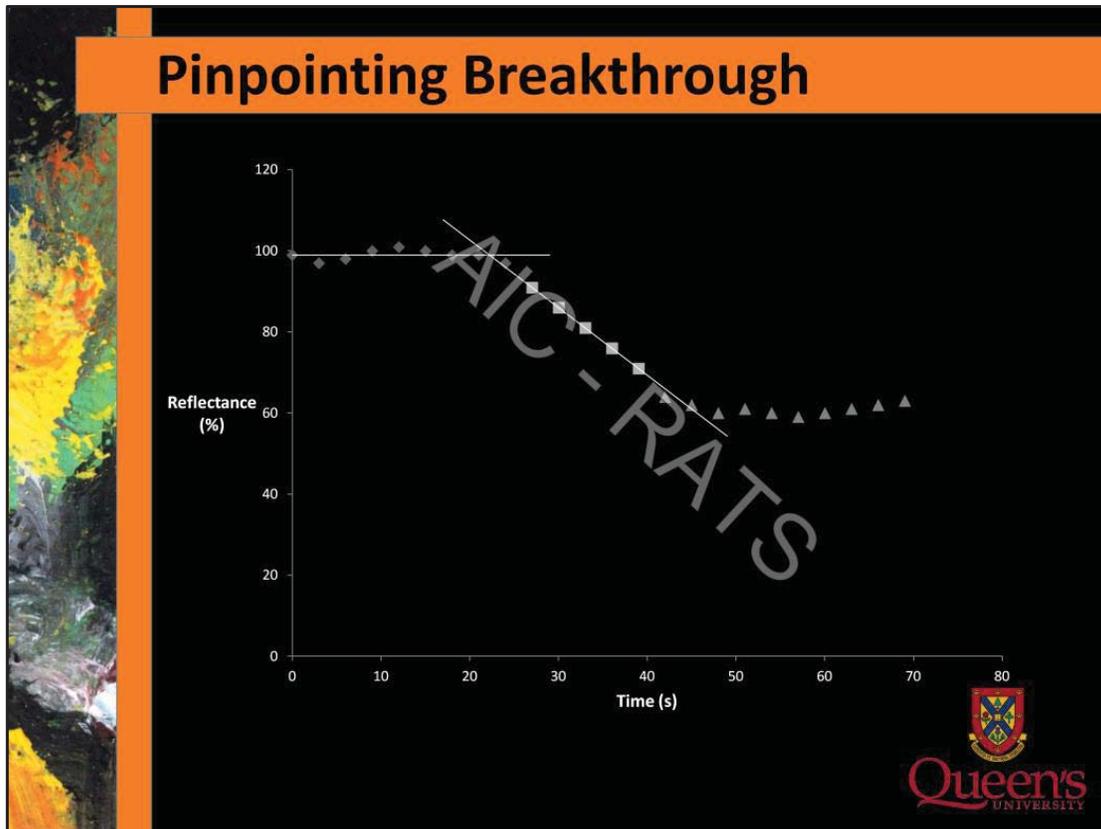


-FT-IR ATR works well as a method of breakthrough characterization as it detects chemical composition up to roughly a micron into the sample.

-This very thin sampling area means that effectively only the surface is being measured, allowing an accurate measurement of the breakthrough time of a liquid going through the full film.



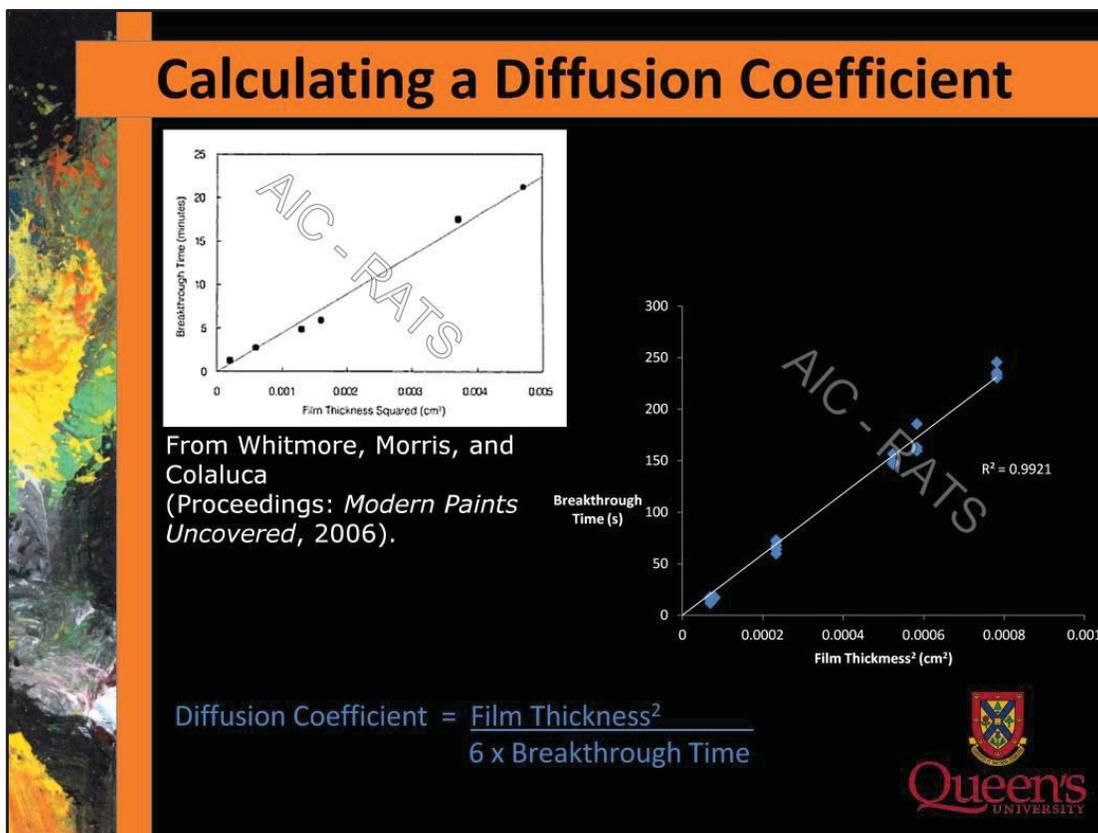
-For this study all the examined solutions had water as a component. So, to detect breakthrough, the  $3400 \text{ cm}^{-1}$  OH stretching band was monitored, beginning at the initial contact of the solution droplet and the gesso film.



-To improve the accuracy of the breakthrough characterization, instead of just using the first observed OH peak, the OH reflectance was plotted against time.

-A linear regression was performed on the decreasing OH reflectance and this was regressed back to the baseline.

-The time where the regression crossed the baseline was taken as the breakthrough time.



-As with the paper by Whitmore *et al.*, the determined breakthrough times were plotted against the square of the films thickness to examine the diffusion coefficient relation.

-Our definition of breakthrough time was found to produce a highly linear result. As this relation is consistent with the definition of the diffusion coefficient, this validates our procedure as a feasible way of characterizing the diffusion behavior of these materials.



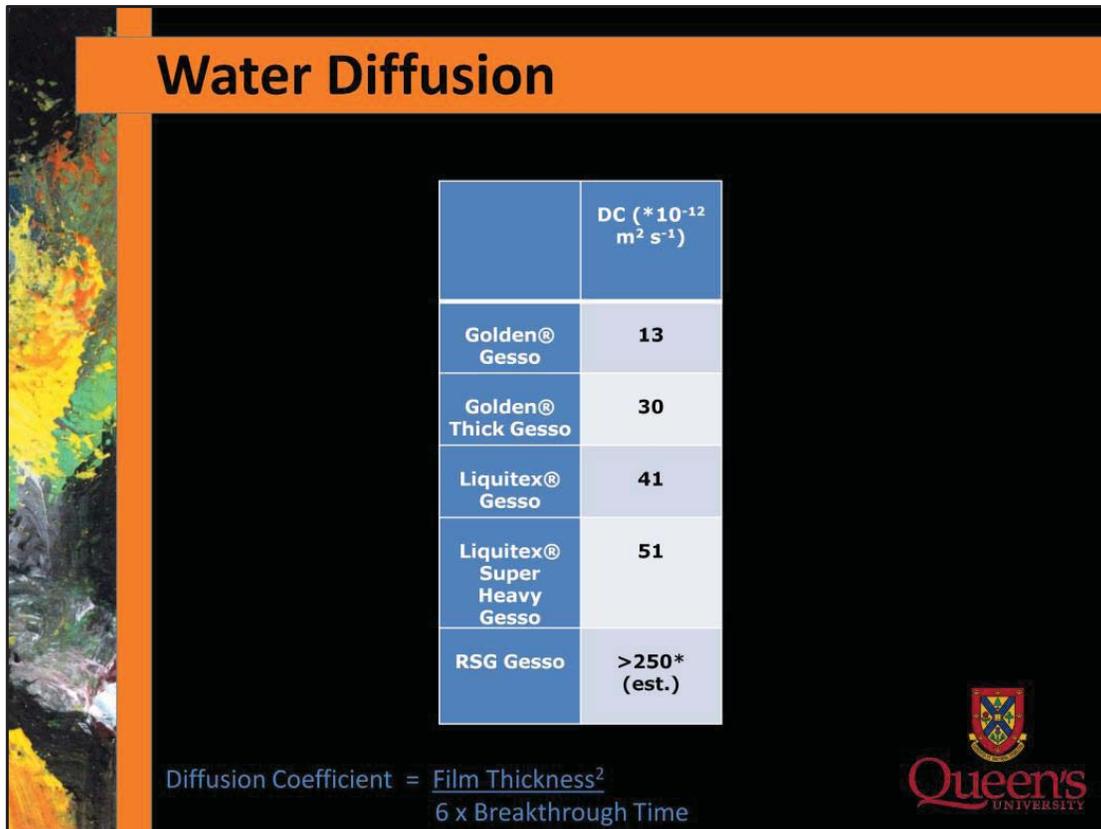
## Materials Investigated

- **Traditional Gesso**
  - 56 g calcium carbonate in 50 ml 10% (w/w) rabbit skin glue (RSG gesso)
- **Acrylic Gessos**
  - Golden® Gesso
  - Golden® Thick Gesso
  - Liquitex® Gesso
  - Liquitex® Super Heavy Gesso
- **Cleaning Solutions**
  - Distilled Water
  - 10% Ethanol
  - 2% Tri ammonium citrate
- **Inpainting Media**
  - Watercolour
  - Golden Gel Medium
  - 25% Aquazol 200



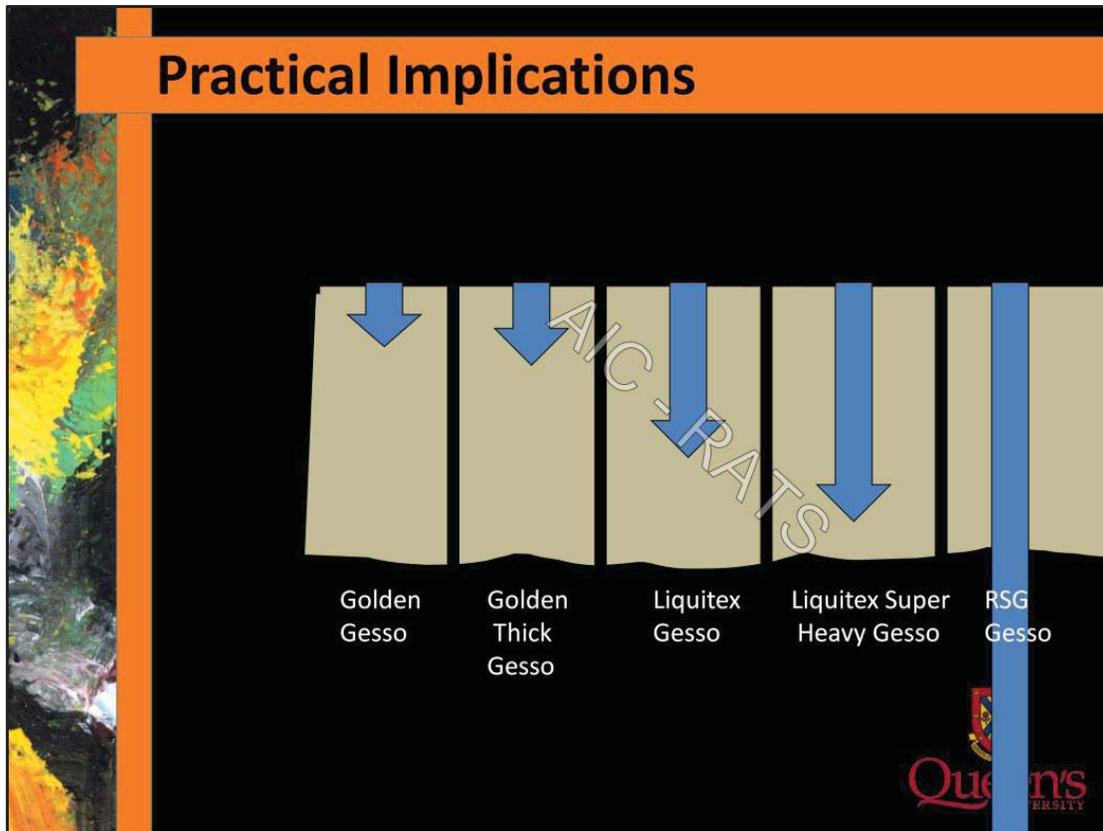
-For our research we have selected a variety of commercially prepared and lab prepared gessos commonly used in art and conservation.

-The diffusive behavior of these materials with a variety of cleaning solutions and inpainting media was investigated.



-Due to the extremely fast diffusive behavior of the RSG based gesso compared with the acrylic materials, **much** thicker RSG samples are needed to characterize the diffusive behavior of this material accurately.

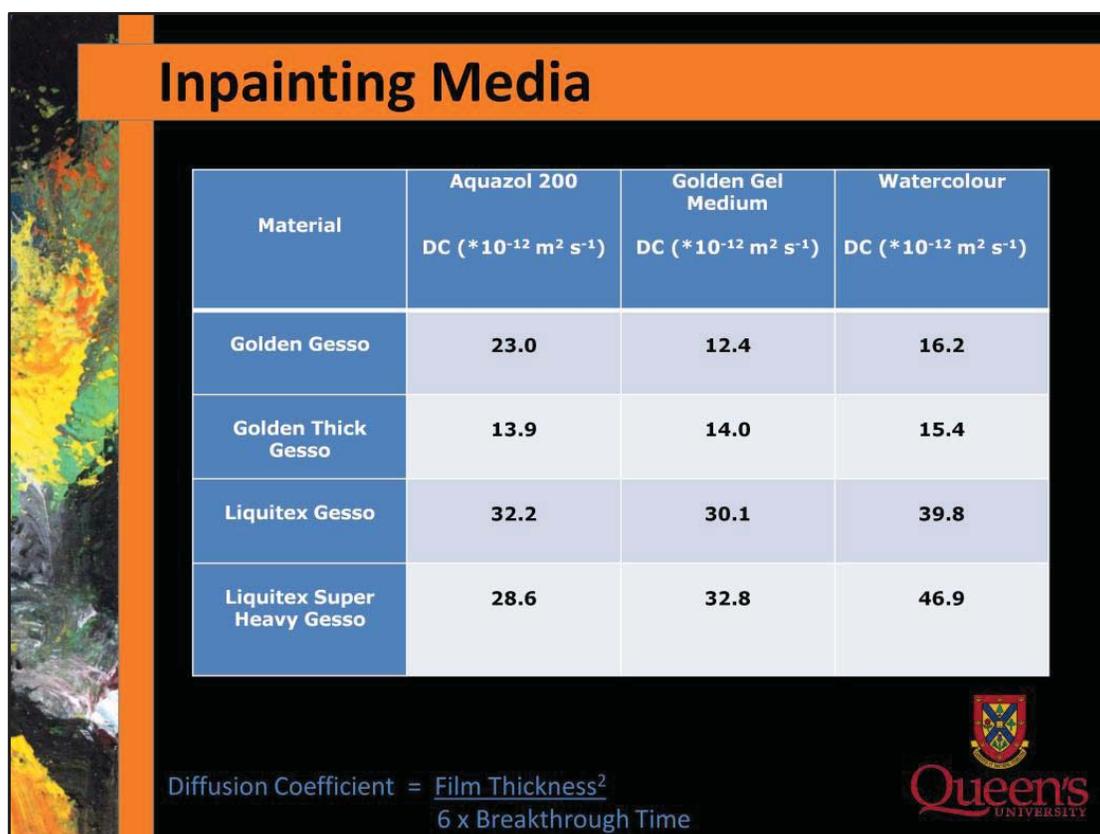
-(\*)While the exact rate of the RSG gesso is still being determined, it is known to be much greater than any of the other materials.



-To illustrate the implications of the difference in diffusion coefficients, here is a diagram of how far water would travel into the film for a given exposure time.

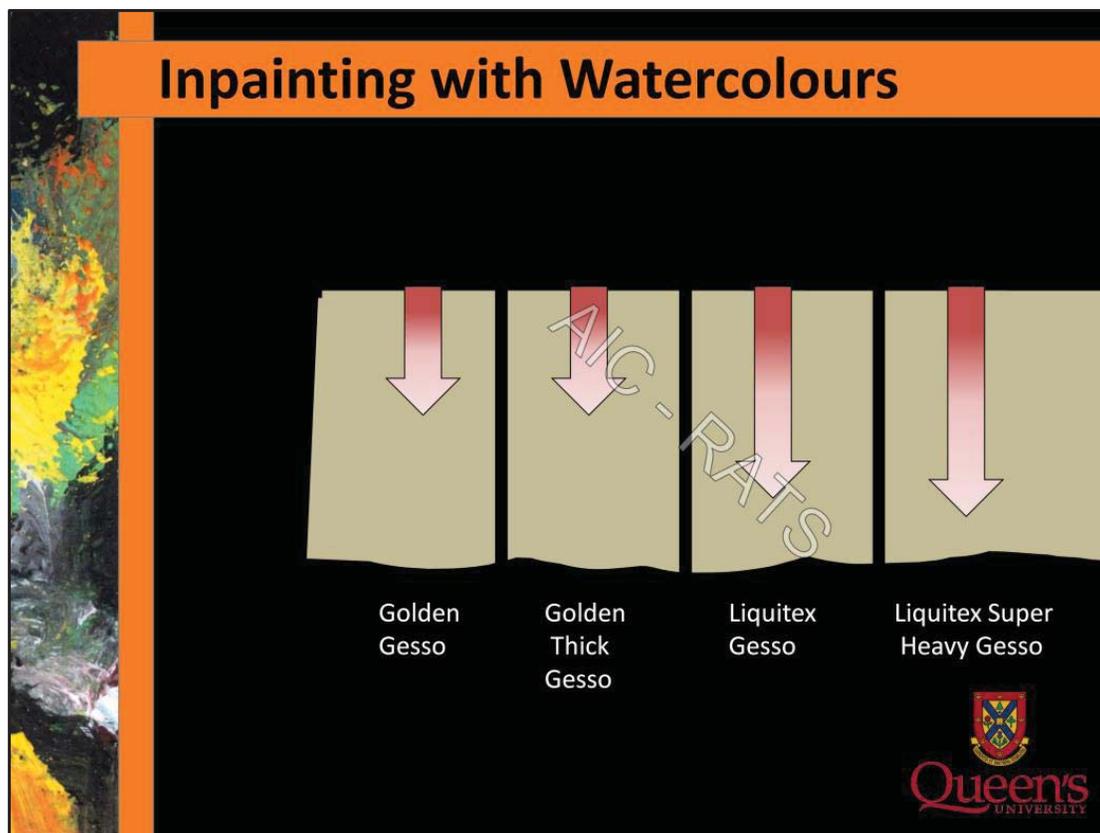
-In terms of conservation, this means that if you were to apply a treatment, such as cleaning with a wetted swab, identically to each material, the water would permeate far less into a Golden gesso sample than an otherwise identical Liquitex sample.

-While the exact rate of the RSG gesso is still being determined, it is known to be much greater than any of the other materials.



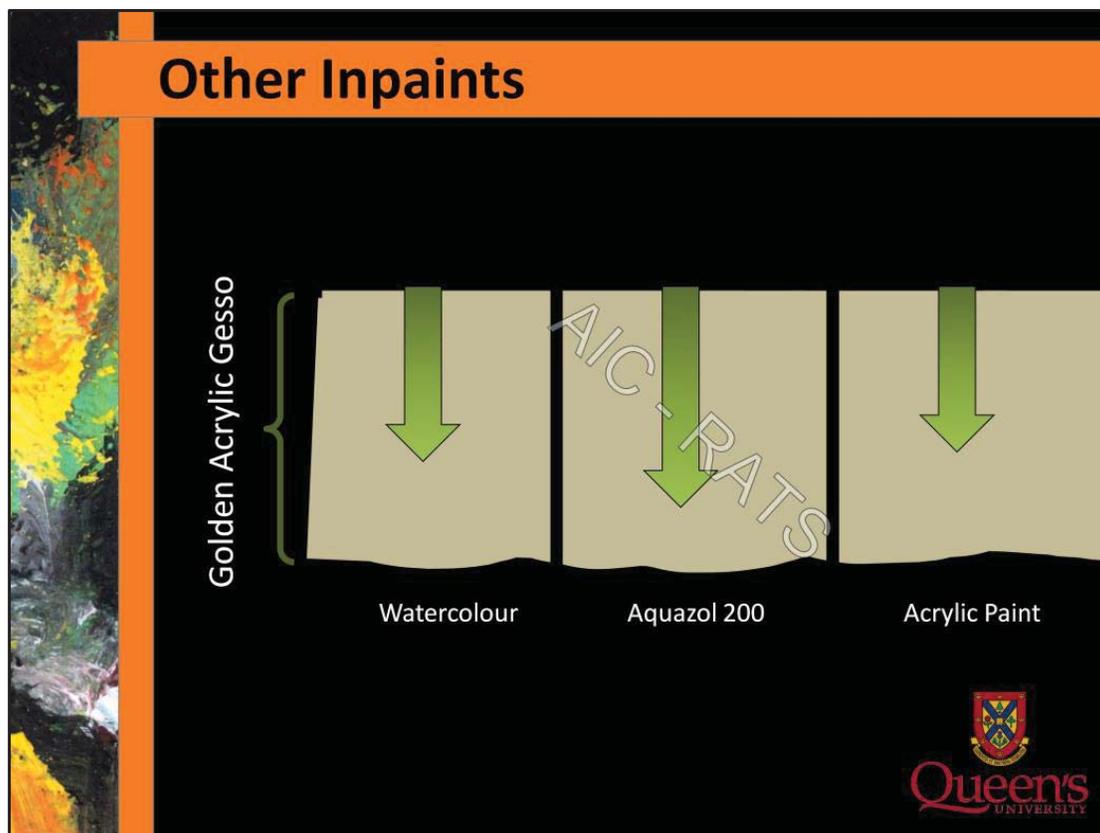
-For each inpainting media, the relative rates of diffusion across the different materials were found to be similar to water.

-The rates of all the inpainting media were found to be surprisingly similar for each gesso given the huge compositional and physical differences between the inpainting media.



-Here is a diagram of how far a watercolour paint would travel into the film for a given exposure time.

-The relative speed of diffusion follows the same trend across the gessos as with water.



- Here is a diagram of how far each inpainting media would travel into a Golden gesso film for a given exposure time, demonstrating the relatively small differences between the paint media.

## Cleaning Solutions

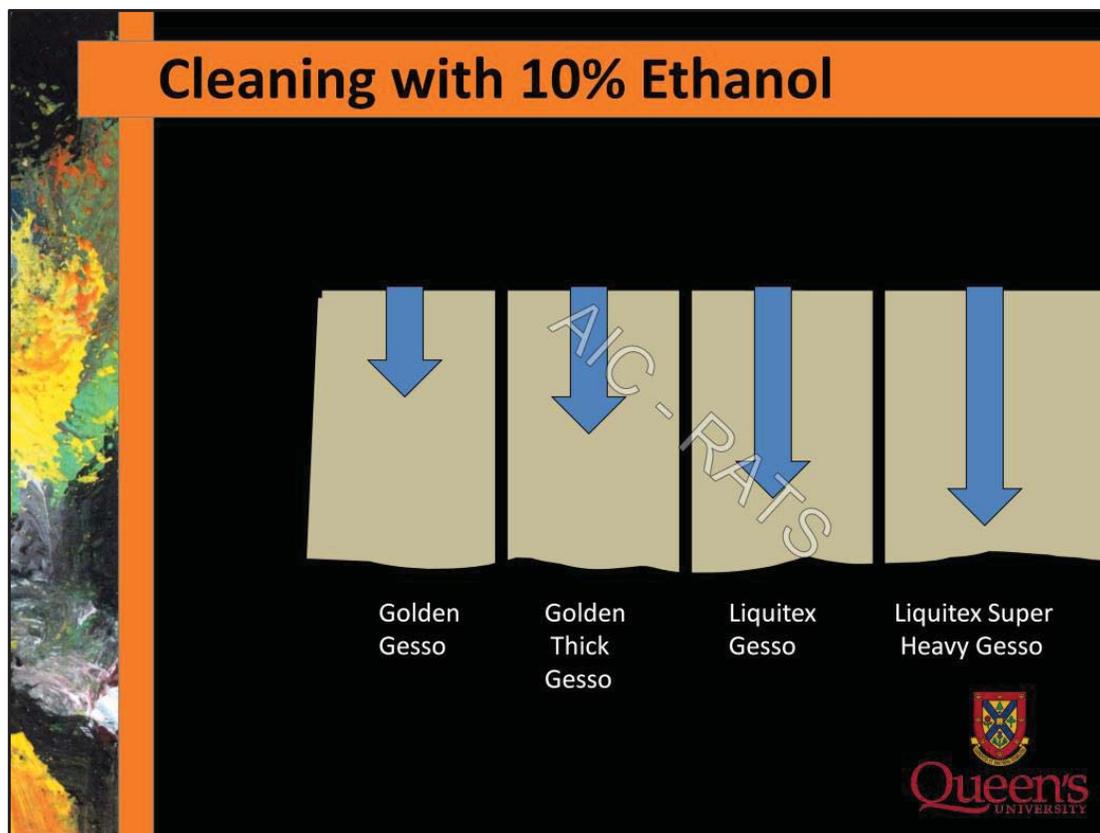
Material	Distilled Water	10 % Ethanol	2% Tri ammonium citrate
	DC ( $\times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ )	DC ( $\times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ )	DC ( $\times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ )
Golden Gesso	<b>7.8</b>	<b>5.6</b>	<b>5.8</b>
Golden Thick Gesso	<b>10.4</b>	<b>9.13</b>	<b>10.5</b>
Liquitex Gesso	<b>18.6</b>	<b>14.1</b>	<b>21.5</b>
Liquitex Super Heavy Gesso	<b>34.4</b>	<b>25</b>	<b>27.3</b>

Diffusion Coefficient =  $\frac{\text{Film Thickness}^2}{6 \times \text{Breakthrough Time}}$



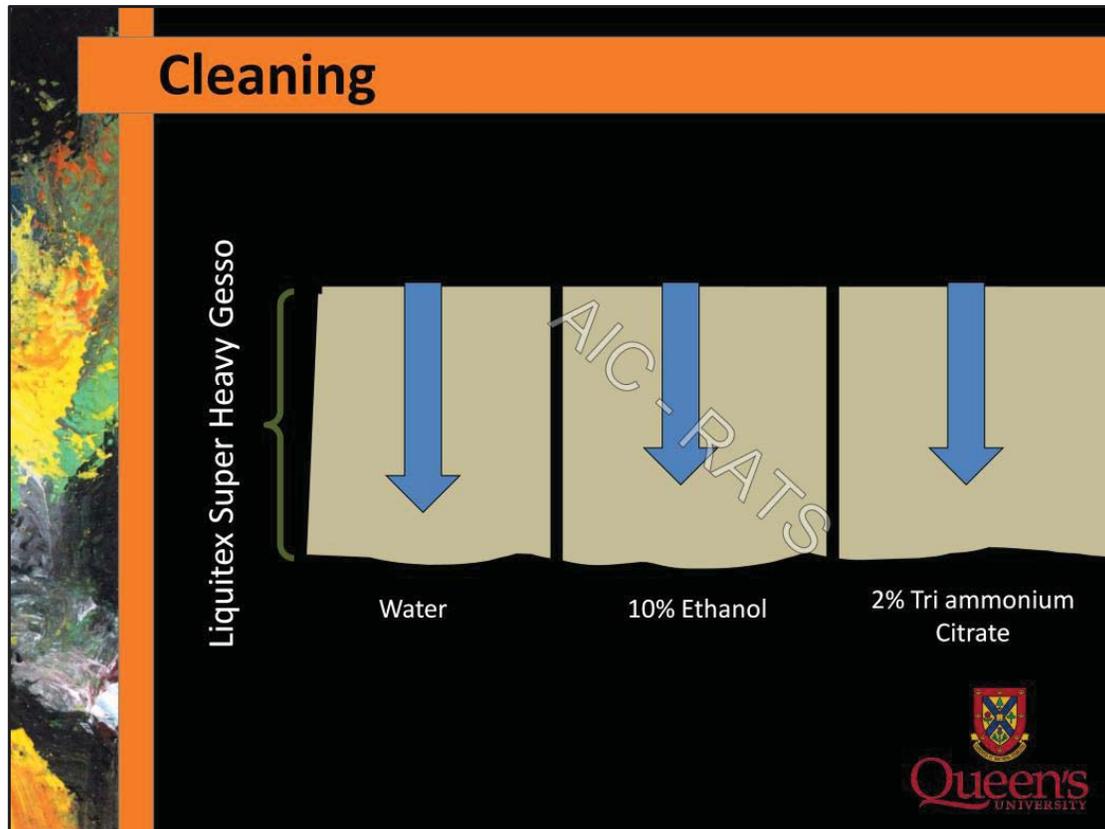
-Within each cleaning solution, the relative rates of diffusion across the different materials were found to follow the same trend as for water and the inpainting media.

-As with the inpainting media, rates of all the cleaning solutions were found to be similar for each gesso, even though there are huge compositional and physical differences between the solutions.



-Here is a diagram of how far a solution of 10% ethanol in water would travel into the film for a given exposure time.

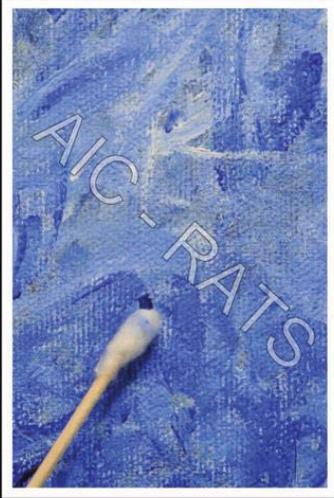
-Once again the relative speed of diffusion follows the same trend across the gessos as with almost every fluid examined.



- Here is a diagram of how far each cleaning solution would travel into a Liquitex Super Heavy gesso film, for a given exposure time showing the relatively small differences in diffusion rates between the various cleaning solutions.

## Summary

- Gessoes are highly active fluid transport media.
- Diffusive behaviour can vary hugely with even apparently similar materials.
- A material can respond surprisingly equally to dissimilar treatments.



-Gessoes are highly active fluid transport media.

-Diffusive behaviour can vary hugely for even apparently similar materials.

- A material can respond surprisingly equally to dissimilar treatments.



Roy S. Berns<sup>1</sup> and James Coddington<sup>2</sup>

<sup>1</sup> Richard S. Hunter Professor in Color Science, Appearance, and Technology and Director of the Munsell Color Science Laboratory, Center for Imaging Science, Rochester Institute of Technology

<sup>2</sup> Agnes Gund Chief Conservator, Museum of Modern Art

Presented at the Paintings/RATS joint session  
41st Annual Meeting of  
The American Institute for Conservation of Historic and Artistic Works (AIC)  
Indianapolis, In, May 29-June 1, 2013



Digital technologies present conservators with numerous new tools on many fronts including core activities like documentation. Often, though, the cost and complexity of the new technology is a barrier to its full implementation by the field. This paper will present the development and refinement of a multispectral imaging system (Dual-RGB) that uses off the shelf hardware and simple custom software, thereby reducing cost and complexity, to demonstrably improve the color accuracy for conservation documentation through a spectral estimation technique.

This system consists of a standard digital camera of reasonably high spatial resolution, two custom filters and standard studio lights for capture of the images. The camera has the IR filter removed to extend sensitivity beyond 600nm. Processing of the images is done with a GUI based program generated in Matlab and executable on any OS.

Fundamentally the system increases the number of channels captured from the standard 3 rgb channels to 6 by placing the two filters in the optical path and capturing images with each filter, hence the name Dual-RGB. First a white board is imaged with the filters so that the object images can be flat fielded to remove lighting artifacts and further improve the spectral estimation. A target such as a ColorChecker Classic with known spectral measurements is then imaged by the system to calculate a transformation matrix. This matrix will then be used to derive the spectral estimation of the object being imaged, which is also imaged with the two filters. Finally the object is captured with the two filters after which the image processing steps are done. The calibration images of white board and known target can be used for processing multiple objects provided the camera and lighting set up does not change.

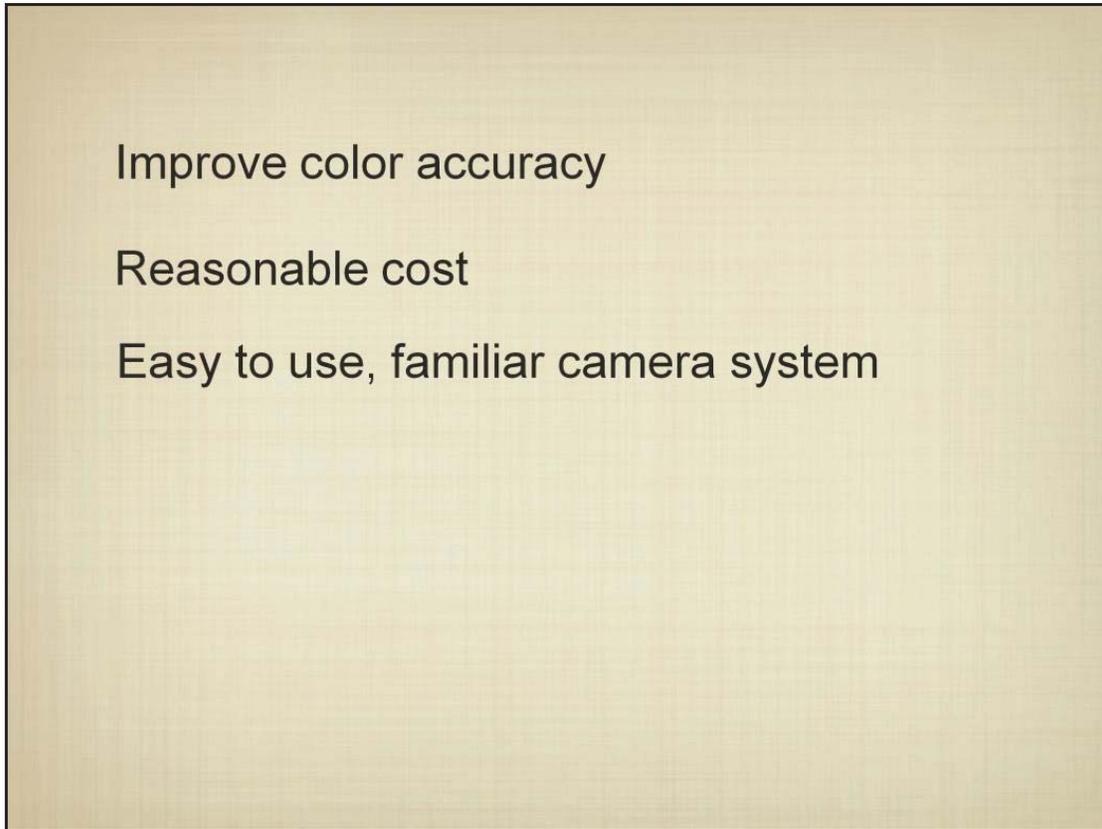


Four computational steps are required for the Dual-RGB approach: flat fielding, image registration, colorimetric processing, and spectral processing. Flat fielding includes spatial low-pass filtering, effectively removing noise artifacts from the sensor and smoothing any texture or dirt of the diffuse white board. The image registration is calculated at either the pixel or sub-pixel level. The archived image is a nine-channel ProPhotoRGB Tiff file. The first three channels are ProPhotoRGB encoded data. Channels 4-6 are image data from filter 1 and channels 7-9 are image data from filter 2. Channel 4-9 data have been flat fielded, registered, rescaled and encoded nonlinearly using the sRGB standard, and quantized to 16 bits.

The colorimetric and spectral processing achieves high color accuracy, reasonable spectral accuracy, and minimal noise propagation. The average DeltaE2000 for a color chart is less than 1 versus a range of 1.3 to 5.8 using the standard capture for a range of medium format digital camera backs. Perhaps more importantly the maximum error of the Dual-RGB system is 8.3 versus a range of 15 to 32 with the standard capture.

This is joint research between  
MoMA and Roy S. Berns'  
research group at the Munsell  
Color Science Laboratory at  
Rochester Institute of  
Technology

See <http://art-si.org>



The goals of the project, the results of which will be outlined in this paper, are listed here.

# Three Approaches



- Monochrome camera and liquid crystal tunable filter (31 bands)

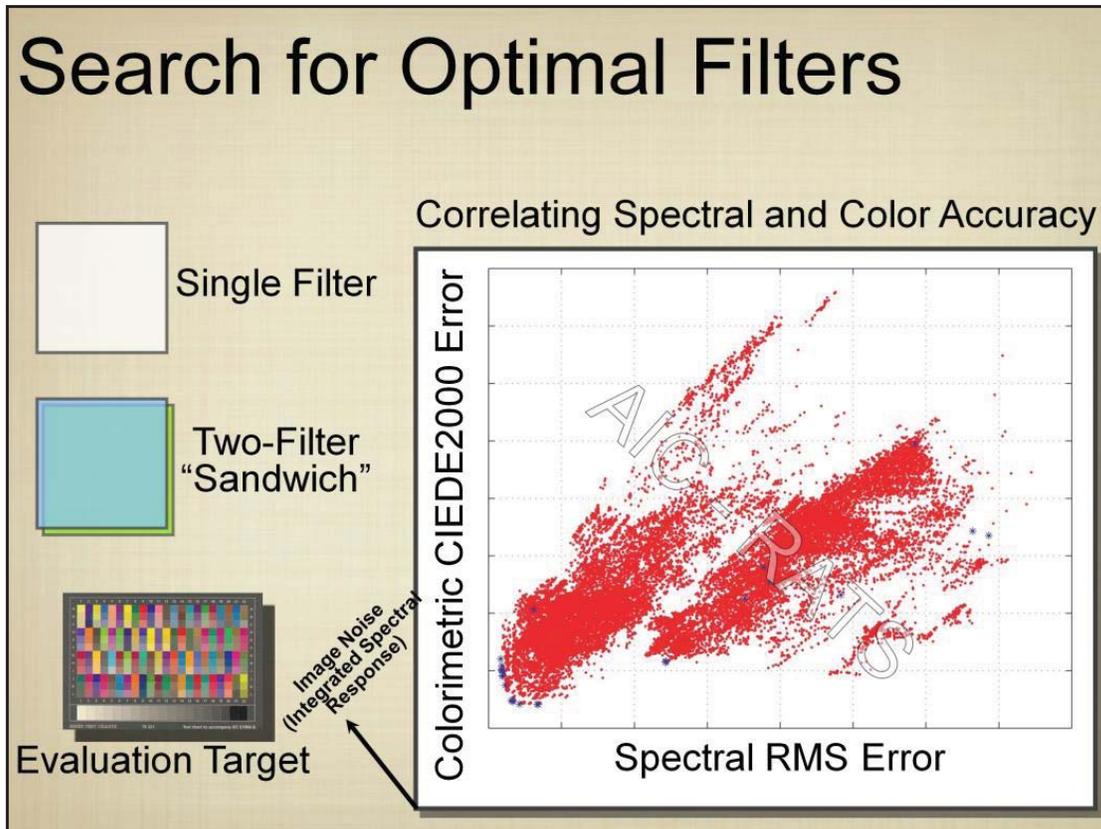


- Monochrome camera and six position colored glass filter wheel (6 bands)



- RGB digital camera and either two colored filters or two different light sources (6 bands)

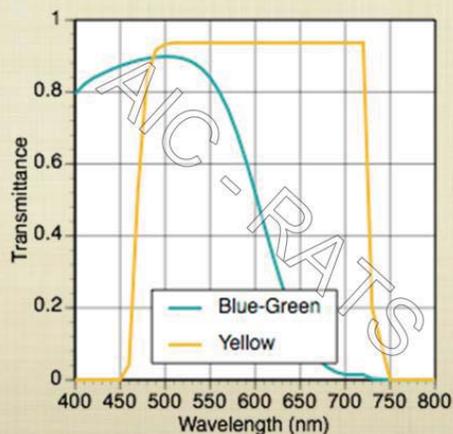
RIT developed and evaluated three approaches. The system that most closely met the criteria outlined was the use of an RGB camera with 2 colored filters to create 6 bands of data. Other systems, shown here, while improving color accuracy did not meet the cost of the ease of use criteria.



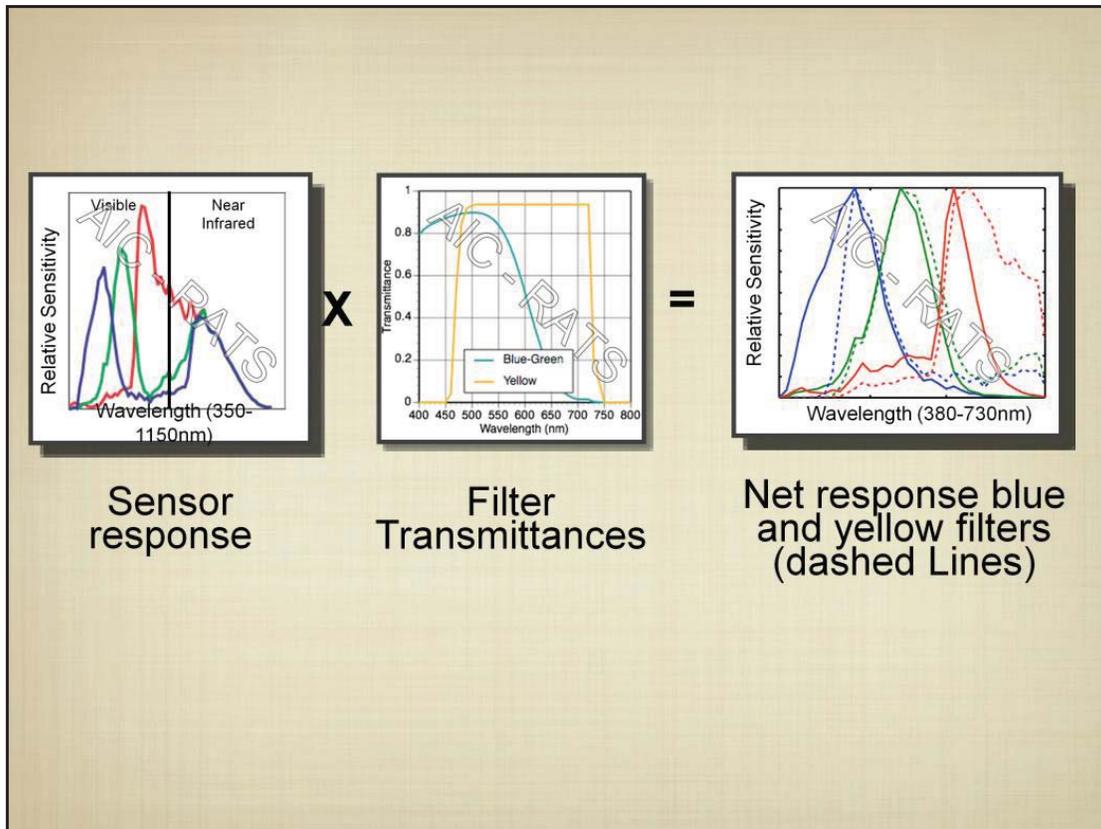
After choosing the 2 filter approach the first step was to identify the optimal set of filters. This was done through a optimization process and identified a set of one blue and one yellow filter. This plot compares color and spectral accuracy. Ideally, the pair of filters should achieve both AND not introduce image noise caused by low throughput caused by dark filters.

# Results

- Blue-green and yellow filters
- Blue-green nearly identical to stock filter
- Could operate either RGB or Dual-RGB

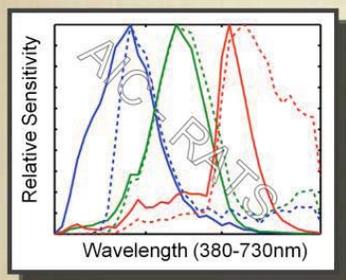


This slide shows the transmittance for both of the selected filters. The custom filters contain IR filters as well so that there is no transmittance in the IR range. The blue filter almost exactly matched the throughput of the filter supplied by the manufacturer for the camera when used in single rgb mode, thus allowing images captured with this filter to function as standard rgb captures if desired.

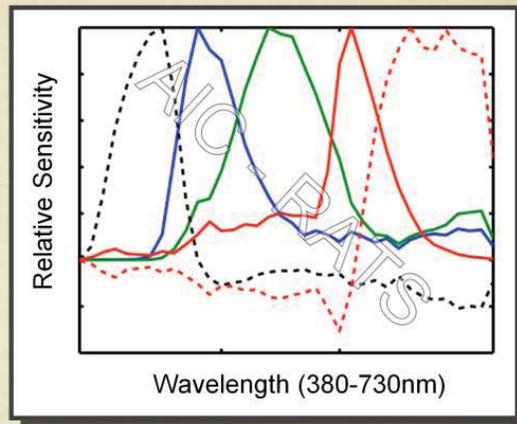


This slide illustrates the channels and spectra that are captured through the dual rgb system. The solid line represents the capture with the blue filter and the dotted line the capture with the yellow filter.

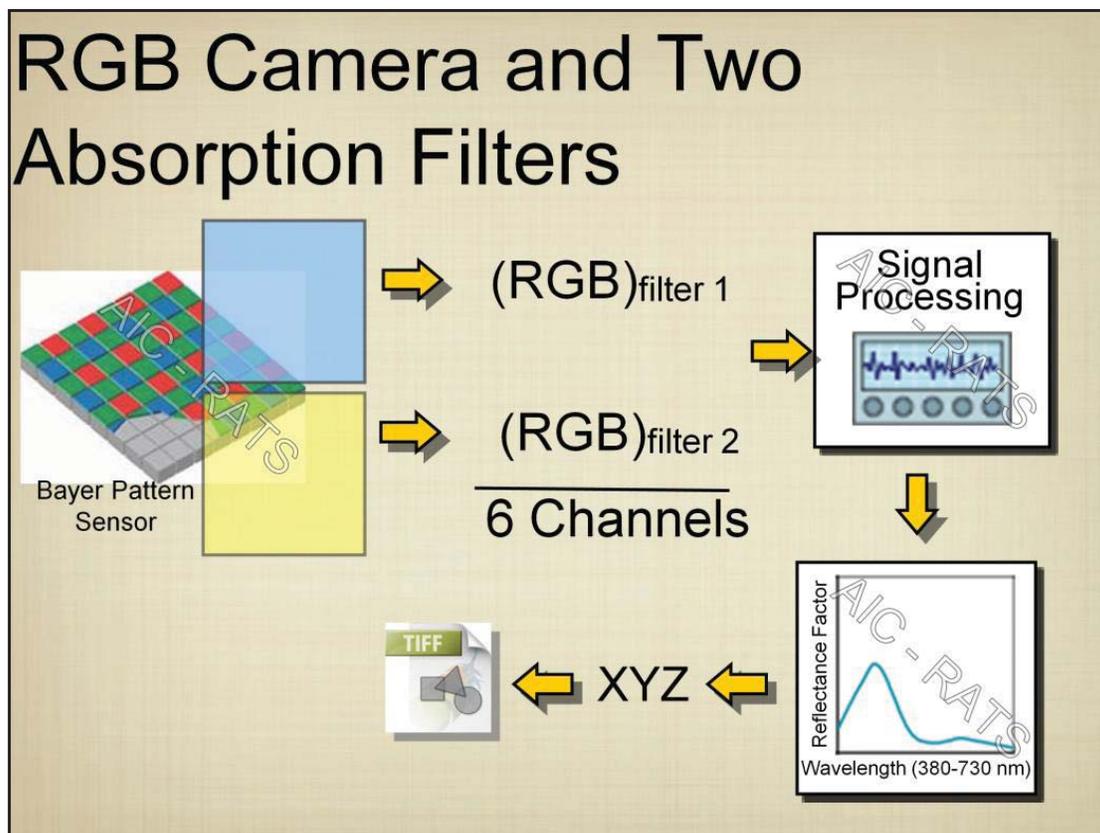
# Spectral Processing Yields Five Channels



$\times \mathbf{M} =$



As the green channel is almost identical in both captures the data are reduced to five channels. A matrix,  $\mathbf{M}$ , transforms the camera to sample the visible spectrum in five distinct spectral regions, resulting in a multi-spectral camera.



The basic data collection procedure is simply to capture a calibration target, a white board and the object under identical lighting conditions with each filter. The images are then flat fielded and aligned, indicated by signal processing here. The captured values for the target are then compared to the known spectral values for the target and an optimization that yields the most accurate spectral estimation for the target is calculated. This estimation is then applied to the 6 channel object image to achieve more accurate color than with a simple **rgb** image.

## Implemented in 2004 with Commercial RGB Camera

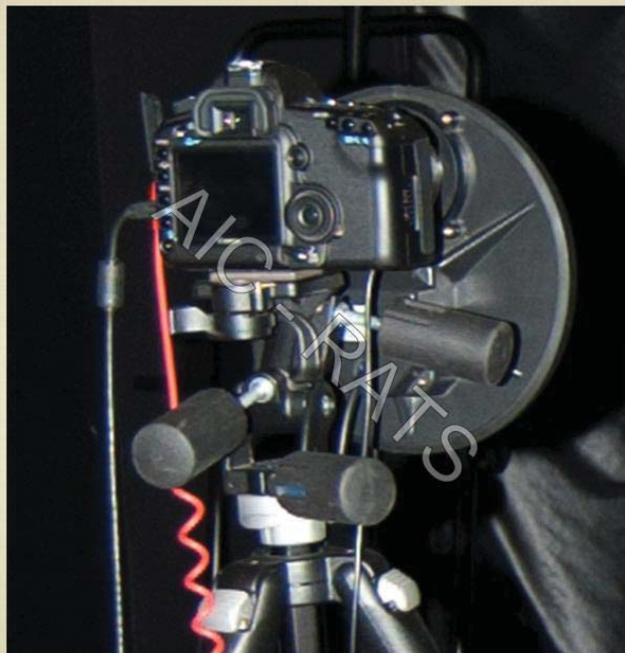
- photographer friendly,
- high resolution,
- less complex,
- less expensive.



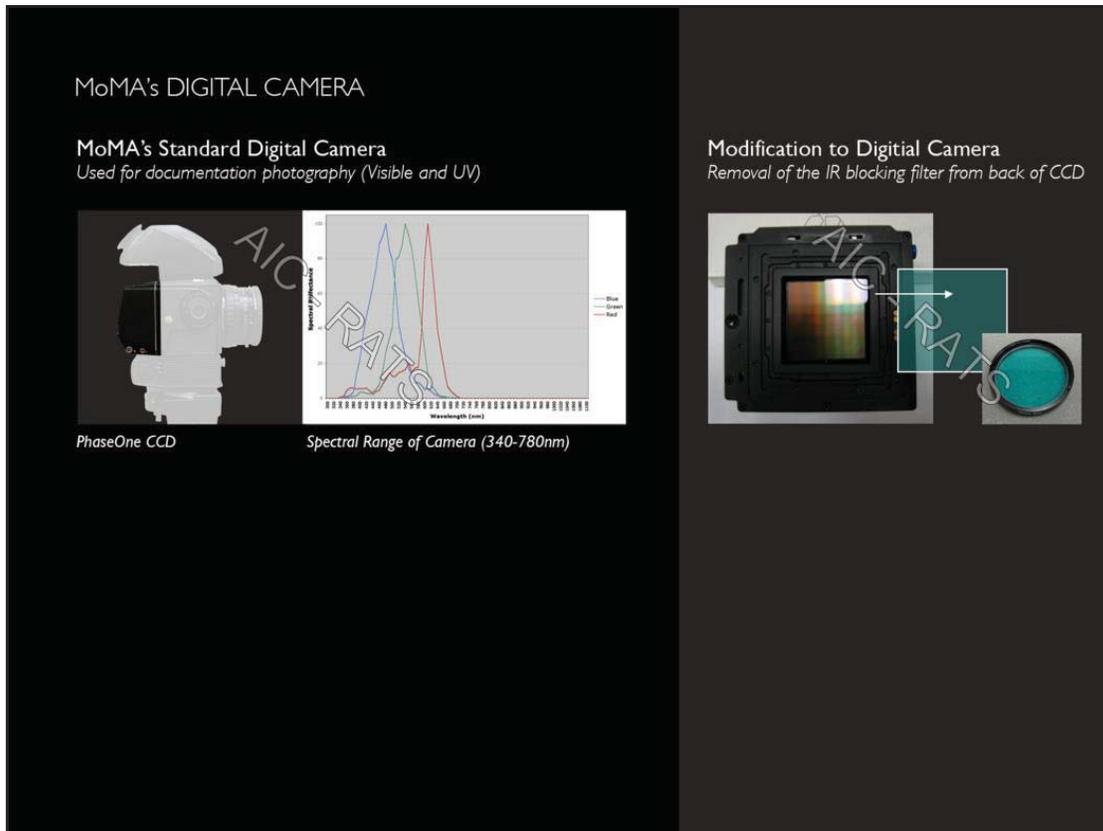
Sinar 54H, P3, M shutter

The first system developed at RIT used a Sinar 54H and a custom filter slider for the B and Y filters.

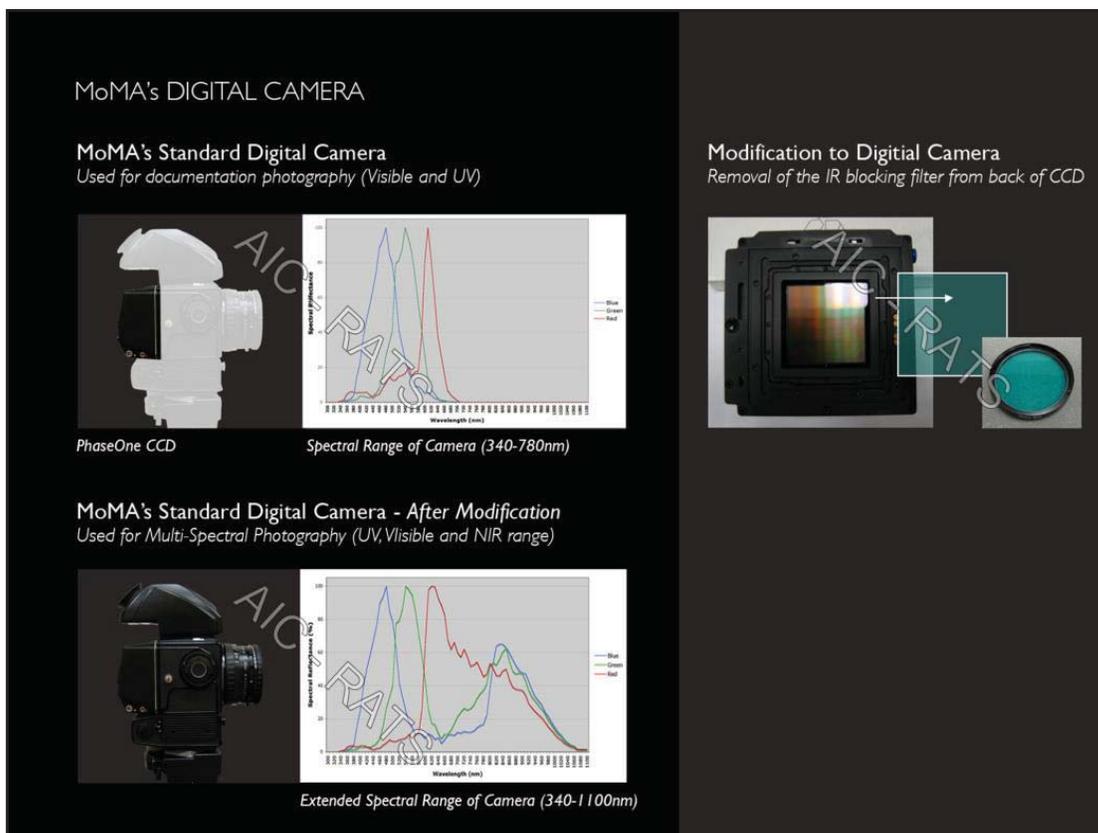
## Canon 5D Version



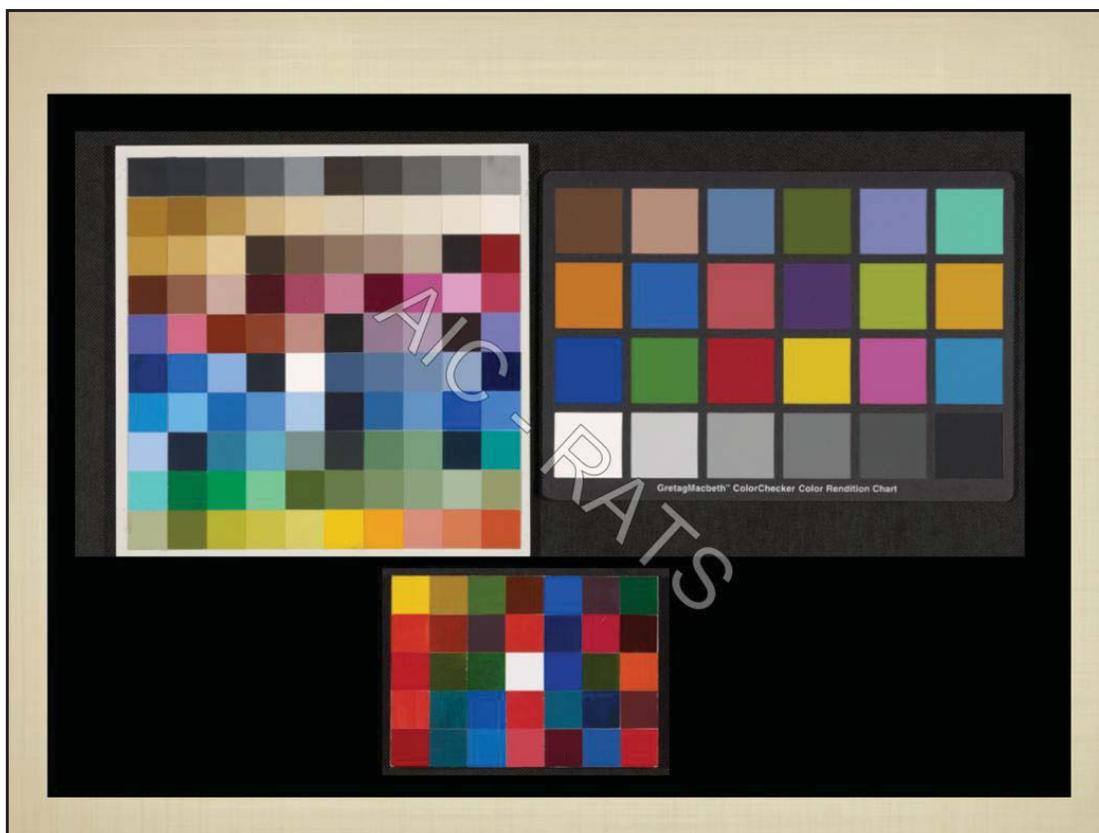
The basic system outlined so far is applicable to any high quality rgb camera, shown here on a Canon DSLR camera. In this implementation, a filter wheel was used. The wheel also enables imaging in the NIR.



A PhaseOne camera in use in the Conservation lab was modified by removing its IR cut-off filter (bluish).



This extends the spectral sensitivity to about 1100 nm.



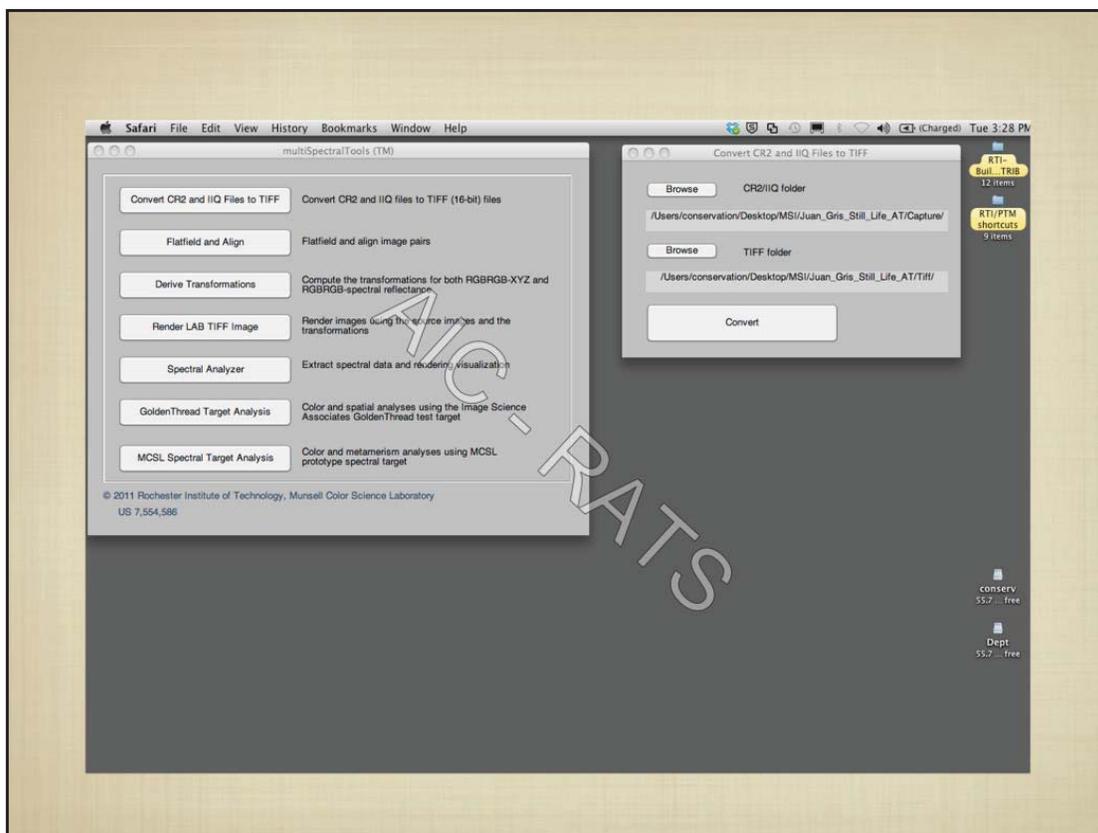
Any target that has been measured with a spectrophotometer can be used for calibration. Two of the targets in this slide are custom targets. The upper left has colors chosen that will minimize metamerism in the spectral estimation while the target on the bottom contains a number of similar red oil paints and a high-chroma yellow paint. This target would be used to evaluate the system, not for calibration.



We have often used the Xrite ColorChecker Classic for calibration. Above it is the Golden Thread target.



The left image shows tape on the floor to orient the lighting at different angles. The right image shows a Pollack painting being lit with fluorescent diffuse lights and the PhaseOne in front.



This is the basic software for the system. The files run as executables through the downloadable matlab runtime compiler.

The various parts of the program are seen here in the order of use and each has prompts for the necessary steps of loading files and running the applicable program. First is conversion of raw files to tif so that the rest of the programs can work with them. This is followed by the flatfield and aligning. The third uses the captured target along with the text file that holds the measured data for that target to derive the optimum transformation. The files generated by the transformation become the basis for the next step which is to render the final 6 channel image of the object. The last programs are various tools for assessing the quality of the images captured. The first presents information on selected pixels from the final image that can be compared to spectral measurements of the same area of the work. The last two are used to compare data within the image to common industry imaging targets.

# Spectral Estimation Accuracy

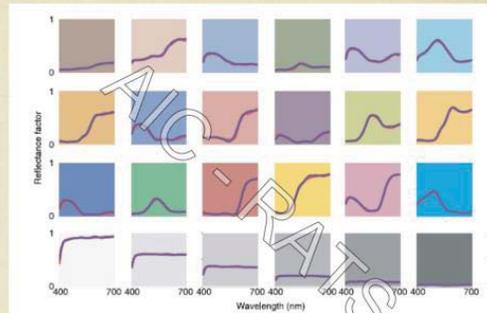
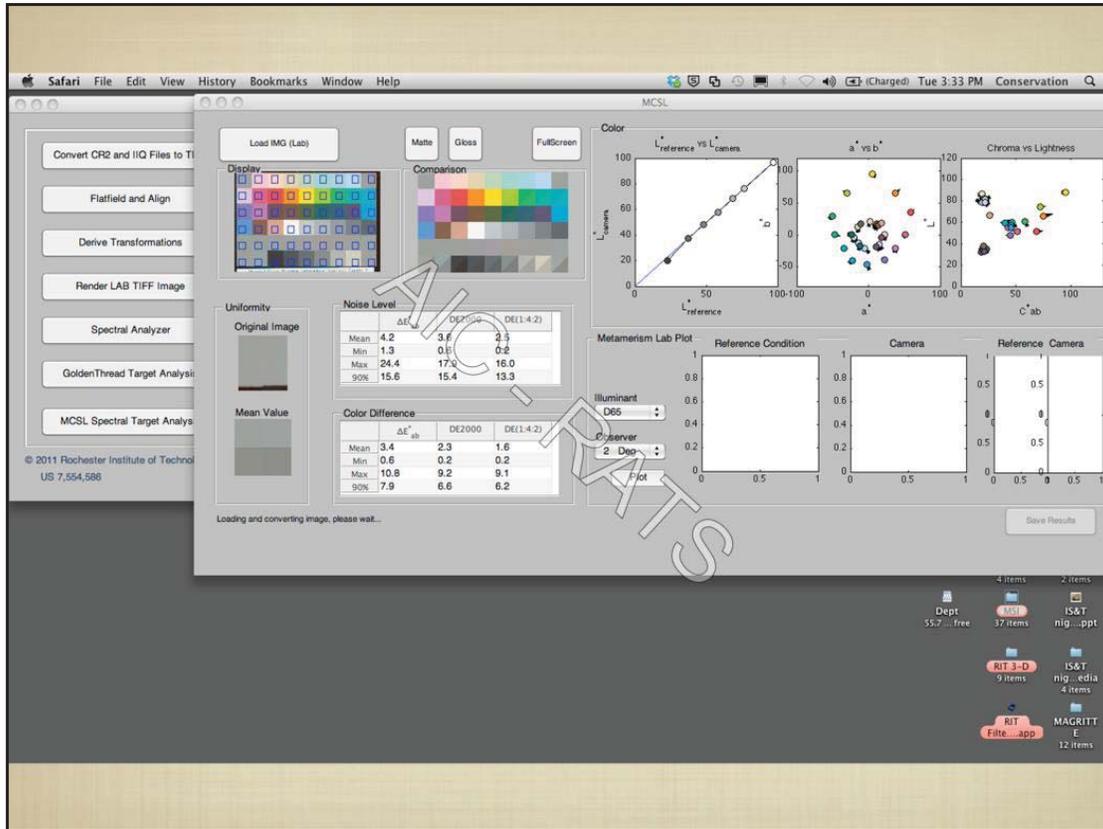


FIGURE 4 Typical spectral-measurement accuracy for the ColorChecker using a two-filter color-filter-array image-acquisition system (blue lines) compared with a small-aperture contact spectrophotometer (red lines).

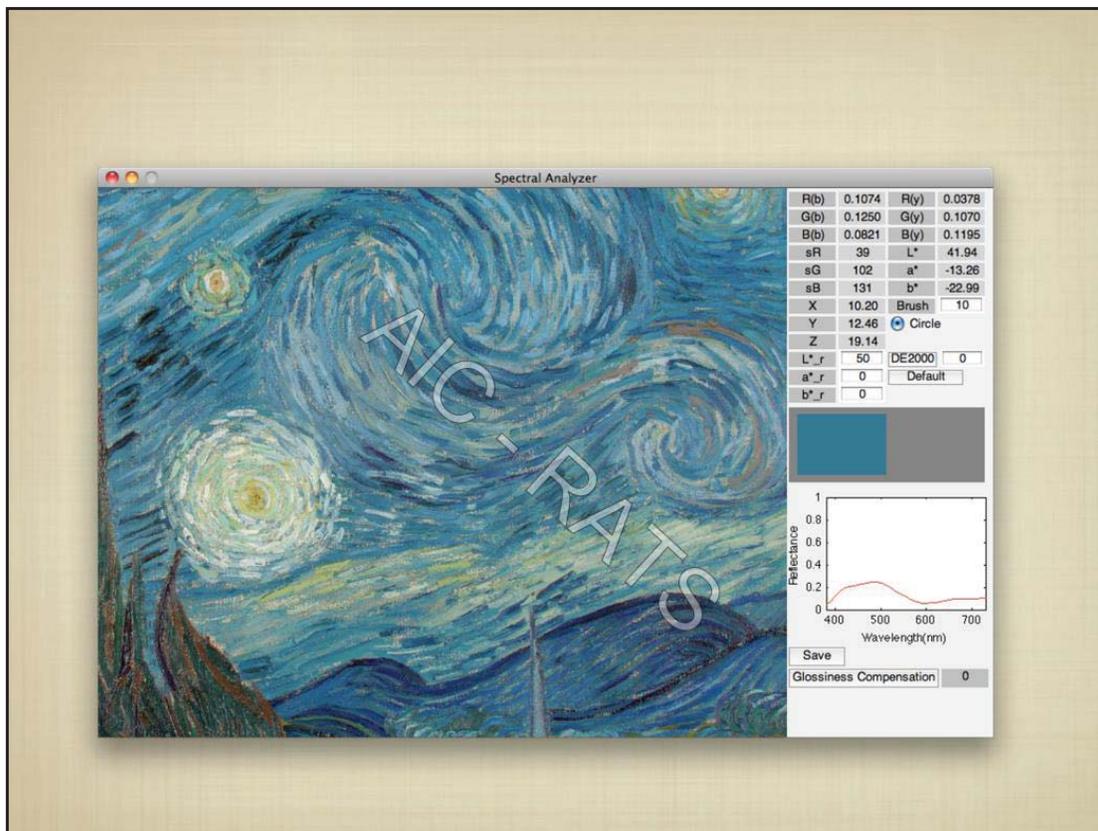
This is typical performance for the calibration data.



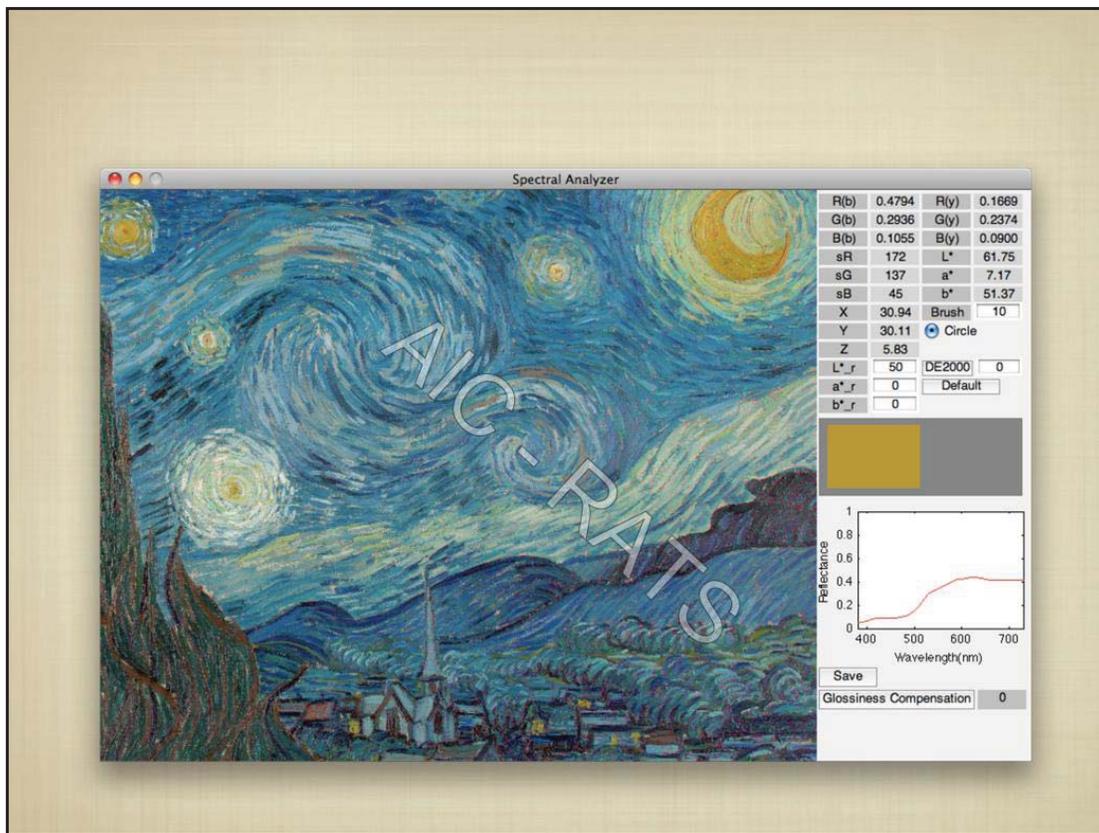
This slide qualitatively demonstrates the increased color accuracy of the system. The circle is the bluish green from the color checker based on the measured Lab values on the target. The upper half is the result using the dual-rgb capture and the bottom half is a standard rgb capture.



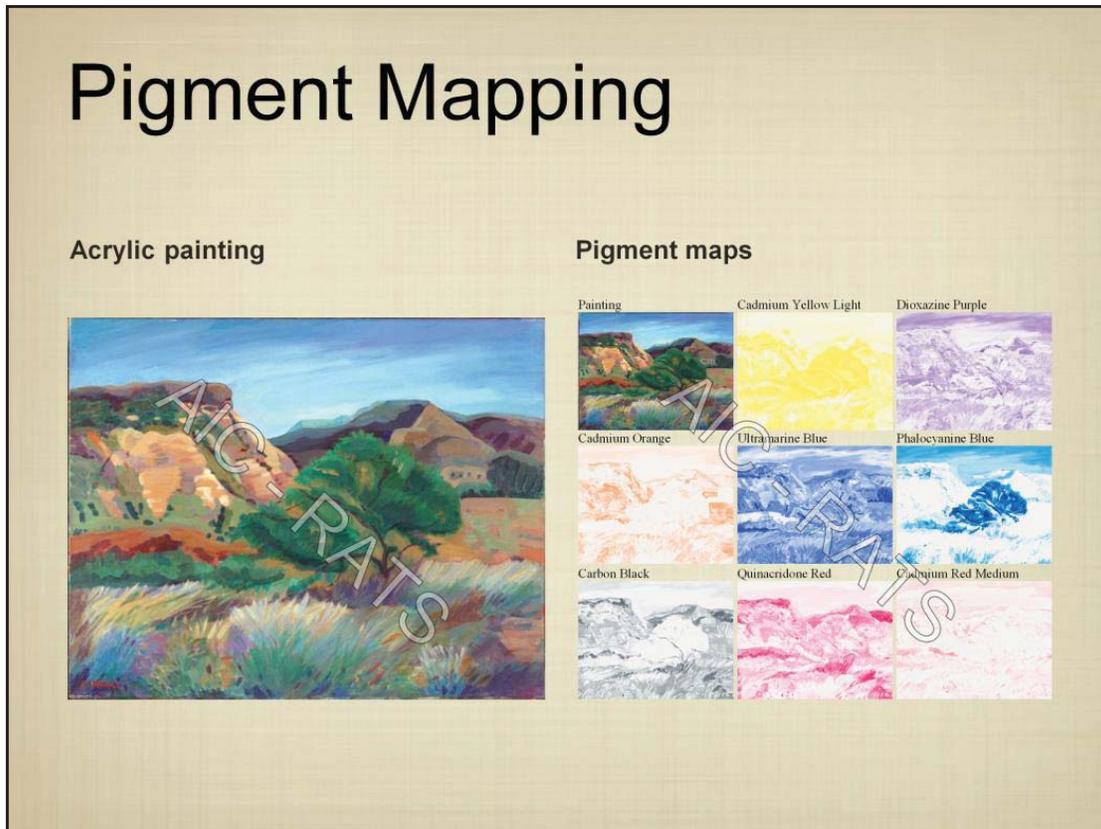
The software has various tools for measuring accuracy of the results.



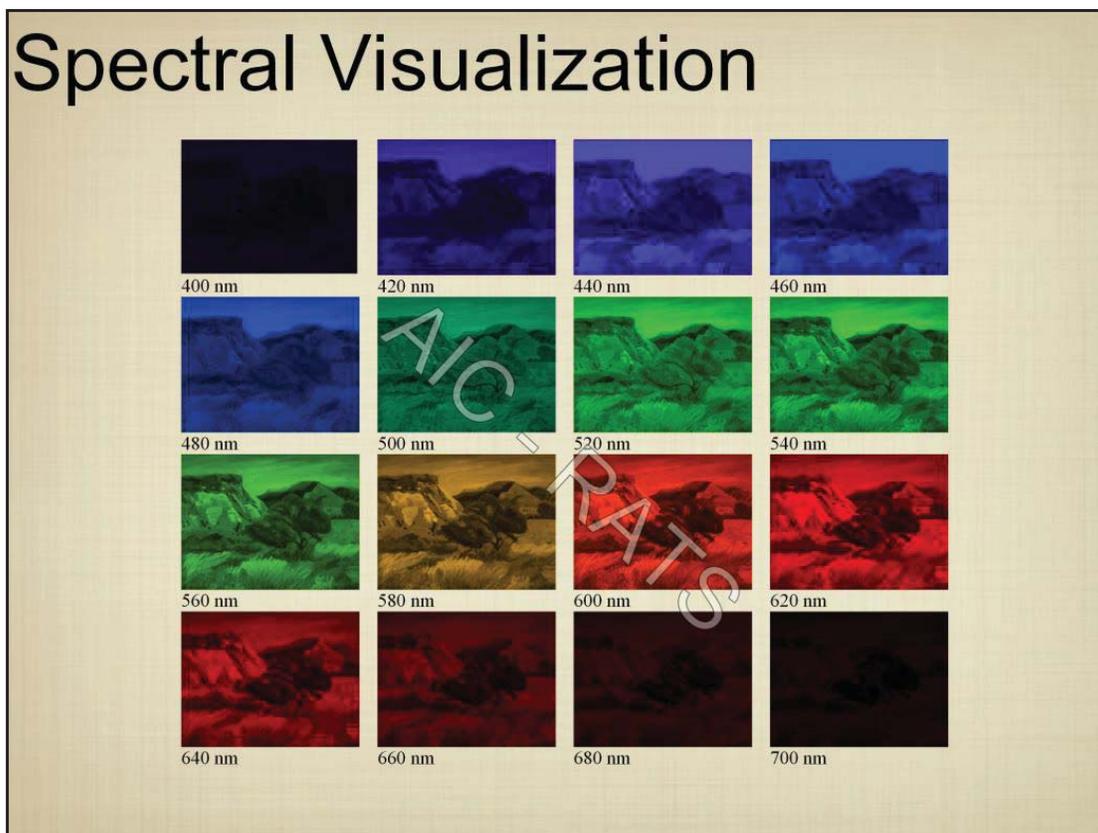
The software also provides a spectral analyzer tool that can plot the spectral estimation of selected pixels.



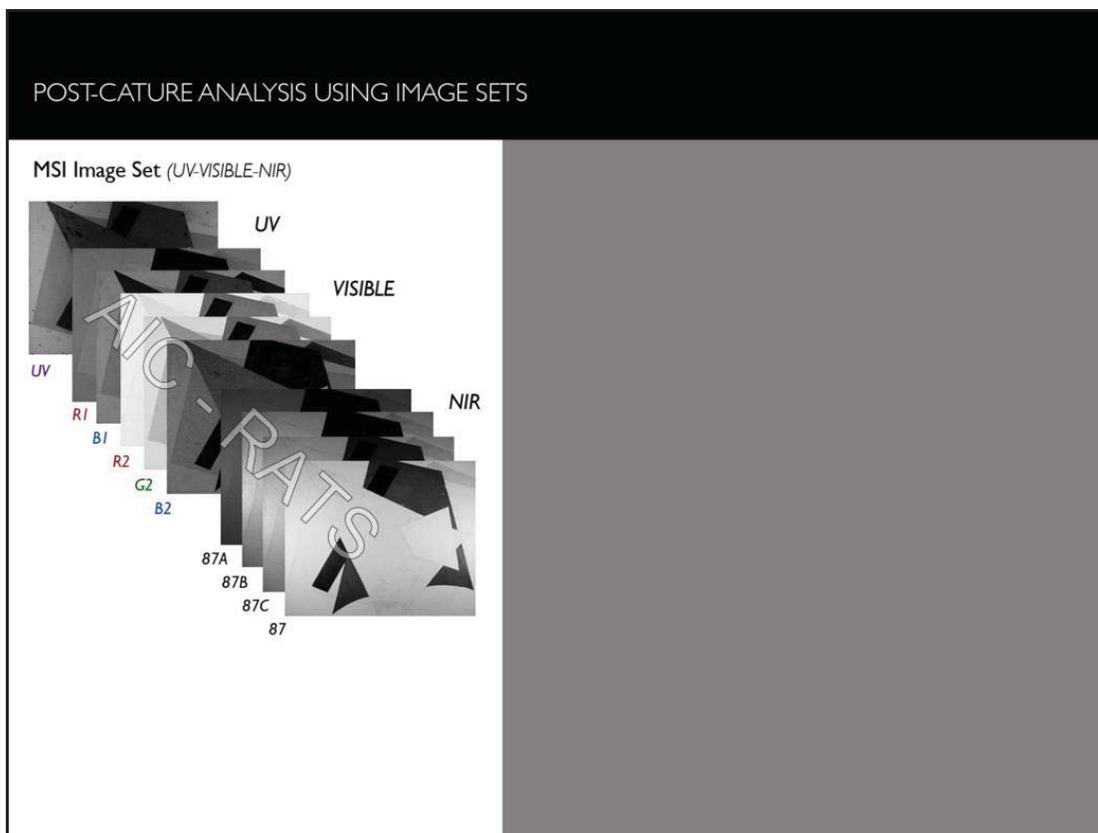
Spectrum of a yellow passage.



The dual-rgb data can be used for pigment mapping. This is ongoing research at RIT. In this example, we assumed this listed set of pigments. Dual-rgb data are sufficient to facilitate the pigment mapping.



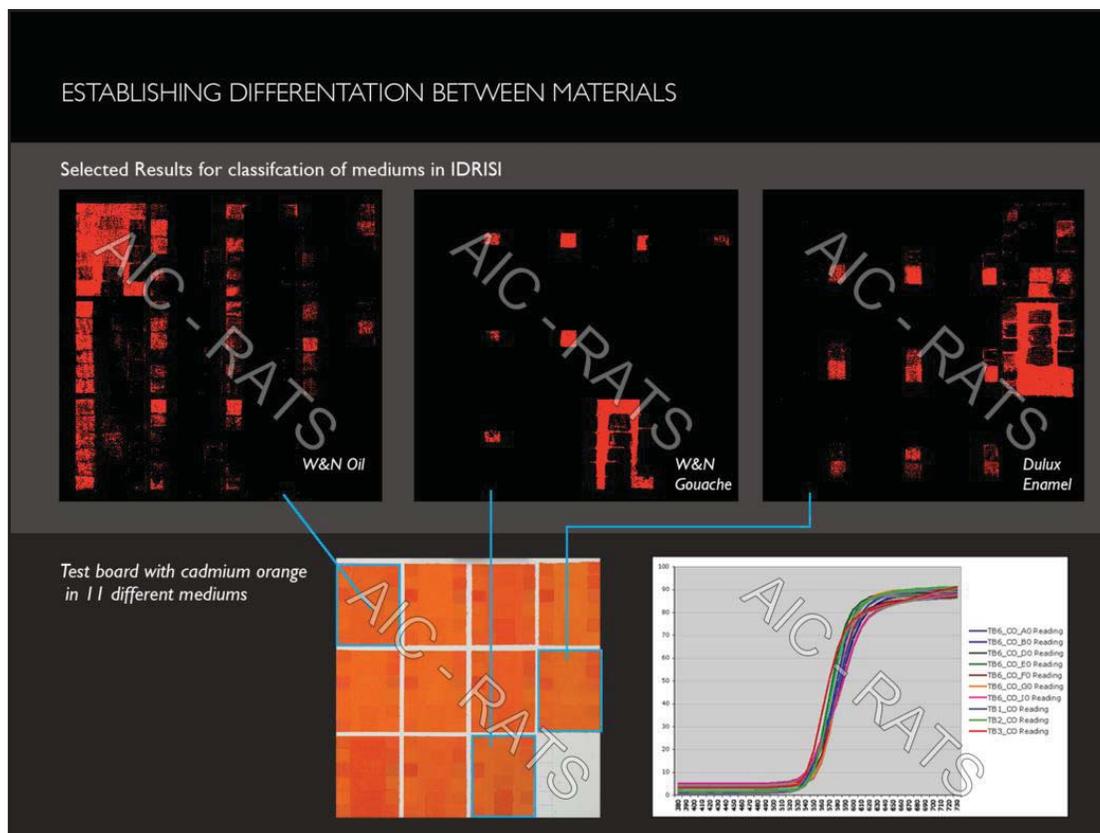
These are spectral band images with color coding that corresponds to the listed wavelengths.



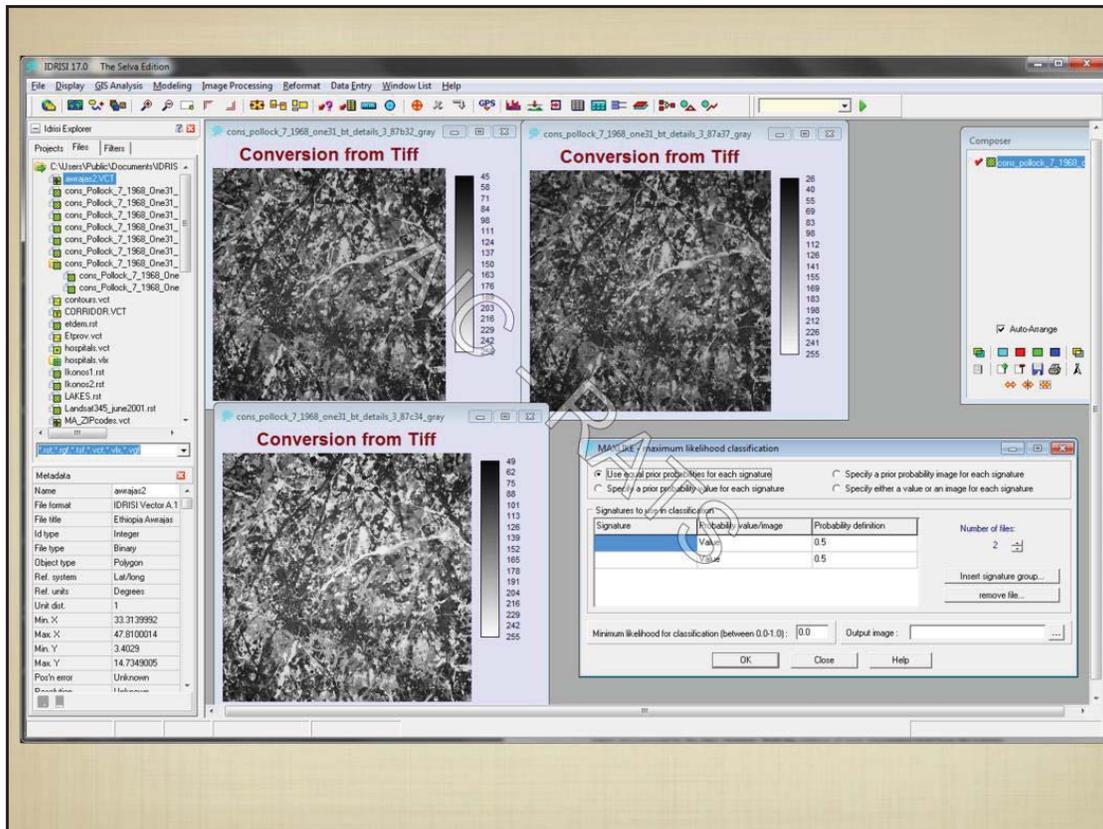
The spectral estimation data is useful not only for more accurate color recording of objects but can also be used for image analytics. When using the system for this it is most useful to include capture of UV and NIR. In our case we capture three separate IR images by using 87A, 87B and 87C filters as well as the usual blue and yellow filters for visible spectrum capture.



A chart was made using these media to test if the dual-rgb system, using its IR sensitivity as well, could qualitatively detect different media. Each section of the chart was begun by laying down a base color of each medium, resulting in 11 sections. On each of these sections smaller patches of each medium with the same pigment as the background, was painted on.



This slide shows the results for the cadmium orange panel made by the procedure outlined in the previous slide. The three top images show the results for separating out oil, gouache and enamel media. The approach is reasonably successful, isolating each of these media's application as a background and then also within the backgrounds of different media. The software used for this is Clark Labs' Idrisi, a package of GIS tools. A maximum likelihood classification of 95% was used for these results but IDRISI offers many other statistical tools as well.

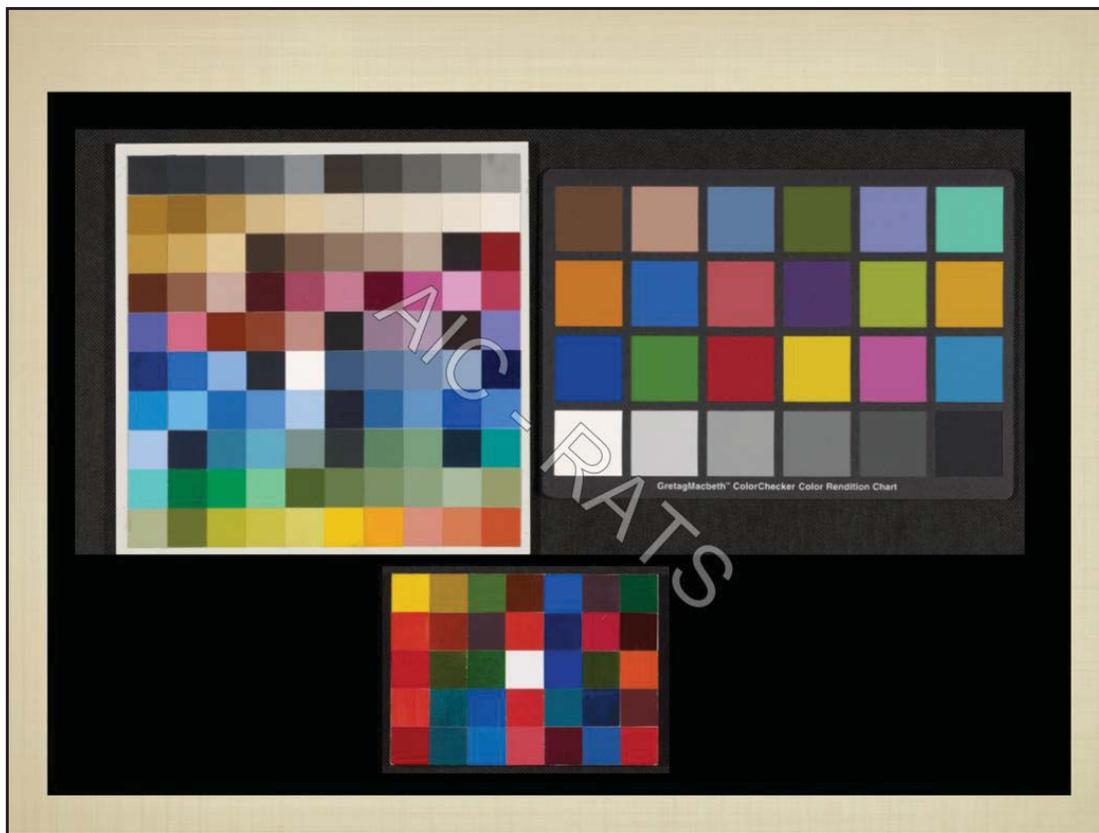


This slide illustrates IDRISI at work.

# Imaging Systems

- PhaseOne 180 IQ (New)
- Leaf Aptos 75 (New)
- Hasselblad H4D-50 (New)
- RIT-Sinar 75H Dual-RGB (Prototype)
  
- Cruse (New)
  
- BetterLight Super 8K with Northlight 900 lighting (Old)

Finally a dual-rgb system that used the Sinar 75H sensor was systematically compared to rgb systems found in many museum imaging services studios.



These three targets were optimally imaged by professional photographers using each system.

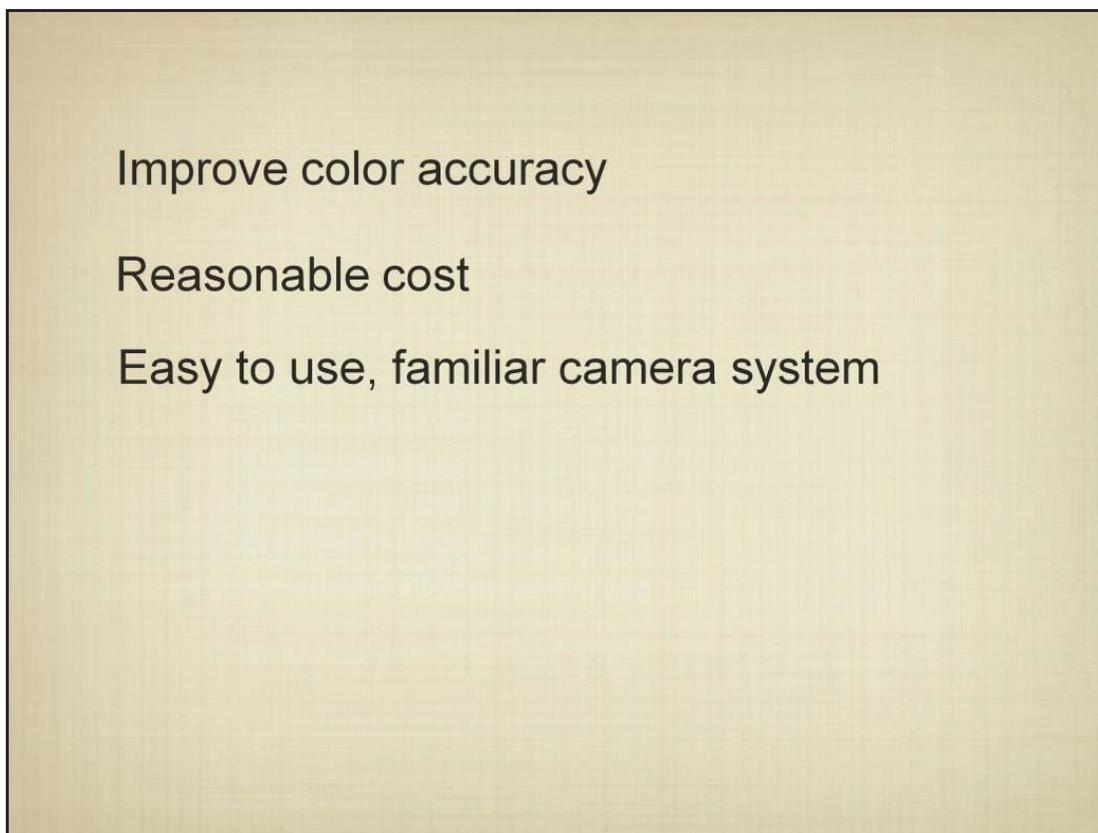
# Results

T-tests for rank order

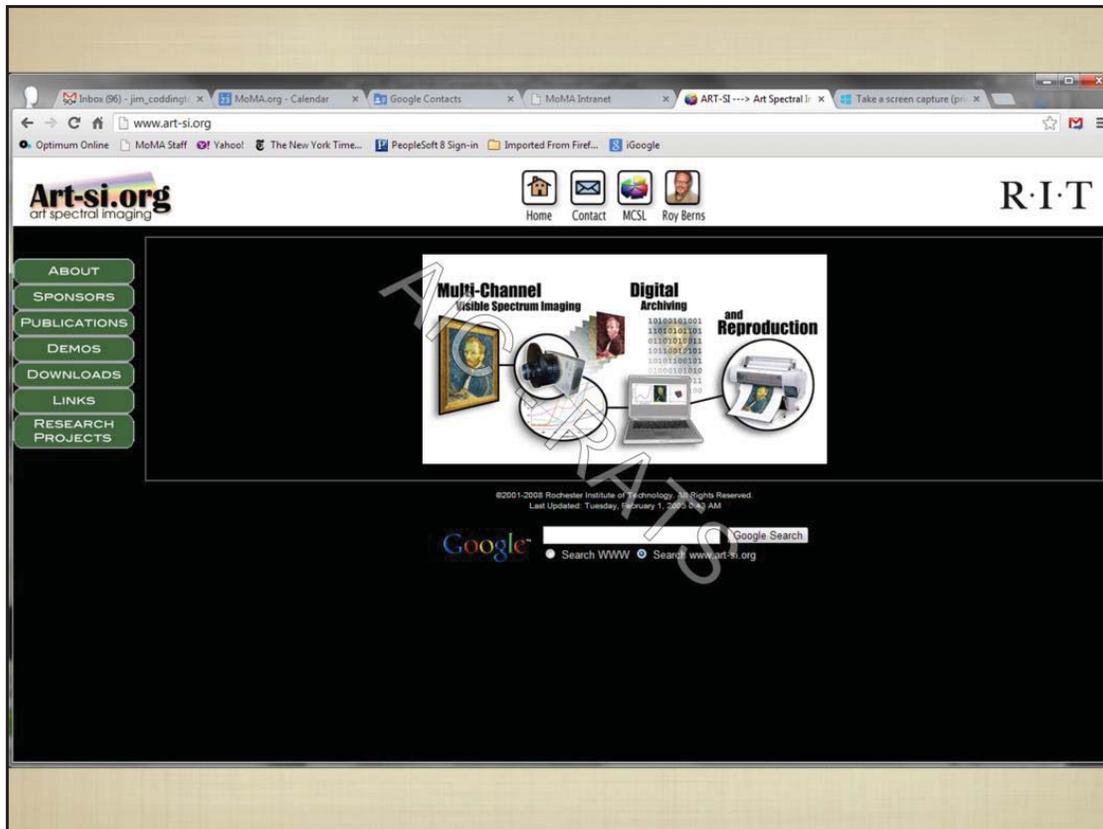
Camera	Statistics	$\Delta E_{00}$	$\Delta E^*_{ab}$
Dual-RGB Sinar 75H Color (1)	Mean	<b>1.5</b>	<b>2.4</b>
	90th	3.3	5.2
	Maximum	6.8	8.3
Dual-RGB Sinar 75H Color and Image Quality (1)	Mean	<b>1.7</b>	<b>3.2</b>
	90th	3.1	5.4
	Maximum	6.2	18.1
Cruse (3)	Mean	<b>2.9</b>	<b>4.4</b>
	90th	5.5	8.3
	Maximum	8.7	14.8
Leaf Aptus 75 (3)	Mean	<b>3.2</b>	<b>5.7</b>
	90th	5.1	9.6
	Maximum	9.0	19.1
Hasselblad H4D-50 (5)	Mean	<b>4.6</b>	<b>9.1</b>
	90th	6.7	13.4
	Maximum	9.8	20.3
Phase One IQ 180 (6)	Mean	<b>5.3</b>	<b>8.3</b>
	90th	8.5	13.5
	Maximum	11.6	30.6
BetterLight Super 8K (7)	Mean	<b>6.0</b>	<b>10.3</b>
	90th	9.9	19.5
	Maximum	18.3	32.0

The colorimetric and spectral processing achieves high color accuracy, reasonable spectral accuracy, and minimal noise propagation. The average DeltaE2000 for a color chart is less than 1 versus a range of 1.3 to 5.8 using the standard capture for a range of medium format digital camera backs. Perhaps more importantly the maximum error of the Dual-RGB system is 8.3 versus a range of 15 to 32 with the standard capture. The maximum error is often the color that requires the most time to 'fix' in any visual post-processing, indicating that the dual-rgb system can save considerable time during documentation, especially in high work flow environments.

More details have been published: R. S. Berns and S. Smith, "Analysis of color management default camera profiles for museum imaging applications," *IS&T Archiving 2012*, 111-115 (2012).



To summarize the initial goals of the dual-rgb of improved color accuracy at a reasonable cost with a fairly simple user experience have been met.



RIT publications about the development of the dual-rgb approach to multi-spectral imaging can be found at [www.art-si.org](http://www.art-si.org).

# Sinar System (Release Imminent)

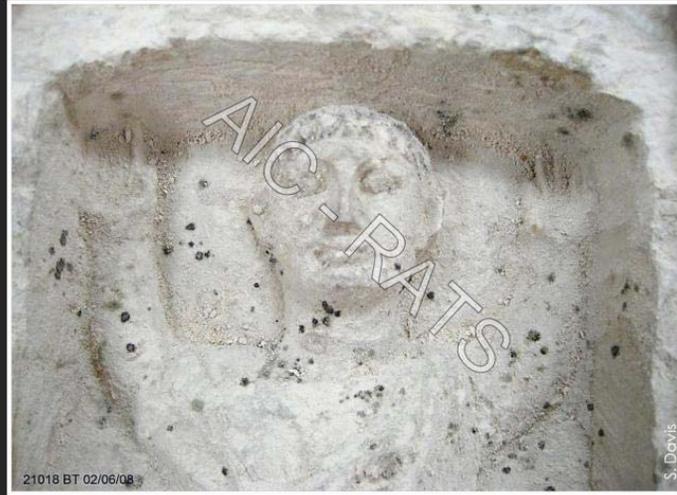
- RePro camera
- 86H sensor (Dalsa 48MP ftf6080c)
- eShutter, HR 100 lens
- CTM software (“color to match”)
- Dual-rgb slider



RIT and Sinar have a partnership to commercialize the dual-rgb approach. The system was released in November, 2013.

See <http://www.sinar.ch/en/category/products/ctm-en/>

## Examination, Technical Study and Treatment of Funerary Stelae from the Roman-Egyptian Site of Terenouthis



**Caroline Roberts**

2013 AIC Annual Meeting, Indianapolis

Caroline Roberts<sup>1</sup>, LeeAnn E. Gordon<sup>2</sup>, and Cathy Selvius-DeRoo<sup>3</sup>

<sup>1</sup> Graduate Intern, J. Paul Getty Museum

<sup>2</sup> Sherman Fairchild Fellow in Objects Conservation, Museum of Fine Arts, Boston

<sup>2</sup> Research Scientist, Detroit Institute of Arts

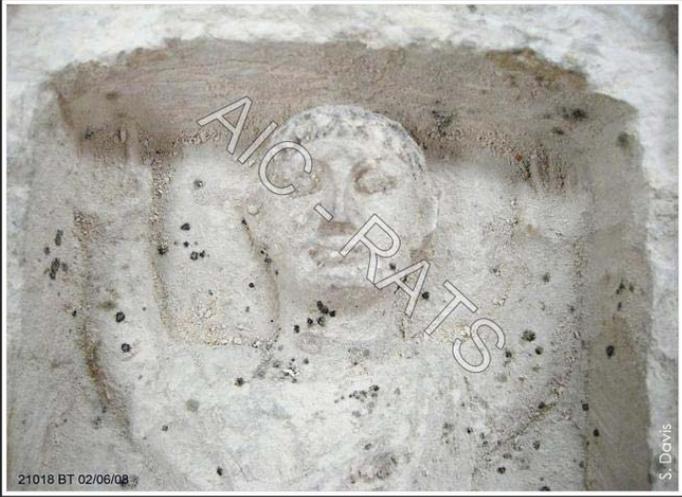
Presented at the RATS session

41st Annual Meeting of

The American Institute for Conservation of Historic and Artistic Works (AIC)

Indianapolis, In, May 29-June 1, 2013

**Examination, Technical Study and Treatment of Funerary  
Stelae from the Roman-Egyptian Site of Terenouthis**



**Caroline Roberts**  
2013 AIC Annual Meeting, Indianapolis

This paper shares some observations and discoveries from my recent study of a group of Roman-Egyptian funerary stelae (or grave markers) from the ancient city of Terenouthis, which are preserved at the Kelsey Museum of Archaeology, at the University of Michigan.

The project, which developed a flexible plan to preserve a large collection of artifacts and incorporated materials and techniques used in specializations outside the conservation field, represents a what I observe to be a contemporary, collaborative approach to research – one that makes the best use of limited resources and looks to professional allies for ideas and support.

Image credit:

Suzanne Davis

## OUTLINE

- **History**
- **Examination**
- **Analysis**
- **Treatment protocol**



KMA Photo Caption Database

My paper presents four main highlights of my study, starting with the stelae's collection history – where they were found, why they are significant, and how they came to reside in Ann Arbor, Michigan.

I'll then touch on the information revealed by examination and analysis, including results obtained through collaborations with scientific laboratories at the Detroit Institute of Arts, and the University of Michigan.

Finally, I'll talk briefly about the treatment protocol that was developed from this research, as well as the aims this project has set for the long-term preservation of the stelae.

Images:

Kelsey Museum of Archaeology Photo Caption Database.



The stelae were discovered in 1935 by a team of archaeologists employed by the University of Michigan, at a site known in antiquity as Terenouthis. Terenouthis is located in the Fayoum region of Egypt, about 150 kilometers northwest of Cairo. There is evidence that the site was a thriving commercial center as early as the Late New Kingdom Period, between 1300 and 1050 BCE. However, most of the artifacts excavated in 1935 are from the Graeco-Roman period, between the 3<sup>rd</sup> and 4<sup>th</sup> centuries CE.

References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

Talay, L. E. and S. E. Alcock. 2006. *In the field: the archaeological expeditions of the Kelsey Museum*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

Images:

c.o. Suzanne Davis

HISTORY



Enoch Peterson and Kelsey Museum staff at Karanis, Egypt

KMA Photo Caption Database

University of Michigan Professor Enoch Peterson, pictured here with Kelsey Museum namesake Francis Kelsey and other staff, led the expedition to Terenouthis.

References:

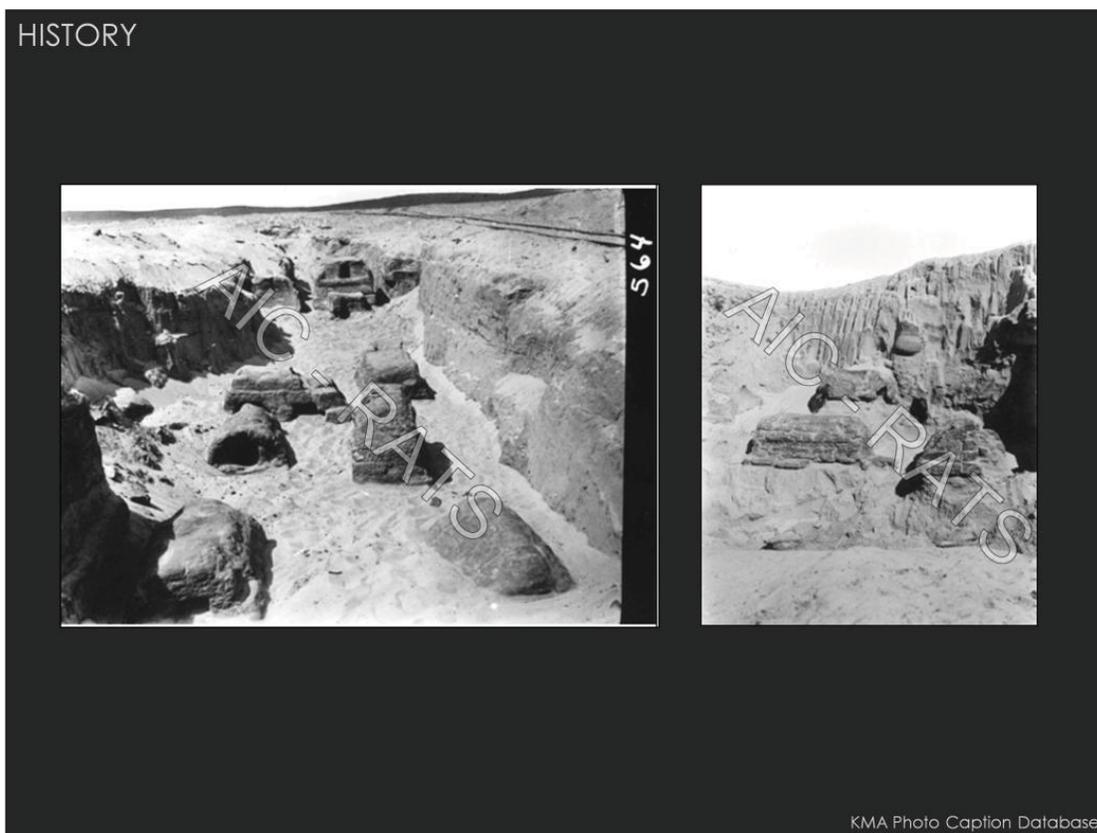
Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

Talalay, L. E. and S. E. Alcock. 2006. *In the field: the archaeological expeditions of the Kelsey Museum*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

Images:

Kelsey Museum of Archaeology Photo Caption Database.



During the excavation, several meters of sand were removed to reveal a vast necropolis. Nearly 1000 tombs were uncovered ...

#### References:

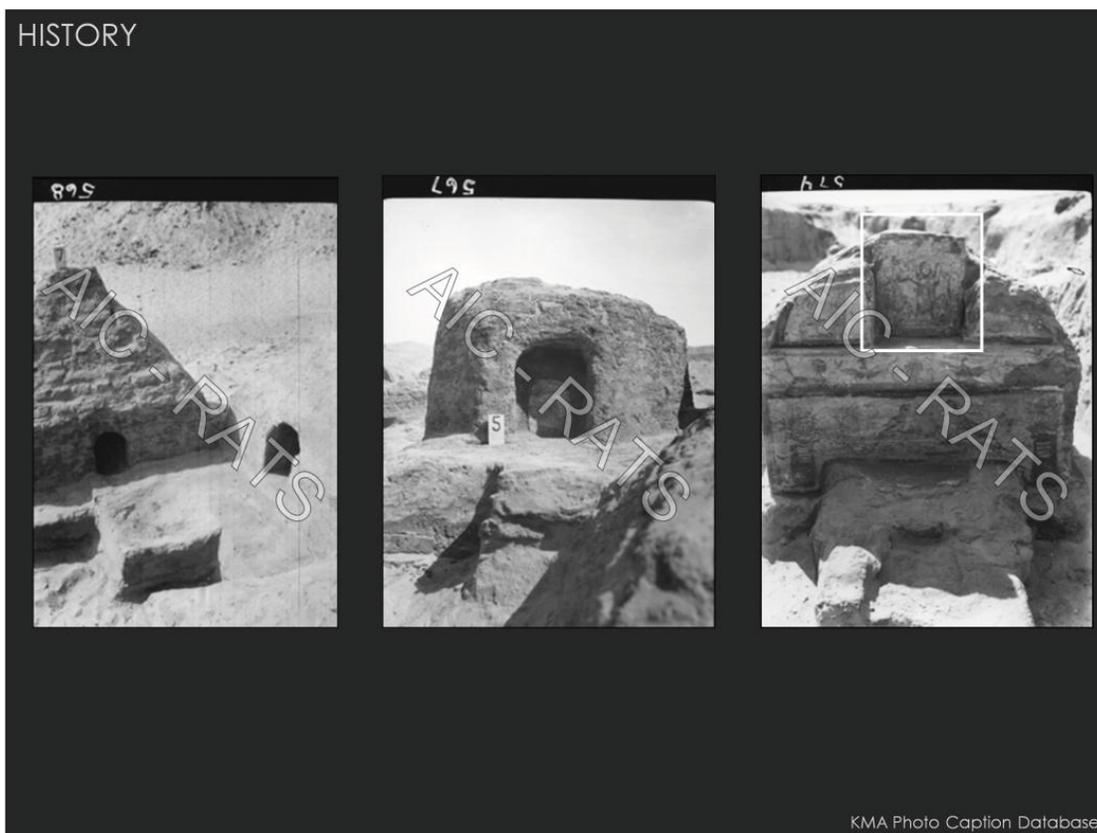
Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

Talalay, L. E. and S. E. Alcock. 2006. *In the field: the archaeological expeditions of the Kelsey Museum*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

#### Images:

Kelsey Museum of Archaeology Photo Caption Database.



... including barrel- and pyramid-roofed structures made of fieldstone, mudbrick and clay, many of whose surfaces were plastered and painted. Niches were cut into the east-facing end of each tomb, and in each niche was placed a carved slab of limestone, or stela. The box in the image on the right shows one of the stela in situ.

#### References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

Talalay, L. E. and S. E. Alcock. 2006. *In the field: the archaeological expeditions of the Kelsey Museum*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

#### Images:

Kelsey Museum of Archaeology Photo Caption Database.

HISTORY



Each stela is carved with an image of the deceased, who are depicted as standing or reclined.

References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

Images:

Kelsey Museum of Archaeology Photo Caption Database.

## HISTORY



Most of the stelae are carved in incised relief, where the contours of the figure lie below the flat surface of the stela's front façade, as shown on the left. Some, however, were carved in more rounded, high relief as shown on the right.

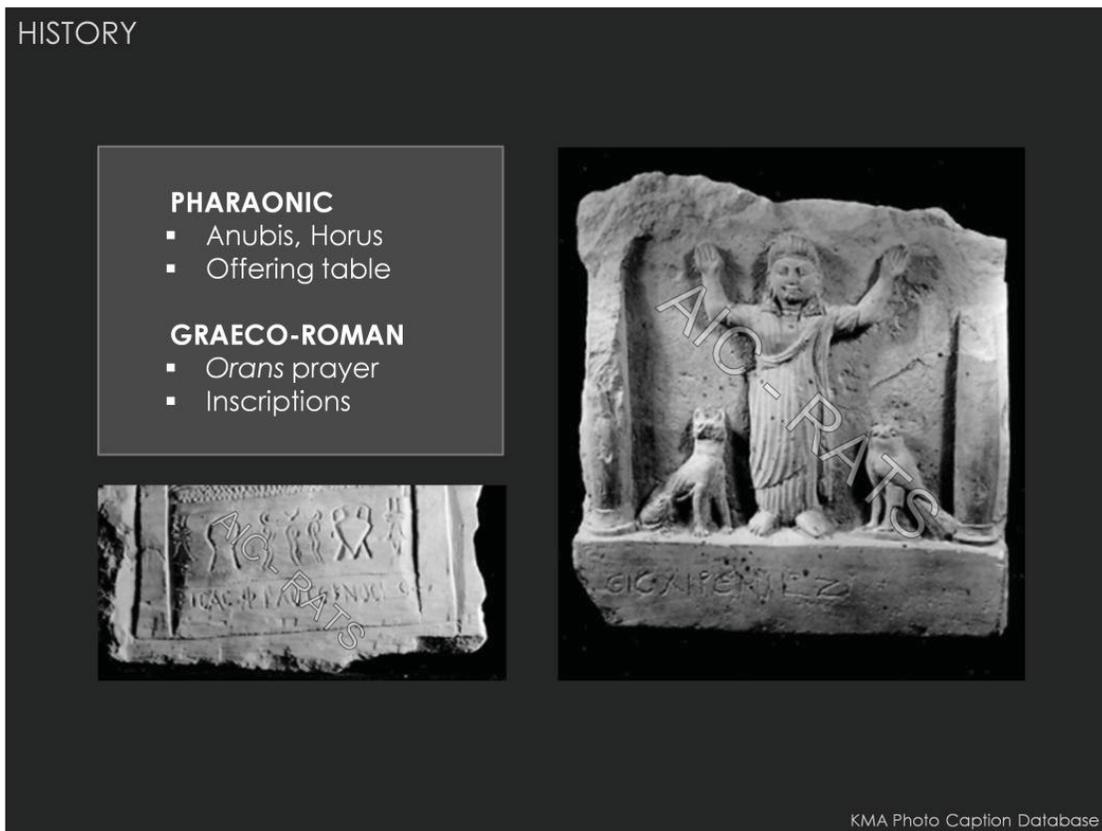
### References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

### Images:

Kelsey Museum of Archaeology Photo Caption Database.



The mixed symbolism of the stelae represent the hybrid belief system of Terenouthis's mixed Greek and Greek-Egyptian population.

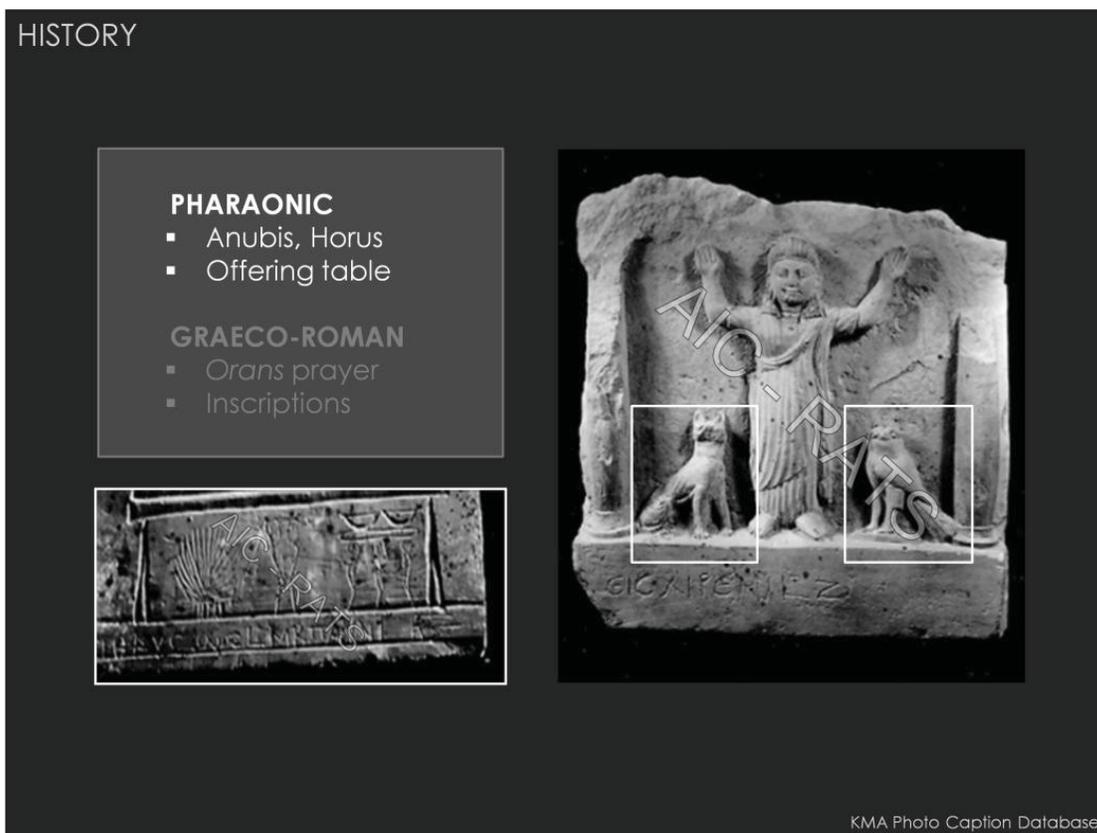
#### References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

#### Images:

Kelsey Museum of Archaeology Photo Caption Database.



Egyptian motifs, including canine and hawk figures representing the gods Anubis and Horus, are often seen flanking the deceased. Offering tables – another motif seen in earlier Egyptian carvings, on the left – are also seen on many of the stelae.

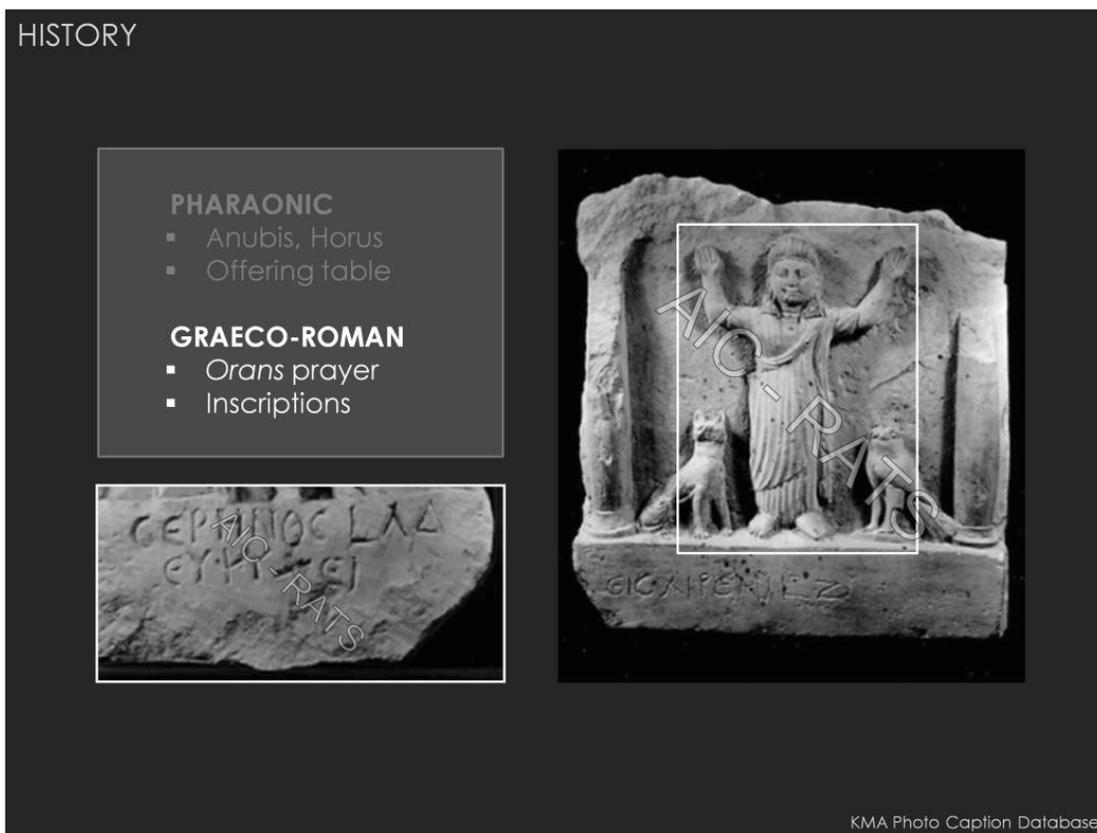
#### References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

#### Images:

Kelsey Museum of Archaeology Photo Caption Database.



Alongside these essentially Egyptian motifs are more classicising elements. For example, the names and ages of the deceased are carved in Greek (again on the left), while the raised arms of standing figures represent a prayer position – the *orans* – that is notably Greek in origin.

#### References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

#### Images:

Kelsey Museum of Archaeology Photo Caption Database.

## HISTORY



Also important is the architectural framework surrounding many of the figures, or the more simplified, incised arch or arch shape seen on many of the stela. These are thought to represent a more ancient (Pharaonic era) symbol for the gateway between the living world and the afterlife.

### References:

Hooper, F. A. 1961. *Funerary stelae from Kom Abou Billou*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

McCleary, R. 1987. *Portals to eternity: the necropolis at Terenouthis in lower Egypt. The University of Michigan's reconnaissance expedition to Kom Abou Billou, the necropolis of ancient Terenouthis (March to April 1935)*. Ann Arbor, Michigan: Kelsey Museum of Archaeology, The University of Michigan.

### Images:

Kelsey Museum of Archaeology Photo Caption Database.

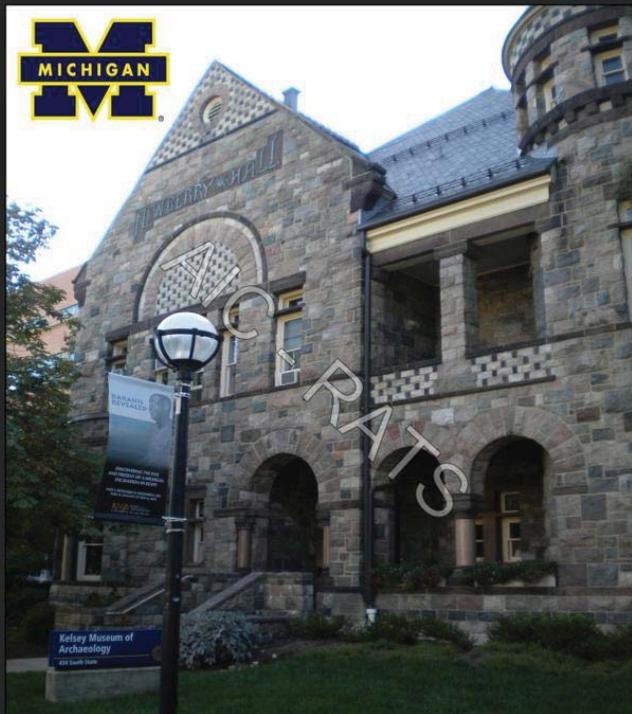
## HISTORY



KMA Photo Caption Database

The excavation at Terenouthis took place during a period when institutions like the University of Michigan were granted, by the Egyptian government, a portion (or 'division') of the finds. Director Peterson was allowed to transport a number of objects, including approximately 200 stelae, back to the Kelsey Museum at the University of Michigan.

HISTORY



**Kelsey Museum of Archaeology**, University of Michigan

The Kelsey Museum of Archaeology houses over 100,000 artifacts, many from the University's numerous archaeological expeditions. The Kelsey's collections serve as an important resource for teaching and research, as Michigan hosts one of the country's top programs in classical archaeology.

## EXAMINATION



**LeeAnn Barnes Gordon**, KMA conservation intern 2010 - 2011

The Terenouthis stelae have been a subject of renewed interest during the past few years, starting with conservator LeeAnn Barnes Gordon's survey of the collection during her 2010 – 2011 internship at the Kelsey. LeeAnn conducted archival research to gain insight into the stelae's conservation history.

Pictured: LeeAnn Barnes Gordon

Photo credit:

Bruno Pouliot

## EXAMINATION



when exposed to wind and weather, as stone and wood. In the excavations conducted at Terenouthis, for instance, some hundred specimens of soft limestones stelae were uncovered. Due to the prevalence of considerable dampness in the soil in certain areas on this site, extreme care had to be exercised in touching the painted and sculptured surfaces of the stone stelae and painting upon lime plaster. Some had to be left in situ, shielded from the direct rays of the sun and action of the wind, until they were sufficiently dry to receive thin coats of **duco cement**. This treatment had to be administered by brush, although a spray would have

Enoch Peterson, 1941. **Lecture notes** from Kelsey Museum papers, 1891 – 1948

KMA Photo Caption Database and Archives

.. which led to an important discovery – a note from a 1941 lecture by excavation director Peterson recalling his use of Duco cement as a protective coating for the stelae. Duco is a cellulose nitrate lacquer that was first produced by DuPont chemical in the 1920's.

Peterson's use of Duco cement as a stabilizing treatment for the stelae reflects early, 'historic' techniques in archaeological conservation. Alfred A. Lucas, a preservation specialist active in Egypt in the 1920's and 1930's, singled out 'celluloid cement' as a preservative coating for unstable surfaces, and gives specific instructions on how to prepare and apply the celluloid solution. In other lectures following his excavation at Terenouthis, Peterson mentions Lucas as an advisor on these early, post-excavation conservation treatments.

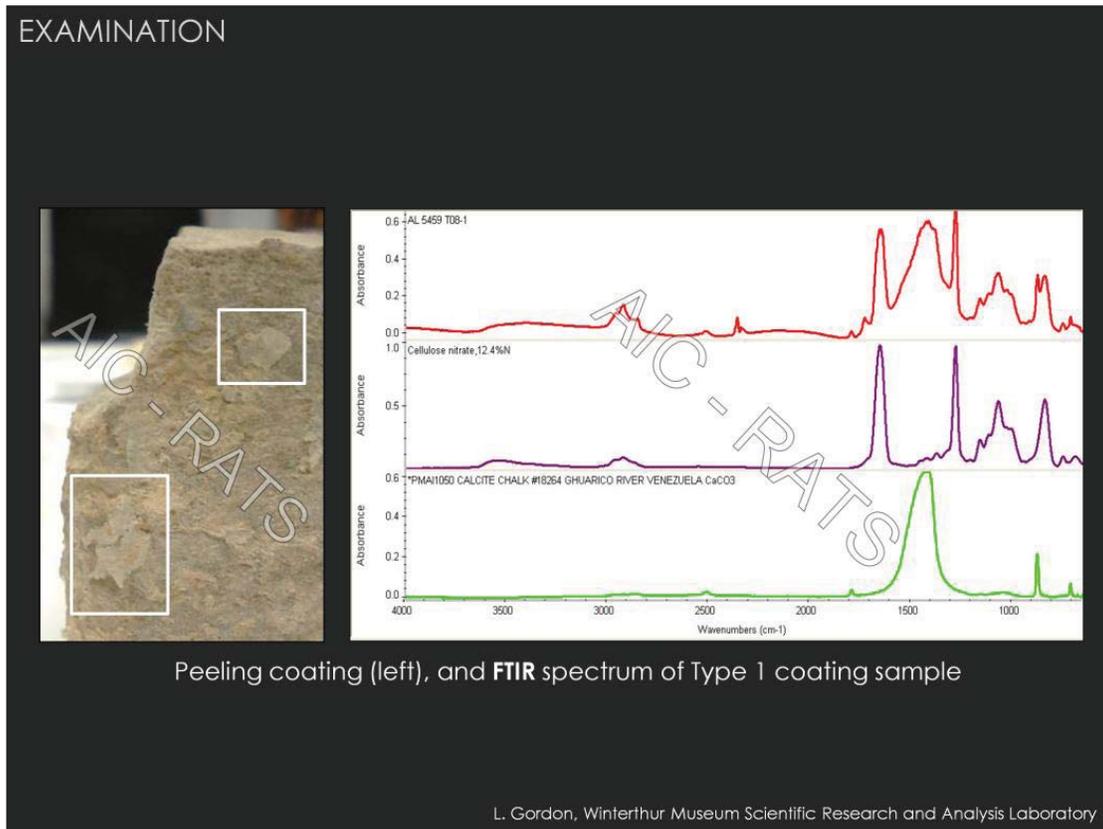
### References:

Lucas, A. 1932. *Antiques: their restoration and preservation*. London: Edward Arnold & Co.

### Images:

Kelsey Museum of Archaeology Photo Caption Database.

Kelsey Museum of Archaeology Archives.



Indeed, a majority of the stelae have this coating – shown here at an advanced stage of deterioration – which LeeAnn was able to confirm as being cellulose nitrate-based.

Documentation of the context and subsequent conservation of the stelae have served as welcome tools for this research, as such information is so often missing from museum archaeological collections.

Images:

Winterthur Museum Scientific Research and Analysis Laboratory

## EXAMINATION



**KMA**  
KELSEY MUSEUM OF  
ARCHAEOLOGY  
CONSERVATION DEPARTMENT  
UNIVERSITY OF MICHIGAN

**CONSERVATION CONDITION SURVEY**

---

Date

Surveyor

Primary material

Secondary material

Other Materials

Notes

Coating present

Re-housing recommended

Date re-housing completed

Accession Number

Temporary Registry Number

Object Function 1

Object Function 2

Location at time of survey (high value object location)

Object not present at time of survey

Object misidentified

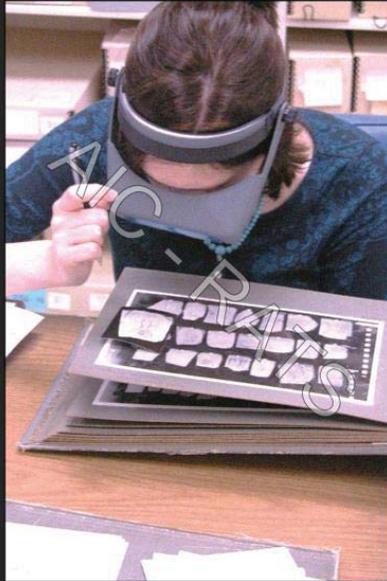
Condition Ranking

---

<p><b>Condition Ranking 1:</b> High priority for treatment; actively deteriorating. <b>This may include:</b></p> <ul style="list-style-type: none"> <li>• major structural problems</li> <li>• mold/mildew</li> <li>• active corrosion on more than 25% of surface</li> <li>• flaking/lifting/powdering/spalling or friable surface, more than 25%</li> <li>• active tearing/breaking</li> <li>• major insect damage/ live bugs</li> </ul>	<p><b>Condition Ranking 2:</b> Needs remedial treatment; condition may worsen quickly over time. <b>This may include:</b></p> <ul style="list-style-type: none"> <li>• active corrosion less than 25% of surface</li> <li>• broken due to failed adhesive</li> <li>• old restorations/failing restorations</li> <li>• deteriorated coatings</li> <li>• flaking/lifting/powdering/spalling or friable surface, less than 25%</li> <li>• needs new housing</li> </ul>	<p><b>Condition Ranking 3:</b> May benefit from or require treatment to improve appearance; condition is stable with little potential for active deterioration. <b>This may include:</b></p> <ul style="list-style-type: none"> <li>• accretions</li> <li>• dirt</li> <li>• dust</li> <li>• losses</li> <li>• old restorations</li> </ul>	<p><b>Condition Ranking 4:</b> No treatment necessary; condition is stable.</p>	<p><b>Condition Ranking 5:</b> No treatment is possible; deterioration is irreversible/irreparable, and/or object is disintegrated/unsalvageable.</p>
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In addition to her extensive contextual research, LeeAnn performed a systematic survey of the entire stela collection, giving each stela a condition ranking of 1 – 4. 42 of the nearly 200 stelae in the collection were given a priority 1 ranking – or high priority for treatment. That’s nearly one fourth of the collection.

EXAMINATION



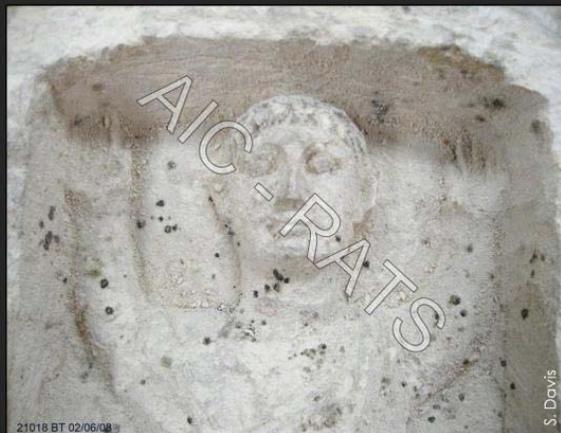
These figures provided a strong argument for research toward a plan to protect the stelae from further deterioration, a task I took on as a Samuel H. Kress fellow at the Kelsey Museum from 2011 – 2012.

Picking up where LeeAnn left off, I began by closely examining a small selection of stelae ranked Priority 1 for treatment in her survey, and whose conditions represented the diverse forms of deterioration seen within the collection. The same group of stelae were then documented, analyzed and treated. I did this work in the museum's conservation lab, the aim being to record initial observations, assess the stelae's deterioration and look for clues as to what could be causing it.

Photo credit:

Sebastian Encina

## EXAMINATION



### Biological formations

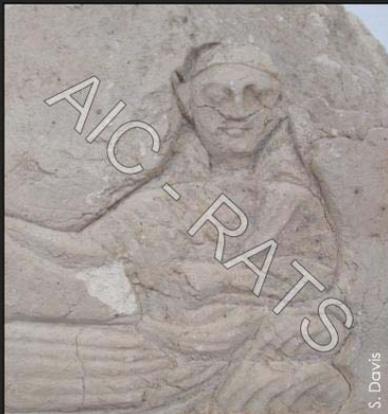
- Round, black spots – possible fungal growth (left)
- Large colonies – possible lichen growth (right)

One of the most visually impacting issues is the presence of dark, seemingly biological formations on many of the stelae. Two discernible types of biological activity can be seen: small, black, circular spots resembling fungal growth, as well as larger colonies resembling lichen growth.

Photo credit:

Suzanne Davis

## EXAMINATION



### Structural deterioration

- Surface spalling (left)
- Delamination along bedding planes (right)

Even more problematic is the major structural deterioration that has occurred on numerous stelae, in the form of both surface spalling and total delamination along the natural bedding planes of the limestone.

Photo credit:

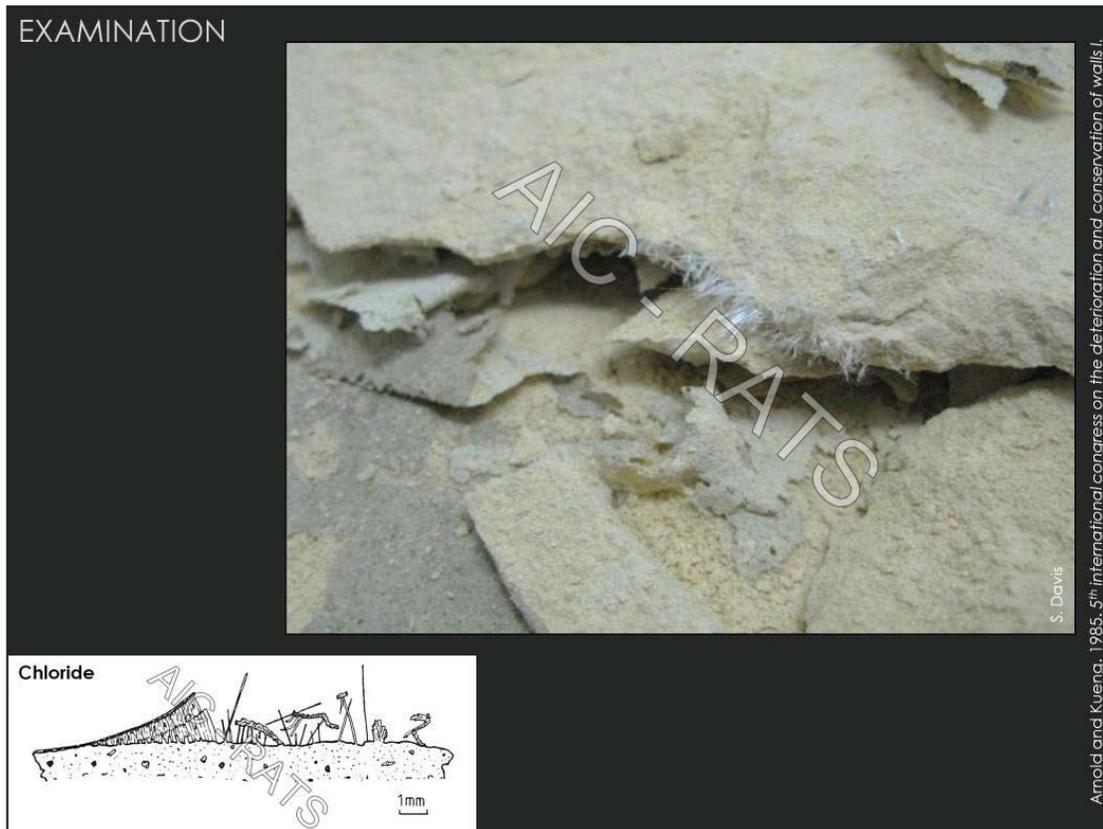
Suzanne Davis



The most prevalent form of deterioration however is the powdering of the stelae's limestone surfaces. This is most visible on stelae whose protective coatings have started to peel, indicating that the deterioration of the coating has contributed to the powdering. But an even more important factor in this is, undoubtedly, salts.

Photo credit:

Suzanne Davis



Salts play a likely and longstanding role in the deterioration of the stelae. Enoch Peterson said so himself, observing that “Antiquities in Egypt are very often encrusted and even impregnated with salt”.

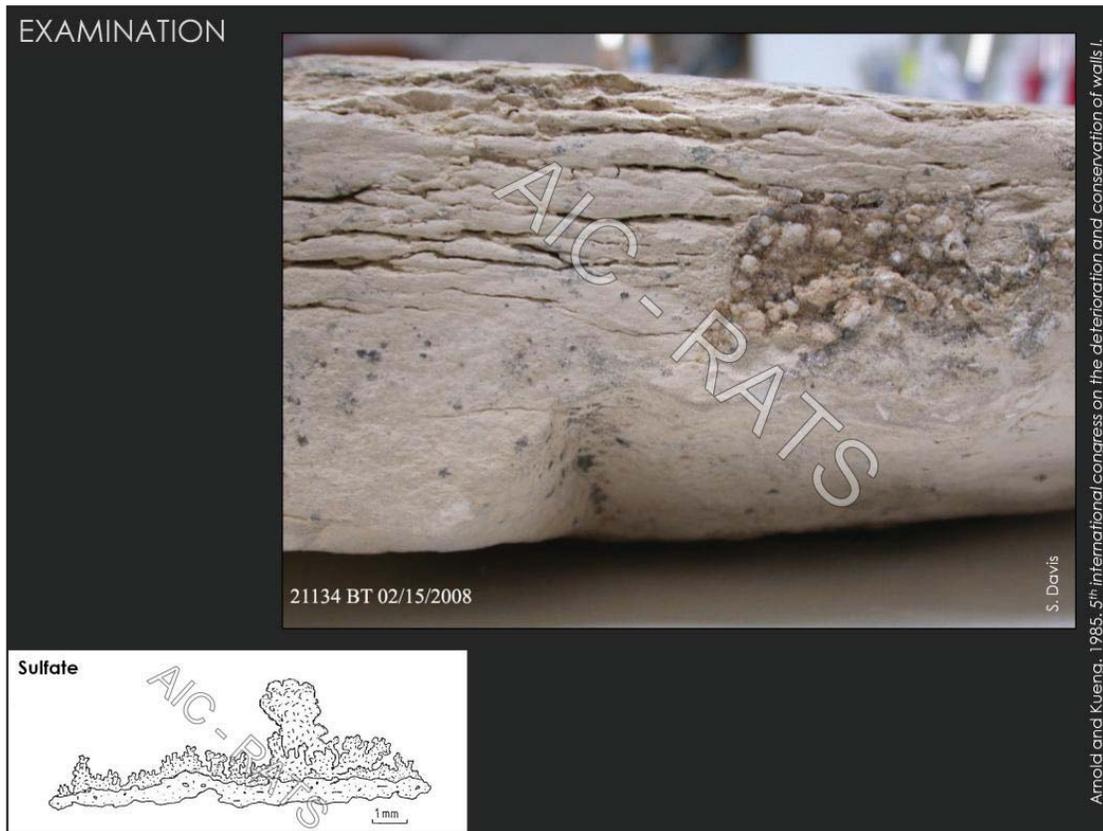
Numerous forms of salt are visible on the stelae, including this spiky, chloride-like salt found efflorescing on stela 21060, which is has unfortunately been reduced to a debris pile.

Images:

Arnold and Kueng, 1985. *5<sup>th</sup> international congress on the deterioration and conservation of walls I.*

Photo credit:

Suzanne Davis



Round, gypsum-like salt formations are also visible on numerous stelae.

Tests for soluble salts found chlorides both from direct sampling and in desalination bath water; a sample taken from a gypsum-like growth tested positive for sulfates.

References:

Odegaard N., S. Carroll, and W. S. Zimmt. 2005. *Material characterization tests for objects of art and archaeology*. London: Archetype, 108, 124.

Images:

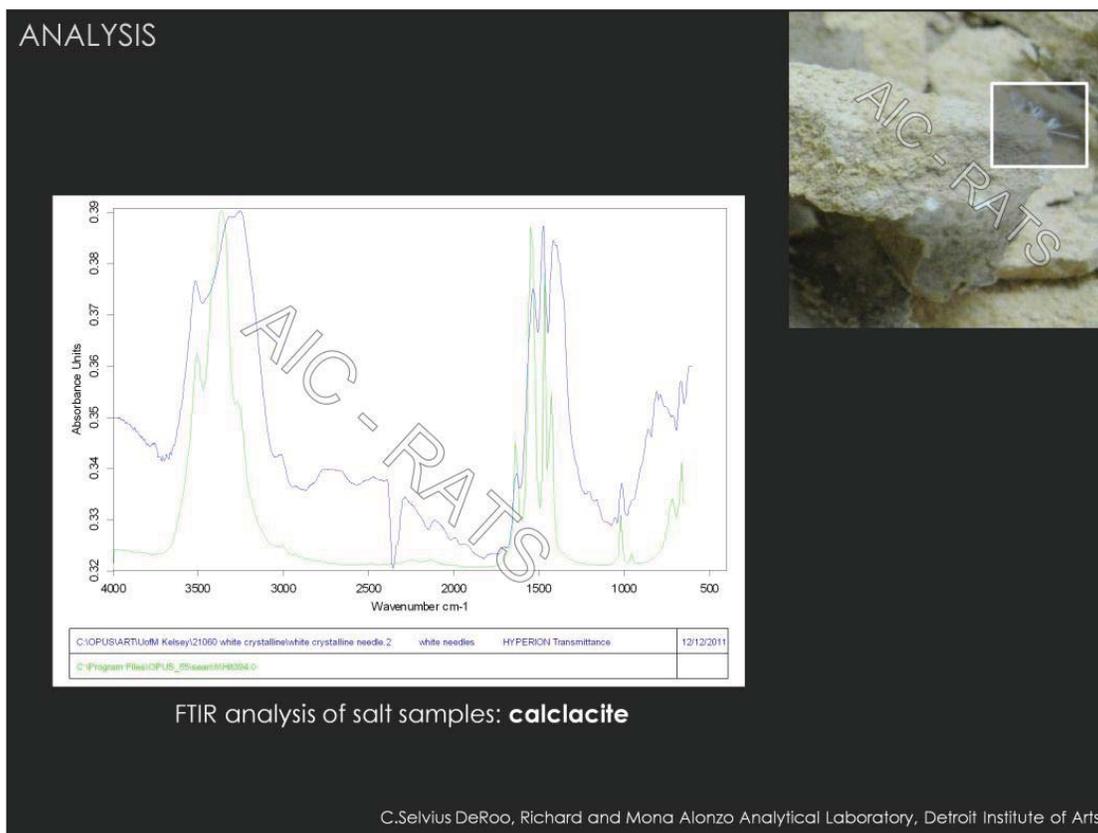
Arnold and Kueng. 1985. *5<sup>th</sup> international congress on the deterioration and conservation of walls I.*

Photo credit:

Suzanne Davis



Analysis was proposed as a way to confirm observations made during these initial examinations, and to more accurately identify the causes of deterioration. This was made possible with the help of scientists both at the University of Michigan, and at nearby museums.

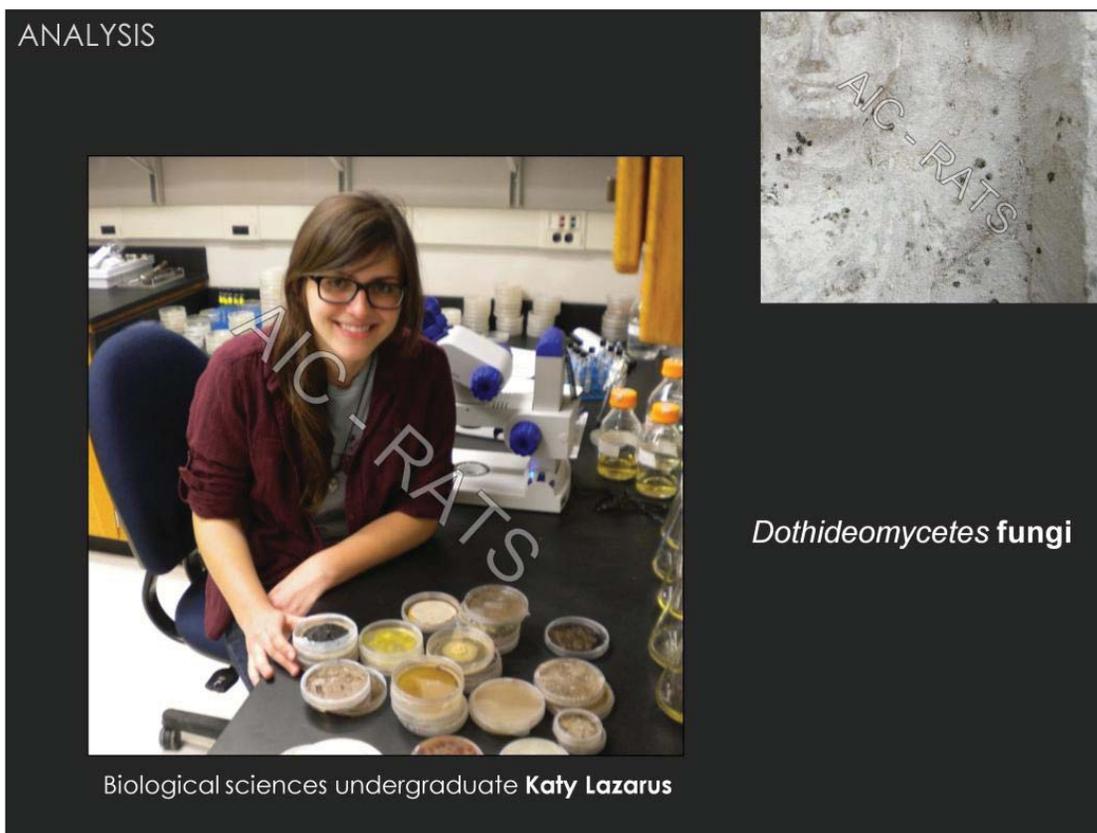


FTIR analysis of salt samples (green spectrum) was carried out by conservation scientist Cathy Selvius DeRoo at the Detroit Institute of Arts. Dr. Selvius DeRoo found gypsum salts, but no halite, which we were expecting to find. Instead she found calcite (blue spectrum), a mineral which forms on calcareous materials through interaction between acetic acid offgassing (from wood storage shelving, cabinets) and chloride salts already present in the stone. This correlates with the previous, wooden shelving used to store the stelae before their rehusing in the 1990's.

Subsequent XRD analysis confirmed presence of halide salts in the stone.

Images:

Richard and Mona Alonzo Analytical Laboratory, Detroit Institute of Arts



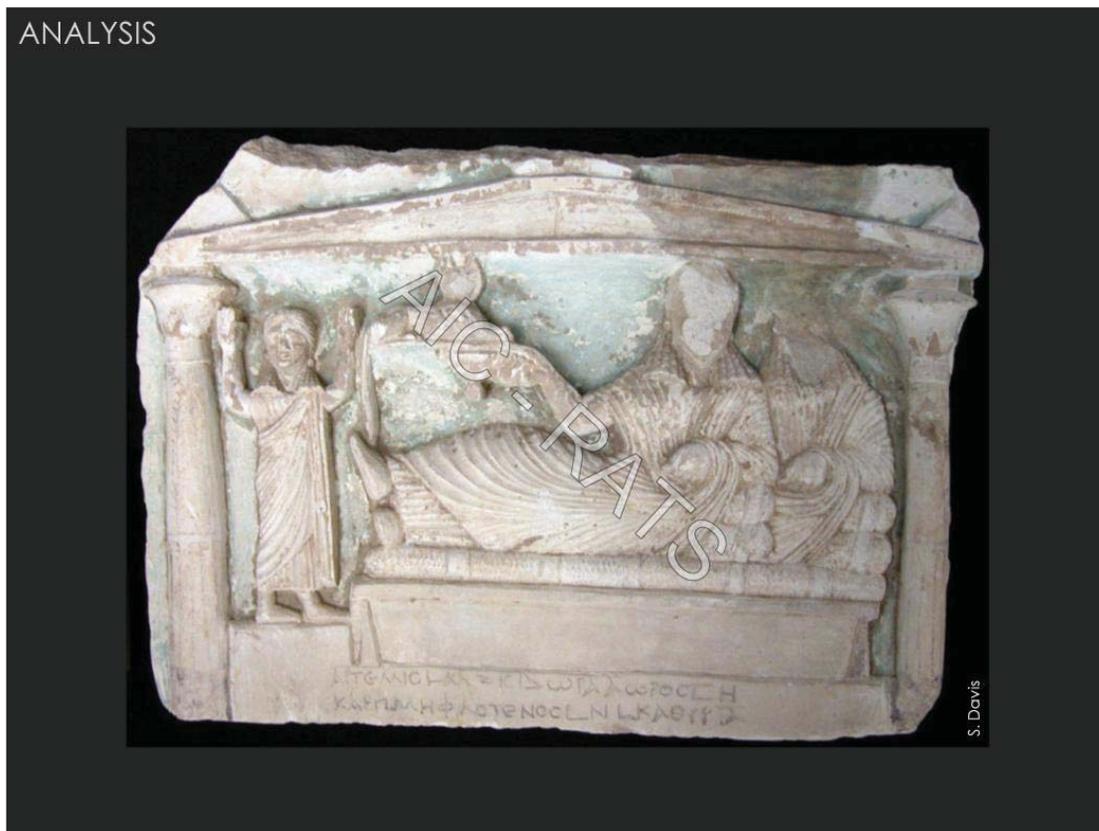
Biological growths were analyzed with the help of University of Michigan undergraduate Katy Lazarus, a student of microbiology professor Dr. Tim James. Katy analyzed both the fungus-like and lichen-like growths using microscopy, culturing, and DNA analysis. The fungal-like spots were identified as *Epicoccum nigrum* and *Leptosphaerulina chartarum*, two types of mold from the class *Dothideomycetes*. Samples taken from the lichen-like growths provided no amplifiable DNA. Katy believes that the *Dothideomycetes* fungi would more likely have colonized after the stelae arrived in Ann Arbor, rather than in Egypt.

Asked whether she thought the growths might be active or alive, Katy reported that they are likely dead or dormant, and that they would likely remain this way as long as the stelae are housed in an RH-controlled environment.



Adding to the complexity of this interplay of deterioration phenomena is the presence of polychromy – traces of which are visible here in the form of a red band running parallel to the stela’s outer edge.

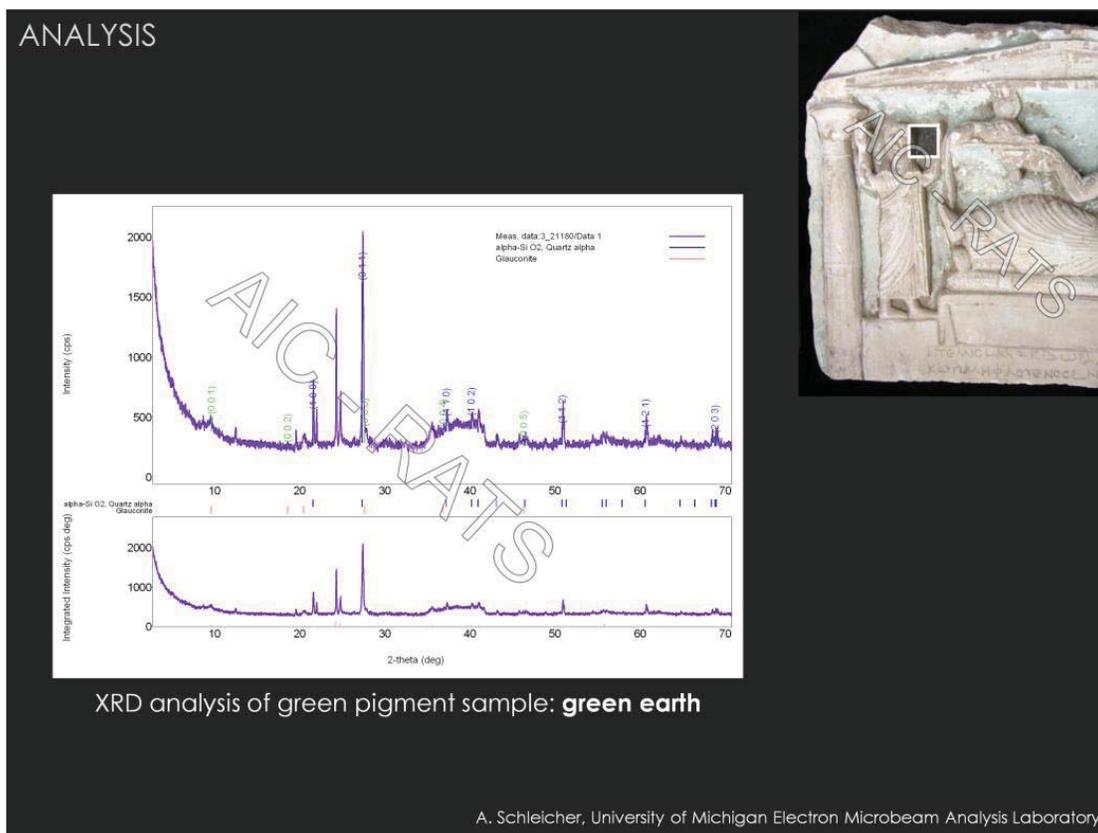
ANALYSIS



Red, yellow, black, and pink polychromy are in fact quite common on the stelae. Far less common is this color – blue-green – seen on the background of stela 21180. XRF analysis carried out with the help of Bruce Kaiser at Bruker instruments revealed, interestingly, no peaks for copper. Curious as to what this pigment could be, an already-detached sample was brought to the University of Michigan Chemistry department for XRD analysis.

Photo credit:

Suzanne Davis



Research chemist Dr. Anja Schleicher assisted with sample prep and XRD instrument setup, as well as with subsequent data interpretation. It appeared that the green paint is in fact a green earth, rather than a copper-based mineral or synthetic pigment. A review of the literature indicated that this is a somewhat rare example of green earth on an Egyptian artifact. Clay-based greens were common in ancient Greece and Rome, and started to be used in Egypt in the Hellenistic period. The only known example of its use before then was found on a Third Intermediate Period cartonnage fragment by Dr. David Scott. Later examples (those we know of) are also few and far between. Dr. Scott continues to puzzle over the question of when and why green earth was used in Egypt, especially when much more vibrant hues of green can be achieved with green frit. The same questions have guided me in my current research on the subject at the Getty Villa.

Dr. Schleicher also helped confirm the stone to be limestone, possibly more than one kind, as well as clay – another potential factor in the powdering and delamination of the stelae.

#### References:

Scott, D. A., S. Warmlander, J. Mazurek, and S. Quirke. 2009. Examination of some pigments, grounds and media from Egyptian cartonnage fragments in the Petrie Museum, University College London. *Journal of archaeological science* 36(3): 923-932.

#### Images:

University of Michigan Electron Microbeam Analysis Laboratory

## TREATMENT PROTOCOL



The information gathered from these initial examinations and subsequent, scientific collaborations, helped inform the decisions that were made when it came time to develop a treatment and preservation strategy for the stelae.

TREATMENT PROTOCOL

### Treatment priorities discussion

1. Stabilization of surfaces (including polychromy) and structures
2. Systematic reduction of coatings
3. Biological stain reduction



Before I began the treatment protocol, I consulted with Graeco-Roman Egyptian curator Terry Wilfong to develop a set of treatment priorities. Staff time and resources at the Kelsey are limited, so I felt it would be important to establish an idea of what about the stelae was most important to the museum – and the to university – and therefore most in need of intervention.

Photo credit:

Suzanne Davis

TREATMENT PROTOCOL

### Treatment priorities discussion

1. Stabilization of surfaces (including polychromy) and structures
2. Systematic reduction of coatings
3. Biological stain reduction

*Preservation of information*



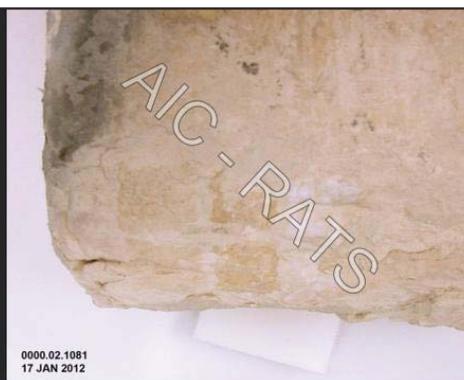
After presenting a list of treatment options, Terry and I agreed that surface and structural stabilization were the highest priority, in the interest of protecting the textual and iconographic information preserved on the stelae.

Photo credit:

Suzanne Davis

## TREATMENT PROTOCOL

- Paraloid B-72
  - 2.5%, 5% in acetone/ethanol
  
- CaLoSil ® nanolime
  - in ethanol, isopropanol and n-propanol
  
- Conservare ® H100 silane
  - alone, + HCT tartrate

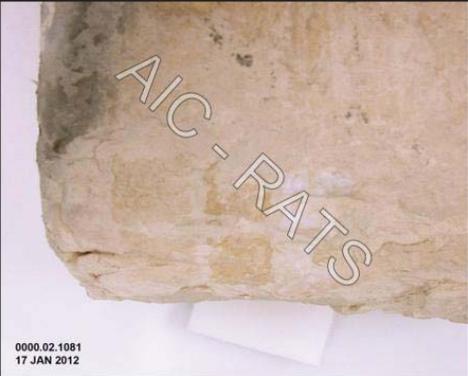


A great deal of research has been done toward solutions to stone deterioration, in large part by conservators and scientists working in the heritage preservation sector. From this research I chose a suite of consolidants that represents what conservators in museums have used, as well as what conservators working in the field and in built environments have used. These included Paraloid acrylic resin in acetone/ethanol, CaLoSil nanolime particles in various solvents, and ethyl silicate consolidant coupled with a tartrate preparation treatment often used on limestone.

Tests were carried out debris pile fragments, as well as the reverse of two different stelae.

TREATMENT PROTOCOL

- Paraloid B-72
  - 2.5%, 5% in acetone/ethanol
- CaLoSil ® nanolime
  - in ethanol, isopropanol and n-propanol
- Conservare ® H100 silane
  - alone, + HCT tartrate



Of these, the material chosen for the protocol was CaLoSil nanolime in n-propanol. CaLoSil is essentially a suspension of calcium hydroxide in alcohol; it is referred to as 'nanolime' due to the small size of the hydroxide particles – about 150nm. This, and the alcohol carrier, allow the material to penetrate more deeply into the stone and act as a true consolidant, rather than a wash, as calcium hydroxide is historically used for.

References:

Online technical leaflet, IBZ-Salzchemie GmbH & Co.KG: [http://www.ibz-freiberg.de/download/pdf/nanomaterialien/CaLoSiL\\_EN.pdf](http://www.ibz-freiberg.de/download/pdf/nanomaterialien/CaLoSiL_EN.pdf)

**TREATMENT PROTOCOL**

Consolidant	Color change?	Applications needed to stop powdering?	Immersion test*
5% B-72 in 85:15 acetone/ ethanol	Yes – darkening of the stone after one application	1 application was sufficient to eliminate powdering	1) Fragment stable 2) Fragment stable 3) Fragment stable
CaLoSil E25	No color change after 1 application; white haze appeared in areas after 2 applications	Consolidant allowed to sit 2 days for carbonation to occur; 1 application eliminated powdering	1) Some loss 2) Minimal loss 3) Minimal loss
CaLoSil E50	N/A	Consolidant too thick to penetrate into the stone	N/A
CaLoSil IP25	Yes – 1 application produced a very slight white haze in areas	Consolidant allowed to sit 2 days for carbonation to occur; 1 application eliminated powdering	1) Some loss 2) Minimal loss 3) Minimal loss
CaLoSil NP25	No color change after 1 application	Consolidant allowed to sit 2 days for carbonation to occur; 1 application eliminated powdering	1) Some loss 2) Some loss 3) Some loss
HCT (Had a soapy appearance – difficult to apply with pipette)	Yes – a barely-visible darkening occurred	3 applications eliminated powdering	1) Some loss 2) Minimal loss 3) Minimal loss
HCT + H100	Yes – a slight darkening occurred	3 applications of HCT + 3 applications of H100 the following day improved but did not eliminate powdering	1) Minimal loss 2) Minimal loss 3) Some loss

1)	>500 mg/L
2)	0 mg/L
3)	0 mg/L

1)	~500 mg/L
2)	0 mg/L
3)	0 mg/L

1)	>500 mg/L
2)	0 mg/L
3)	0 mg/L

\* Successive 24 hr. H<sub>2</sub>O immersion tests on one fragment  
#) = immersion step



IBZ-Salzchemie GmbH & Co.KG

This recommendation was made for a few reasons. First, the CaLoSil in n-propanol produced no color change in the stone or impact on existing polychromy during testing. Only one application was needed to eliminate stone powdering, and most importantly, the acting consolidant is calcium carbonate – a material already present in the stone. Having seen the effects of applying an incompatible consolidant – Duco cement – to the surface of these artifacts, I wanted whatever was applied in this treatment to be as compatible with the limestone as possible, considering that this treatment step cannot be reversed.

Images:

Online technical leaflet, IBZ-Salzchemie GmbH & Co.KG: [http://www.ibz-freiberg.de/download/pdf/nanomaterialien/CaLoSiL\\_EN.pdf](http://www.ibz-freiberg.de/download/pdf/nanomaterialien/CaLoSiL_EN.pdf)

## TREATMENT PROTOCOL



### Paraloid B-72 applications

- Cases where coating is lifting but contains carving details (left)
- Cases where stone is structurally delaminating (right)
- Polychromy

B-72 still proved useful for other applications, including rare cases where the coating itself needed to be stabilized, and for filling delamination cracks. It also helped stabilize areas of thick polychromy.

## TREATMENT PROTOCOL



Poulticing carried out using **Arbocel**® paper pulp

With a strategy for stabilization in place, the issue of salts needed to be addressed. From tests I was able to determine that poulticing is possible, but risky.. but again I felt it was important to include this in the protocol, especially if it is ever to be used by stelae collections where environmental control is not an option.

## TREATMENT PROTOCOL



Temperature and RH monitoring in stelae storage shelving

Fortunately such controls have been in place at the Kelsey since the mid-1990's, and if the types of salts present in the stelae are known, temperature and relative humidity parameters can be set to prevent salt damage. Environmental monitoring over an 11-month period showed that RH levels ranged from 22 percent to 54 percent relative humidity, clear of the critical RH ranges of the halite and calclacite salts present in the stelae.

Environmental control will also ensure that biological activity and cellulose nitrate coating deterioration will progress more slowly.

### References:

Caneva, G., M. P. Nugari, O. Salvadori. 2005. *Plant biology for cultural heritage: biodeterioration and conservation*. Los Angeles: Getty Conservation Institute, 15 – 31.

Shashoua, Y. 2008. *Conservation of plastics*. Oxford: Butterworth Heinemann.

## TREATMENT PROTOCOL

- **Surface stability: Is the stone surface powdering?**
  - No.
  - Yes. Apply CaLoSil® NP25 consolidant in powdering areas using a glass micropipette; test a small area first to make sure white haze does not form.
  
- **Structural stability: Is the stone flaking or delaminating?**
  - No.
  - Yes. If fragments are detached, consolidate the join surfaces with 2.5 – 5% B-72; reattach using a 30 - 50% mixture of B-72 in 85:15 ethanol / acetone to prevent dissolution of the coating and/or polychromy...
  
- **Salt efflorescence: Is there visible salt efflorescence or signs of related deterioration?**
  - No.
  - Yes. Is the object stored or displayed in an environment where relative humidity is well below 75%?
    - No. Desalination can be carried out via poultice. The author recommends Arcobel® BC1000 paper pulp for this particular group of objects...

Contingency-based protocol (excerpt)

From these tests and observations I assembled a contingency-based protocol designed for flexibility, as each stela exhibits varying degrees and forms of deterioration. Also, with 200 stelae to address I knew that multiple conservators would eventually be involved in treating them, and wanted the protocol to read more as a guideline than as a set of instructions.

## FURTHER STUDY

- **Electron imaging** of CaLoSil® consolidant in the stone
- Identification of **all salt and clay species** in the stone
- Biological **stain reduction**
- Protocol for treating **cyclododecane**-coated stelae

Many questions remain, including how the CaLoSil consolidant is distributed in the limestone, as well as the exact nature and behavior of the salt mixtures and clays present in the stone. A more effective method for reducing biological stains might also be discovered in future study, even if this isn't a top treatment priority. And finally, a protocol for stabilizing and treating those stelae that were coated with cyclododecane during their 2009 relocation is something of great interest to the Kelsey Museum's conservators.

Fortunately the Kelsey will have a conservation intern next year, one who like me is very enthusiastic about stone, and therefore an opportunity to address these questions and continue the treatment of the stelae.



I would like to thank these organizations and individuals for their generous support of this project, especially the Samuel H. Kress Foundation, the University of Michigan, my supervisors Suzanne Davis and Claudia Chemello, and my co-authors LeeAnn Barnes Gordon and Cathy Selvius DeRoo. Thank you.

Images:

Kelsey Museum of Archaeology Photo Caption Database.

**Artificial Aging of Paper-Based Cores Wrapped in  
Various Isolating Layers  
for Use as Archival Storage Supports**

**Amy Baker Williams**  
Project Conservator, University of Pittsburgh

**Catherine H. Stephens**  
Art Conservation Research Center (ACRC)  
Center for Conservation and Preservation (CCAP), Yale University

**May 31, 2013: 41<sup>st</sup> Annual Meeting of the AIC, Indianapolis, IN**

Amy Williams<sup>1</sup> and Catherine Stephens<sup>2</sup>

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<sup>2</sup> Senior Conservation Scientist, Art Conservation Research Center (ACRC), Center for Conservation and Preservation (CCAP), Yale University

Presented at the RATS session  
41st Annual Meeting of  
The American Institute for Conservation of Historic and Artistic Works (AIC)  
Indianapolis, In, May 29-June 1, 2013

**Artificial Aging of Paper-Based Cores Wrapped in Various Isolating Layers for Use as Archival Storage Supports**

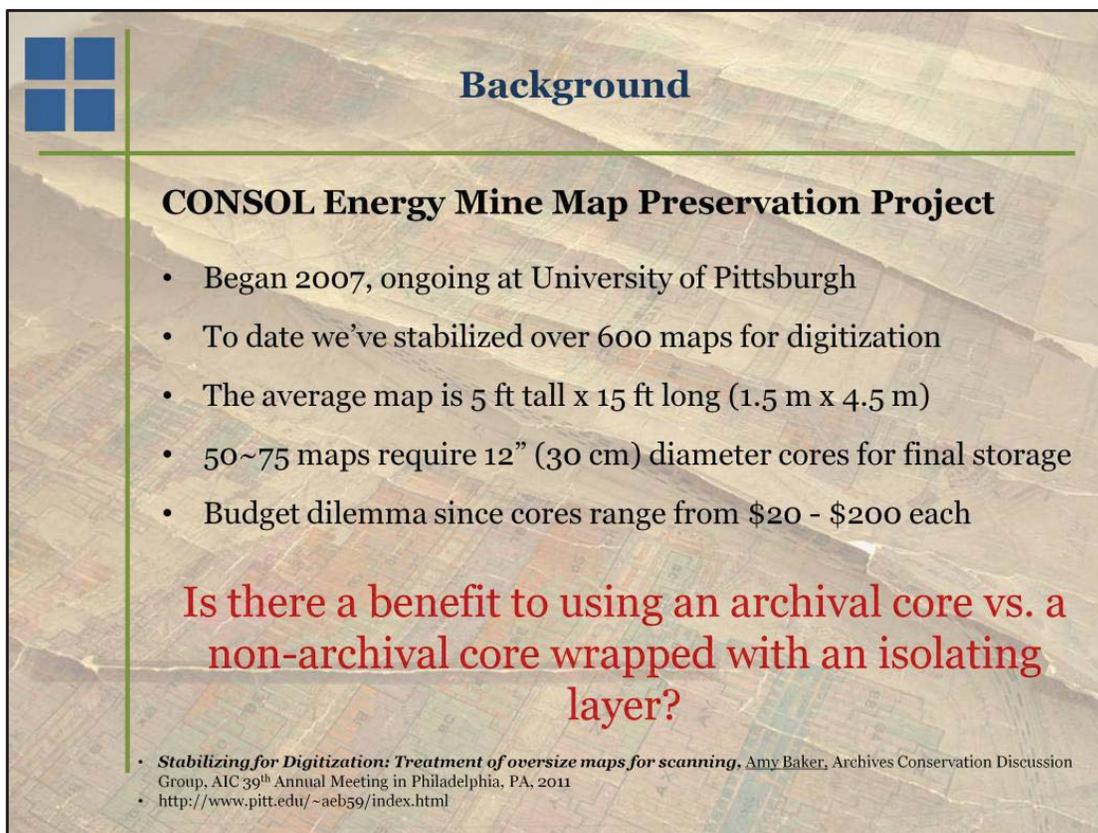
**Amy Baker Williams**  
Project Conservator, University of Pittsburgh

**Catherine H. Stephens**  
Art Conservation Research Center (ACRC)  
Center for Conservation and Preservation (CCAP), Yale University



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- The two co-authors worked on this project together, intermittently, from August 2011 – to January 2013 in Pittsburgh, PA, when Amy Baker Williams was project conservator in the Preservation Department at the University of Pittsburgh and Catherine Stephens was a conservation scientist at Carnegie Mellon University; it was a rewarding collaboration and it provided both individuals an opportunity to learn more about the topic of paper-based cores than they had worked alone.
- The image on the left illustrates the manufacture of rolled, paper-based cores, which we also sometimes refer to as “storage tubes” in this presentation. The image on the right illustrates a map rolled onto a non-archival storage tube with a polyester webbing acting as an isolating layer and Mylar acting as a protective layer on top of the map. The rolled materials are held to the tube using linen ties.



## Background

### CONSOL Energy Mine Map Preservation Project

- Began 2007, ongoing at University of Pittsburgh
- To date we've stabilized over 600 maps for digitization
- The average map is 5 ft tall x 15 ft long (1.5 m x 4.5 m)
- 50~75 maps require 12" (30 cm) diameter cores for final storage
- Budget dilemma since cores range from \$20 - \$200 each

**Is there a benefit to using an archival core vs. a non-archival core wrapped with an isolating layer?**

• *Stabilizing for Digitization: Treatment of oversize maps for scanning*, Amy Baker, Archives Conservation Discussion Group, AIC 39<sup>th</sup> Annual Meeting in Philadelphia, PA, 2011  
• <http://www.pitt.edu/~aeb59/index.html>

- The collaboration had its origins in a grant-funded project to flatten, clean, and preserve maps of coal mines in order that they be digitized. The project began in 2007, with funding from the University of Pittsburgh, The Pennsylvania Dept. of Environmental Protection, The Office of Surface Mining and CONSOL Energy, Inc. The maps were stabilized in the lab, sent out to a scanning facility, and then returned to the University for final archival storage. Amy encountered a budget dilemma because she could use a non-archival core, and wrap it with a barrier layer of mylar for about \$20 each. Or she could purchase a tube sold by an archival products company which is advertised as an 'archival' storage tube for \$150 to \$250 each depending on the quantity purchased and the supplier. The difference in cost for storing 75 large maps (\$15,000 vs. \$1,500) sparked the \$13,500 question, "Is there a benefit to using an archival core vs. a non-archival core wrapped with an isolating layer?"



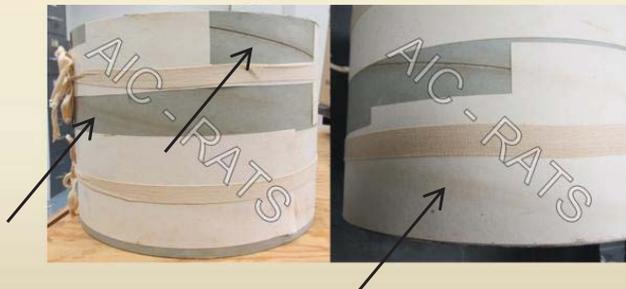
## Background - Early Experiments

- What are the long term effect of a basic storage design:
  - Using linen tape to secure the map to the support core
  - Using Permalife®, buffered tissue, Mylar or bookcloth as an isolating layer
- Conservator prepared models using Whatman No. 1 as ‘map’ & Conservation Scientist aged them in an oven at 90°C and 50% RH

**Unaged**



**Aged 18 weeks**



Observation: Staining at seam-gap of archival tube transfers to the “artwork”  
∴ We need to do a more systematic study of the aging of support cores

- Amy approached Catherine with an “archival” tube and four samples for analysis. Whatman No. 1 paper, substituting for a “map”, was placed in direct contact with the storage tube [1] or with Permalife [2], buffered tissue [3], Mylar [4], or bookcloth [5] acting as an isolating layer between the “map” and the tube. Catherine aged the five samples using the conditions listed above for 18 weeks. Samples of the “map” were removed from each of the tubes periodically and examined to look for changes to the color and to pH. We wanted to know if the isolating layers impeded changes to the color of the “map” as compared to the “map” being in direct contact with the tube and if the isolating layer prevented the “map” from becoming acidified (at this point, we assumed the chemistry would be exclusively hydrolysis).
- As you can see from the images on the right, when the “map” was in direct contact with the tube, it became stained in the areas where it was in contact with the seam gap. You can see the seam gap as it also became stained on the tube. What you don’t see here is that there was also staining where the linen tying tape was in contact with the “map”. It was surmised that the tape acted as a trap, preventing the material emitting off the tube from escaping through the paper and into the air.
- We didn’t know what was causing the staining of the seam gap and the “map”, merely that the “map” was being stained by the tube where there were the gaps and where the “map” was held in place.
- What you don’t see on this slide is that the Permalife and bookcloth didn’t act effectively as isolating layers but that Mylar and buffered tissue showed some isolating properties (inhibited yellowing and decreases to pH).
- As a result of these experiments, Amy and Catherine decided to take a closer look at different types of paper-based cores for use as rolled storage tubes and they decided to reconsider what common materials used as isolating layers might best perform as isolating layers.



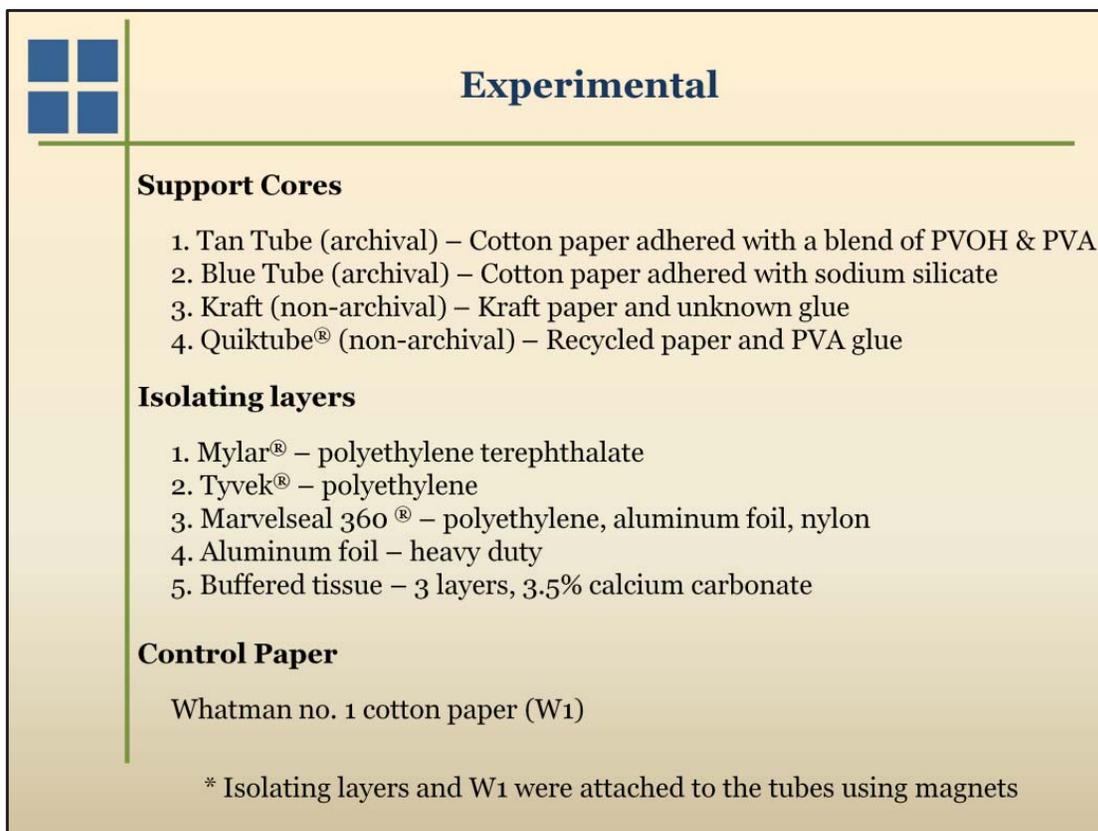
**Goal**

*Determine which paper-based tube storage design causes the least chemical and physical damage to a map rolled around it for support as a final storage solution*

**Approach**

1. Select a series of different tubes, both archival and non-archival
2. Research what isolating layer materials other conservators use when designing rolled tube storage
3. To prevent any damage to the actual mining maps, use a control paper to study the efficacy of the cores and isolating layers in deterring further damage

- The goal of this project and the approaches taken are defined above.



**Experimental**

**Support Cores**

1. Tan Tube (archival) – Cotton paper adhered with a blend of PVOH & PVA
2. Blue Tube (archival) – Cotton paper adhered with sodium silicate
3. Kraft (non-archival) – Kraft paper and unknown glue
4. Quiktube® (non-archival) – Recycled paper and PVA glue

**Isolating layers**

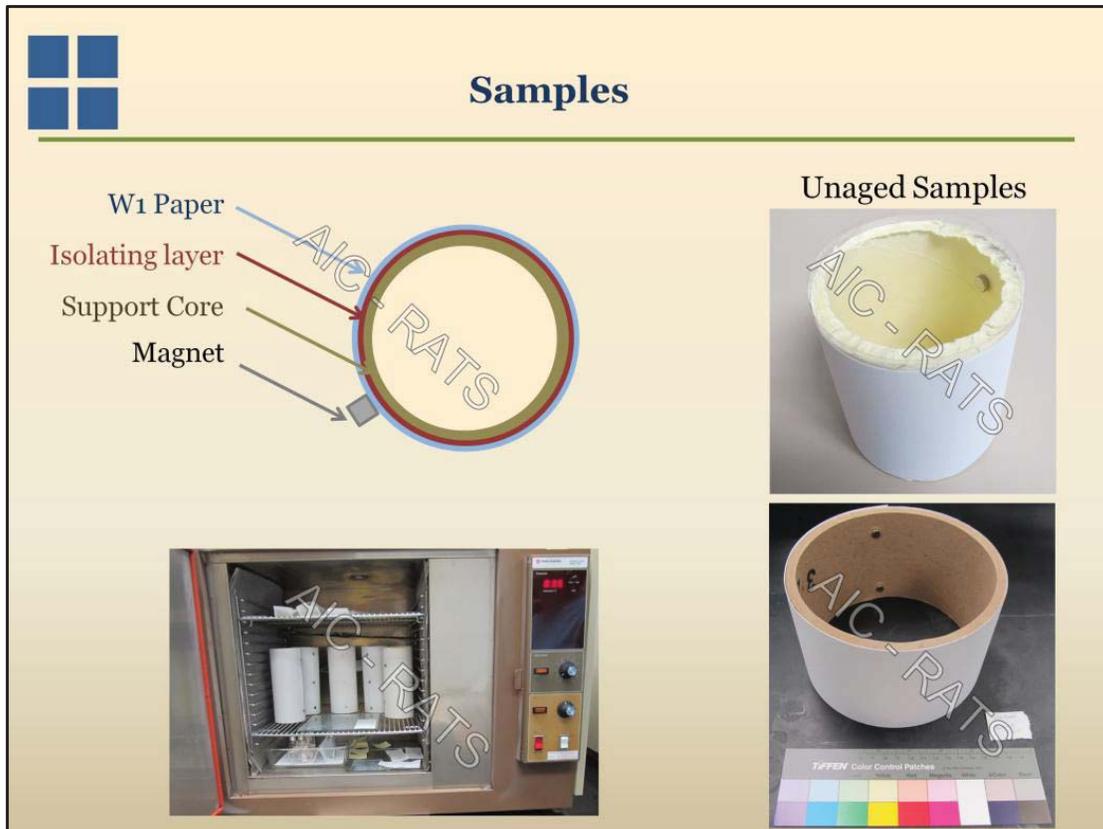
1. Mylar® – polyethylene terephthalate
2. Tyvek® – polyethylene
3. Marvelseal 360® – polyethylene, aluminum foil, nylon
4. Aluminum foil – heavy duty
5. Buffered tissue – 3 layers, 3.5% calcium carbonate

**Control Paper**

Whatman no. 1 cotton paper (W1)

\* Isolating layers and W1 were attached to the tubes using magnets

- This slide enumerates all the materials we used in the study. We chose both archival and non-archival tubes and 5 types of isolating layers. We picked the isolating layers based on:
  1. An e-mail that Amy sent out at the AIC distlist (<http://cool.conservation-us.org/byform/mailling-lists/cdl/2012/0331.html>)
  2. Discussions with objects, paper, and paintings conservators
  3. Isolating layers advertised by archival companies(<http://www.gaylord.com/adblock.asp?abid=1924>)
  4. Conservation articles, blogs, the literature
    - (<http://www.nedcc.org/free-resources/preservation-leaflets/4.-storage-and-handling/4.9-storage-solutions-for-oversized-paper-artifacts>)
    - (<http://blog.lib.uiowa.edu/preservation/2010/02/17/banner-solution/>)  
(<http://www.nps.gov/museum/publications/conservationogram/16-05.pdf>)
    - (<http://cool.conservation-us.org/coolaic/sg/bpg/annual/v07/bp07-09.html>)  
(<http://cool.conservation-us.org/coolaic/sg/bpg/annual/v24/bp24-18.pdf>)
    - (<http://ntserver1.wsulibs.wsu.edu/rssapp/rssviewer.aspx?Story=1271>)
- A Quiktube® is similar in style to a Sonotube®. A Sonotube® is used for pouring concrete to construct concrete columns in building.
- The Whatman No. 1 paper acts as a control and our model “map” and was chosen because we have a good understanding of how cotton papers age under artificial aging conditions. Whatman No. 1 was specifically chosen because it has a slightly higher starting molecular weight and pH than Whatman No. 42 paper



- The upper left diagram illustrates how each sample was constructed for these experiments
- The upper right photograph is of the tan tube with Mylar as an isolating layer and the Whatman No. 1 paper on top
- The lower right photograph is of the kraft tube with three layers of buffered tissue and the Whatman No. 1 on top
- The lower left photograph shows some samples in the oven



## Experimental - Continued

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**Artificial Aging Conditions**

- 90°C, 50%RH
- Collect samples from tubes every 6 weeks for 24 weeks

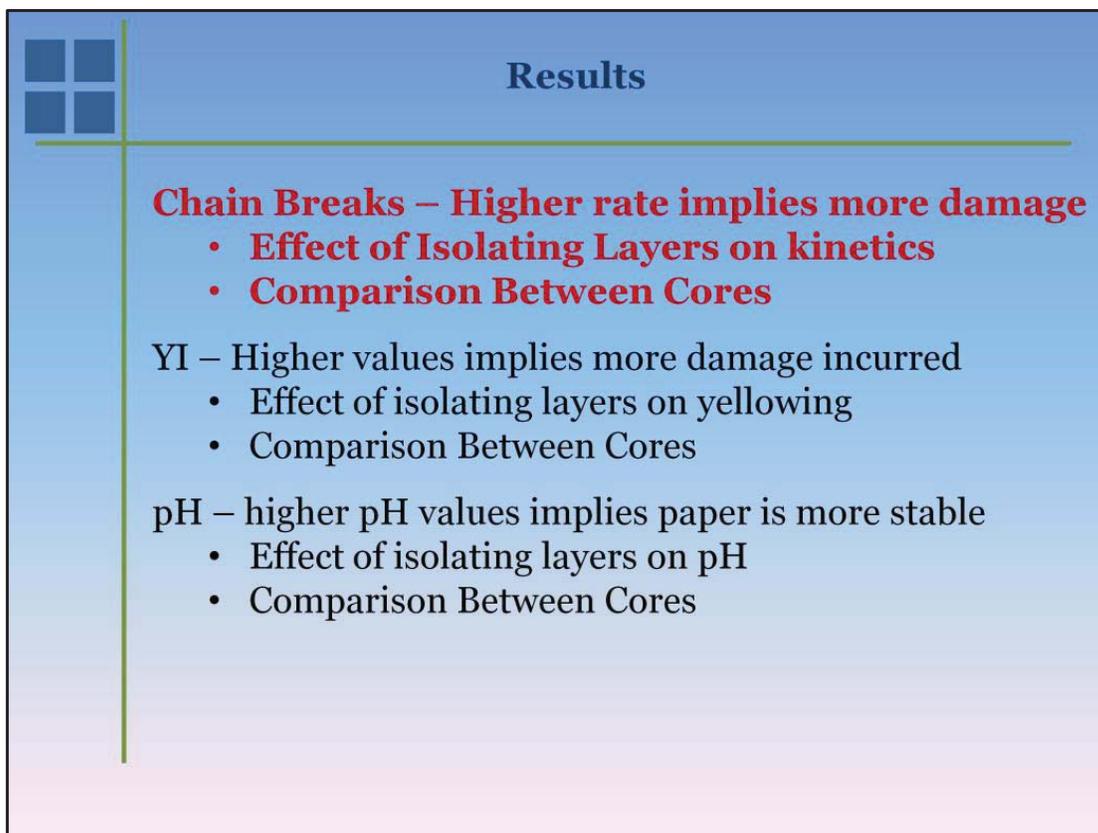
**Analyses**

- **Molecular weight (MW)** – look for rate of degradation
- **Yellowness index (YI)** – monitor how yellow paper gets
- **pH** – look for changes in acidity

**Final Sample Matrix**

Isolating layers	Rolled Storage tubes			
	QT	KT	Tan	Blue
No isolating layer (Direct contact)	✓	✓	✓	✓
Aluminum foil	✓	✓	✓	✓
Buffered tissue	✓	✓	✓	✓
Marvelseal®	✓	✓	✓	✓
Mylar®	✓	✓	✓	✓
Tyvek®	✓	✓	✓	✓
W1 control (not on a tube)	✓			

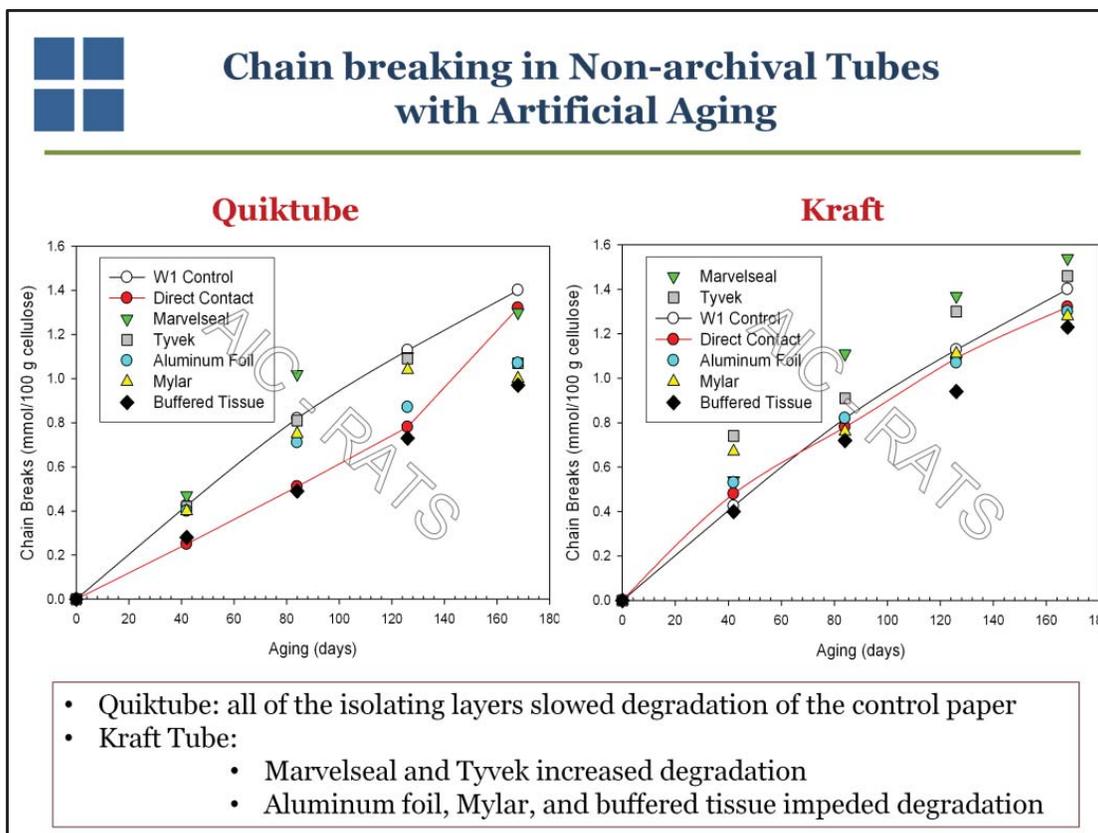
- This slide shows our experimental protocol. Catherine decided to age the samples at 90°C and 50% relative humidity (RH) because she knew that Whatman No. 1 "map" would degrade via hydrolysis using these artificial aging conditions
- Will the "maps" degrade slower or faster when they are in contact with the various rolled storage tube designs?
- At every data point (unaged, 6 weeks, 12 weeks, 18 weeks and 24 weeks), we measured changes to the molecular weight (calculated in terms of chain breaks and measured using gel permeation chromatography), the yellowness (ASTM method E-313), and the pH (TAPPI method T 509 om-11; measured in a glove bag purged of CO<sub>2</sub>)



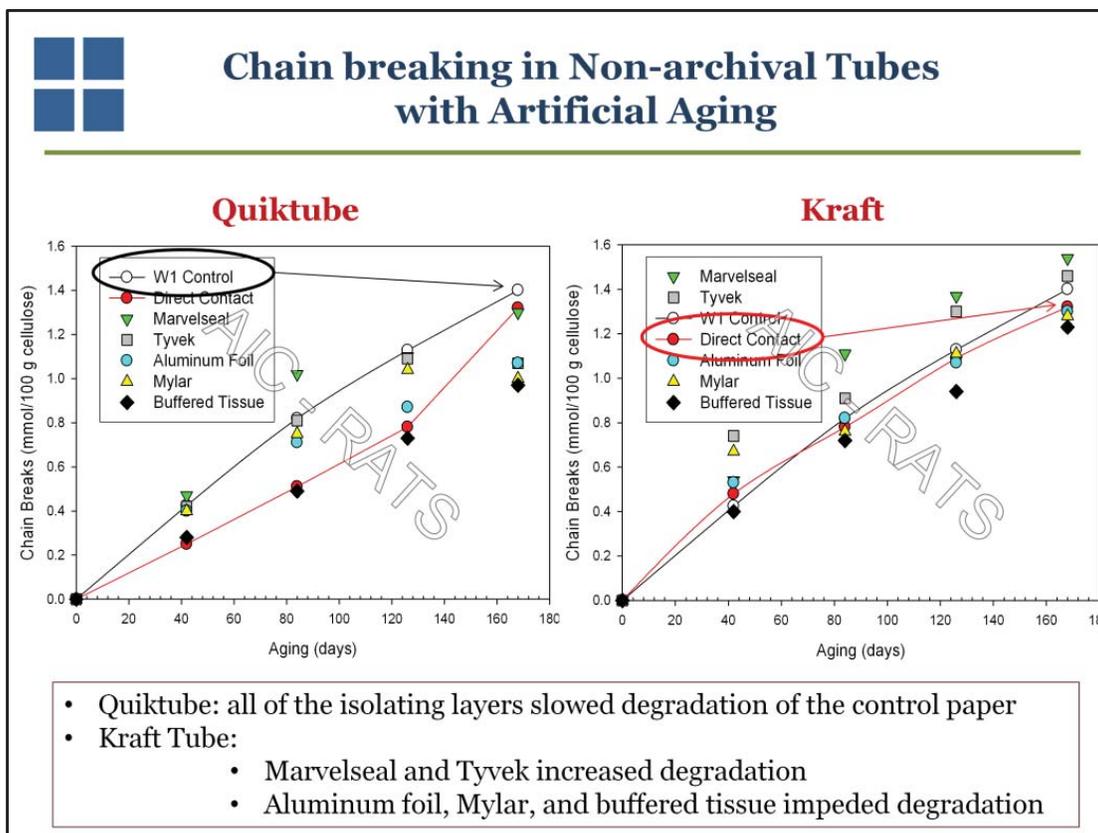
## Results

- Chain Breaks – Higher rate implies more damage**
  - **Effect of Isolating Layers on kinetics**
  - **Comparison Between Cores**
- YI – Higher values implies more damage incurred
  - Effect of isolating layers on yellowing
  - Comparison Between Cores
- pH – higher pH values implies paper is more stable
  - Effect of isolating layers on pH
  - Comparison Between Cores

- This slide is an outline of the order of how we will present the results.
- Further, we will discuss non-archival storage tube results followed by the archival storage tube results.
- Based on the results in terms of rolled storage tube, we will compare how the best performing isolating layers behaved for each of the four different tubes.
- First, let's look at changes to the molecular weight of the Whatman No. 1 "maps" after each has been aged at 90°C and 50% RH by itself, in direct contact with the storage tubes, or when it has been rolled onto tubes with isolating layers.
- Reminder: Lower numbers of chain breaks are affiliated with less degradation and hence, higher strength and stability; higher numbers of chain breaks are affiliated with greater amounts of degradation, lower strength, and lower stability.

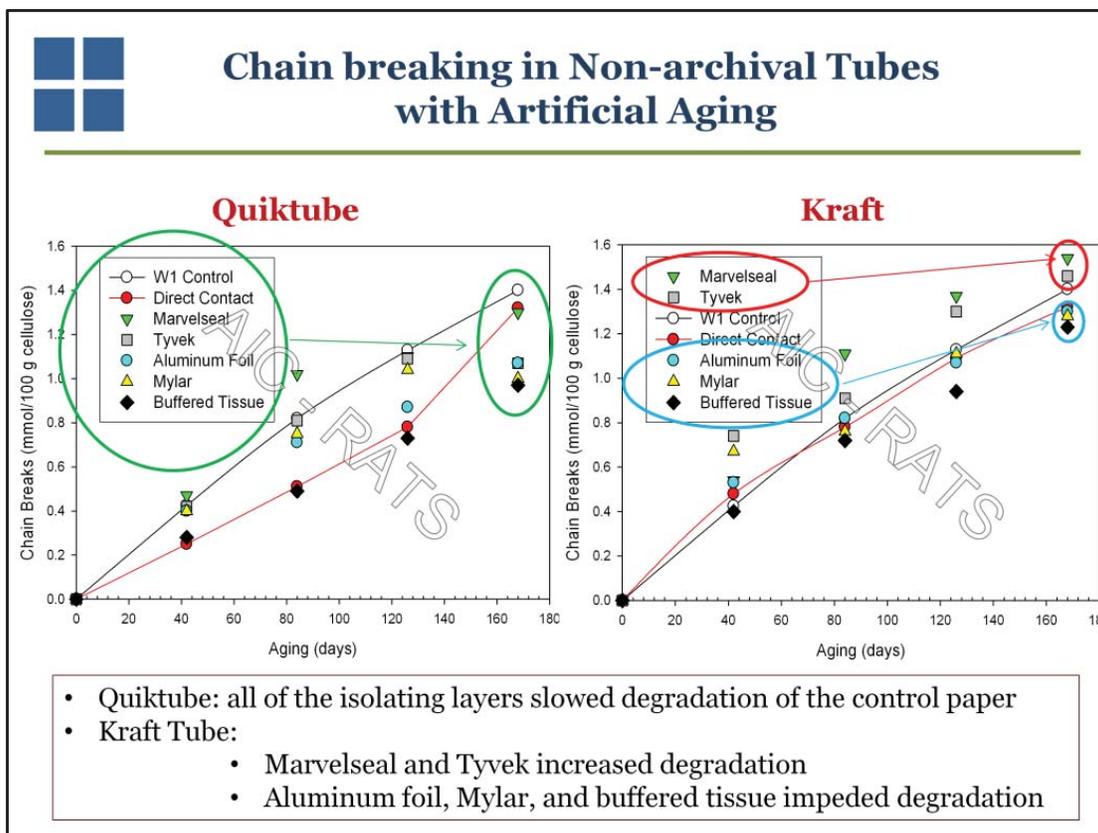


- The next three slides are designed to illustrate how all the data will be discussed throughout the rest of the presentation.



Important concepts with respect to understanding the data are:

- The x-axis is always represents artificial aging time in the oven at 90°C and 50% RH in days.
- The y-axis represents the result from a particular analysis. In this slide, it is chain breaks, as calculated from changes to the molecular weight of the “maps” with time.
- The legend is always organized with respect to the data at 24 weeks, with the first listing representing the data with the largest number of chain breaks over time and the last listing representing the data that exhibited the least number of chain breaks with time. This is intended to help the reader see how one isolating layer ranks against another.
- The black solid line connects the Whatman No. 1 (“W1 control”) data and represents the behavior of a Whatman No. 1 “map” when it is not in contact with any tube. It represents what Whatman No. 1 “control map” would do on its own when aged at 90°C and 50% RH.
- The red solid line connects the Whatman No. 1 “map” data when it is in direct contact with a tube.
- The behaviors of the “maps” when they are in contact with isolating layers are always compared in terms of the “control map” or when the Whatman No. 1 “map” is in direct contact with a tube

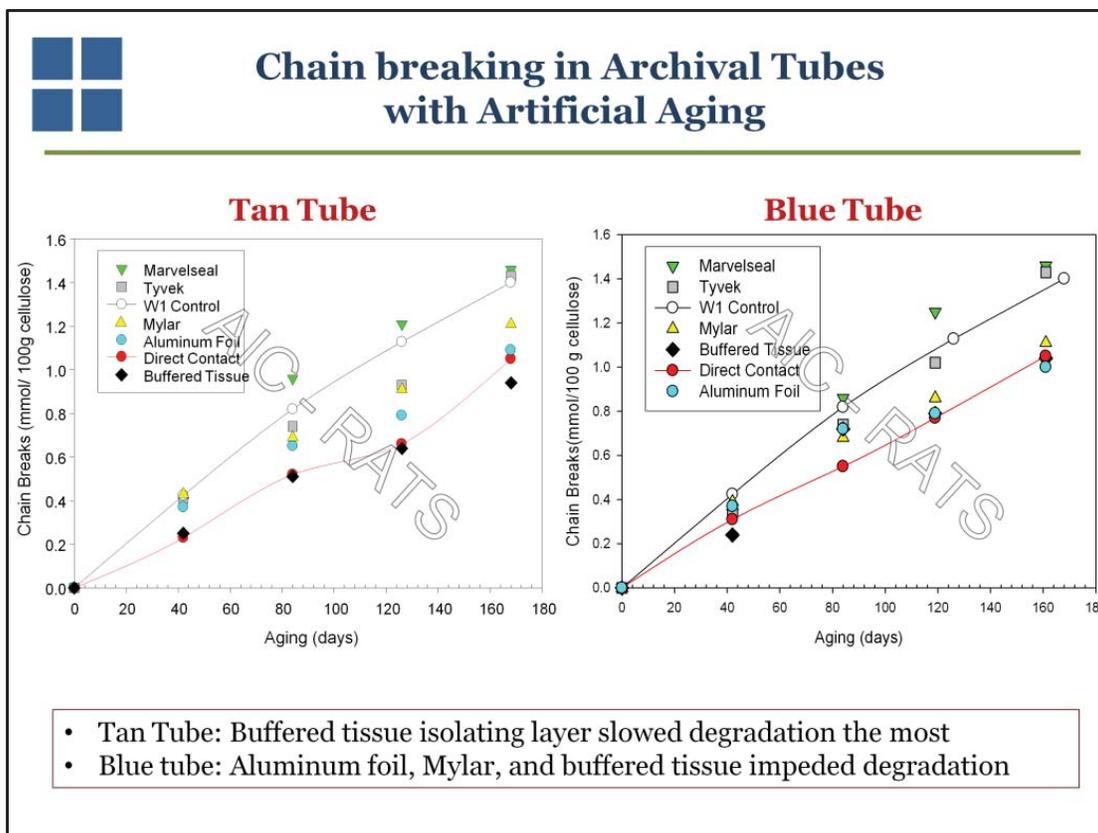


#### Quiktube results:

- The Whatman No. 1 control “map” showed the largest number of chain breaks, which says that rolling a map on a Quiktube may slow down chain breaking.
- All of the isolating layers slow down the degradation of the “maps” even further than having a “map” in direct contact with the Quiktube.
- The Mylar and buffered tissue rolled onto the Quiktube did the best job protecting the Whatman No. 1 “map” from chain breaking reactions.

#### Kraft tube results:

- A Whatman No. 1 “map” in contact with either Marvelseal and Tyvek as isolating layers undergoes more chain breaking than when the “map” ages all by itself (note that they fall above the black line). This indicates that contact with the Marvelseal and Tyvek promote chain breaking reactions.
- By contrast, the aluminum foil, Mylar, and buffered tissue all acted as mild isolating layers, decreasing the degradation of a Whatman No. 1 “map” slightly when compared to the same “map” in direct contact with the Kraft tube.

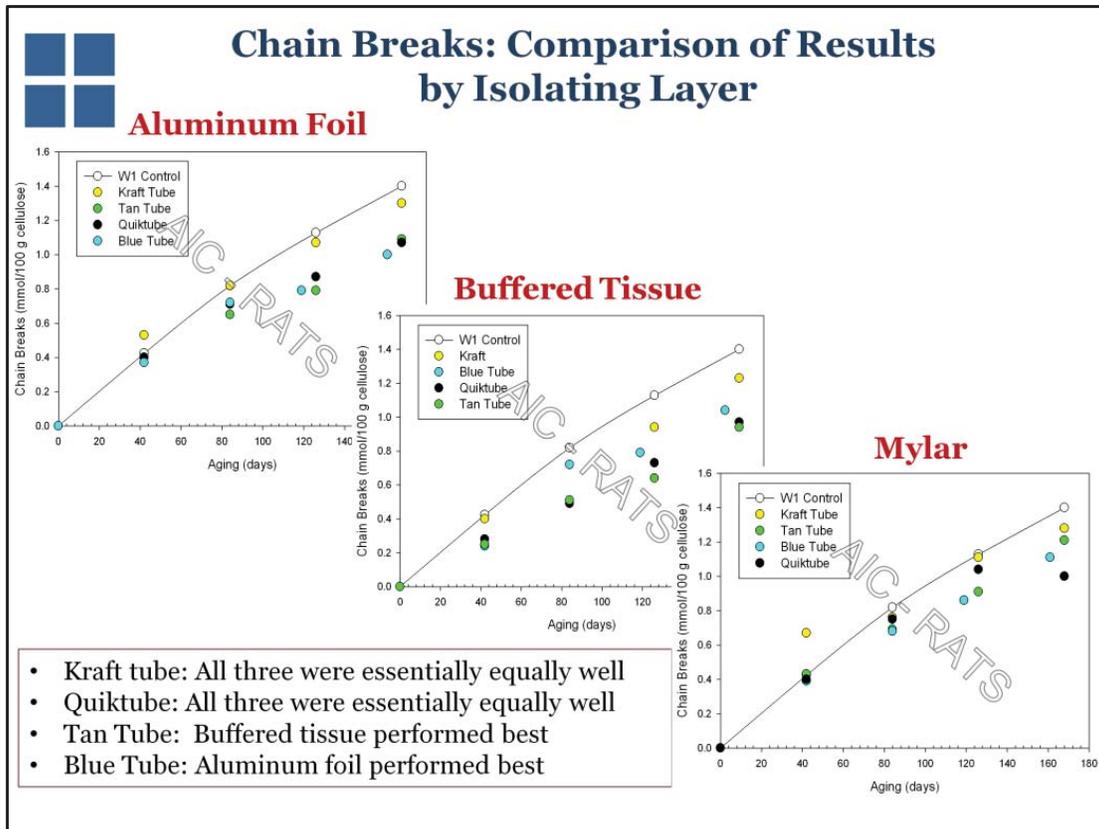


**Tan tube results:**

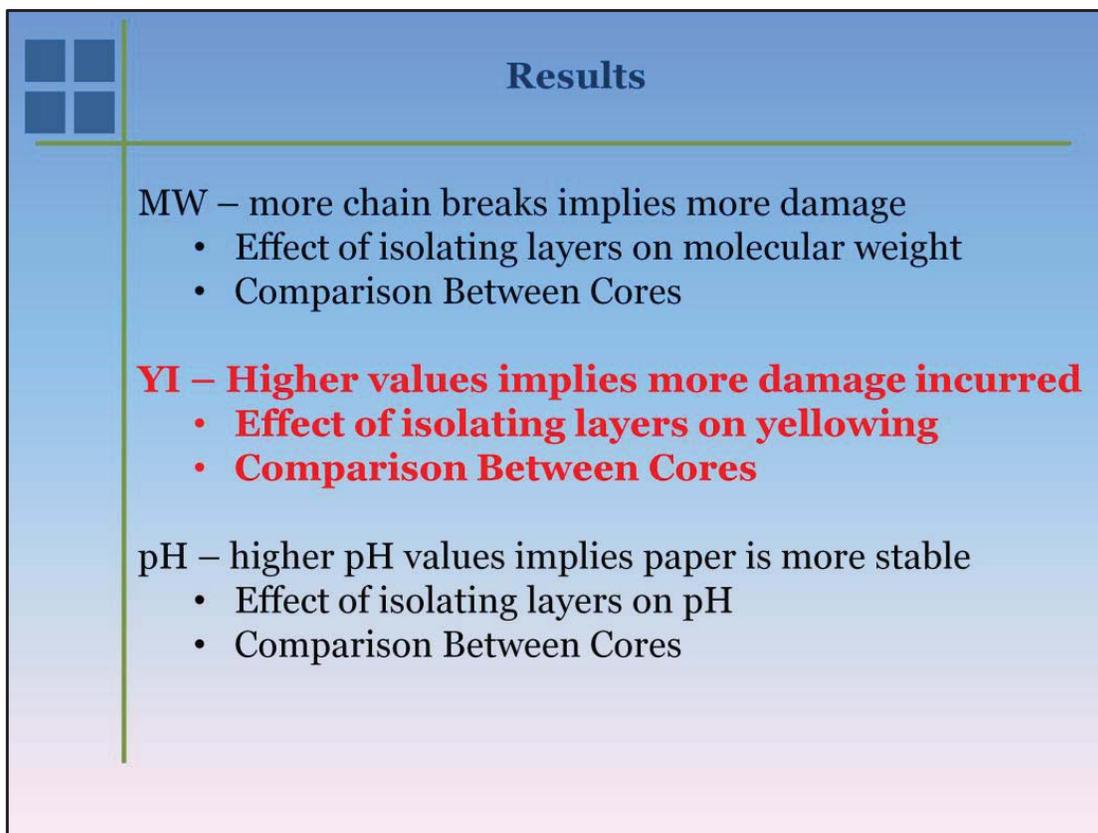
- Under these aging conditions, the Marvelseal and Tyvek isolating layers promoted degradation of the Whatman No. 1 “maps” (data above the black line).
- Whatman No. 1 “map” in direct contact with the tube proved to be better at inhibiting degradation than the Mylar and aluminum foil – this is likely because of the contribution of the alkaline reserve of the Tan Tube.
- The best storage tube design using the Tan tube was to use buffered tissue as an isolating layer, as it inhibited degradation slightly more than when a “map” was in direct contact with the Tan tube.

**Blue tube results:**

- Under these aging conditions, the Marvelseal and Tyvek isolating layers promoted degradation of the Whatman No. 1 “maps” (data above the black line).
- The use of Mylar or buffered tissue as isolating layers was about the same as having the Whatman No. 1 paper in direct contact with the tube, so their barrier properties were minimal.
- The best storage tube design using the Blue tube was to use aluminum foil as an isolating layer, as it inhibited degradation slightly more than when a “map” was in direct contact with the tube.



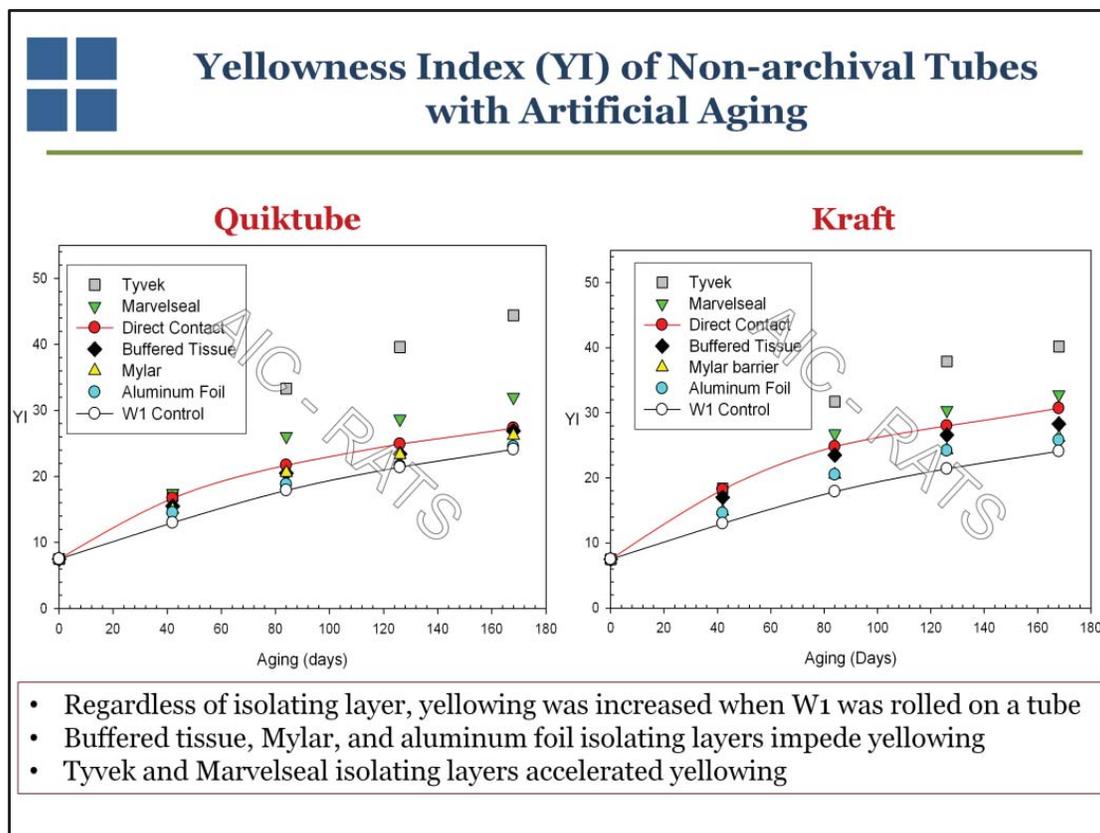
- On the previous two slides, we saw that with accelerated aging at 90°C and 50% RH, the three best isolating layers for inhibiting chain breaking were aluminum foil, the buffered tissue, and the Mylar.
- See the previous slides for recommendations for use of isolating layer for each type of the four tubes.



## Results

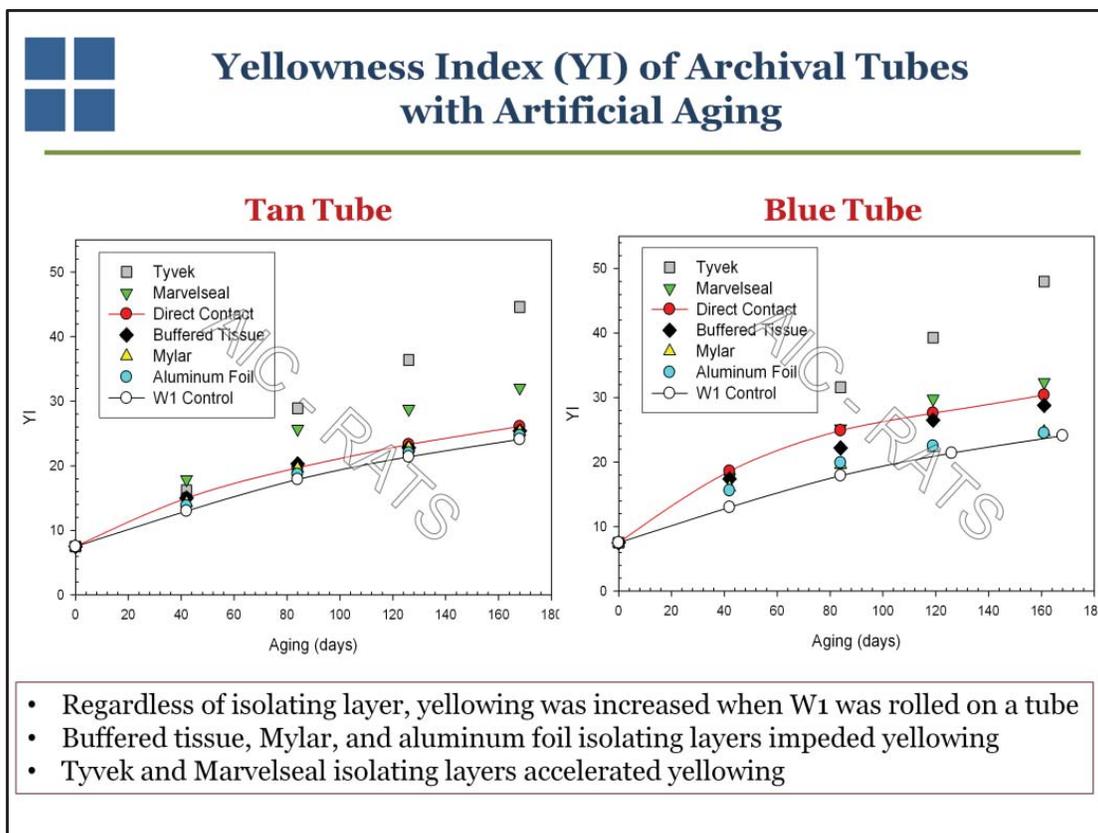
- MW – more chain breaks implies more damage
  - Effect of isolating layers on molecular weight
  - Comparison Between Cores
- YI – Higher values implies more damage incurred**
  - **Effect of isolating layers on yellowing**
  - **Comparison Between Cores**
- pH – higher pH values implies paper is more stable
  - Effect of isolating layers on pH
  - Comparison Between Cores

- Lets look at changes to the Yellowness Index (YI) -- a number calculated from spectrophotometric data that describes the change in color of a test sample from white toward yellow after exposure to light, chemical treatment, or processing -- of the Whatman No. 1 “maps” after they have been aged at 90°C and 50% RH by themselves, in direct contact with the storage tubes, or when they have been rolled onto tubes with isolating layers.
- Reminder: Lower YI values are qualitatively affiliated with less degradation, higher pHs, and hence, are indicative of a stable “map”.



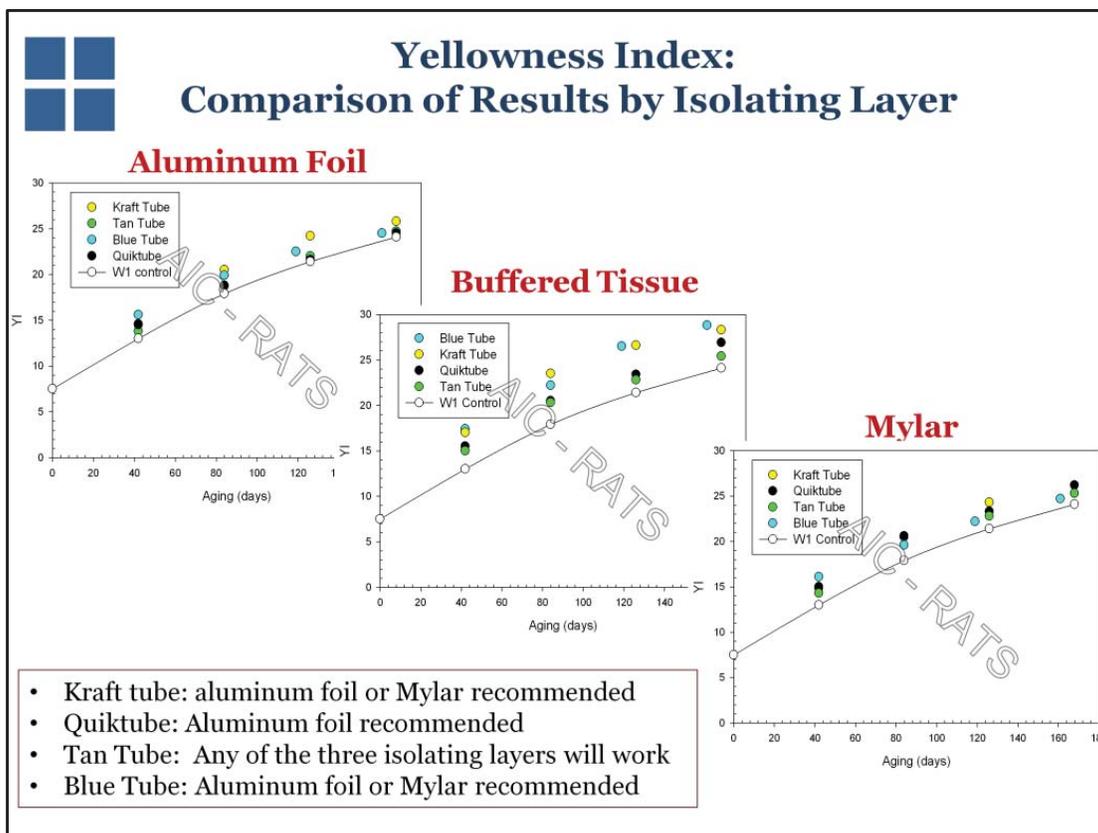
#### Quiktube and Kraft tube results:

- In both cases, the control Whatman No. 1 “map” showed the lowest levels of YI with artificial aging.
- This implies that the ideal method preventing yellowing is to not put a “map” on a rolled storage tube at all. However, given that in Amy’s case this is not possible as many of her maps are too large for flat storage.
- The Whatman No. 1 “map” in direct contact with the Quiktube showed only slightly more yellowing when a “map” was aged by itself.
- The Whatman No. 1 “map” in direct contact with the Kraft tube showed slightly higher levels of yellowing than when a “map” was aged in contact with the Quiktube.
- The Tyvek and Marvelseal isolating layers both promoted yellowing versus using another isolating layer or putting a “map” in direct contact with the Quiktube or Kraft tube.
- The buffered tissue, Mylar, and aluminum foil isolating layers inhibited yellowing of the Whatman No. 1 “maps” compared to direct contact or if a “map” was aged by itself.

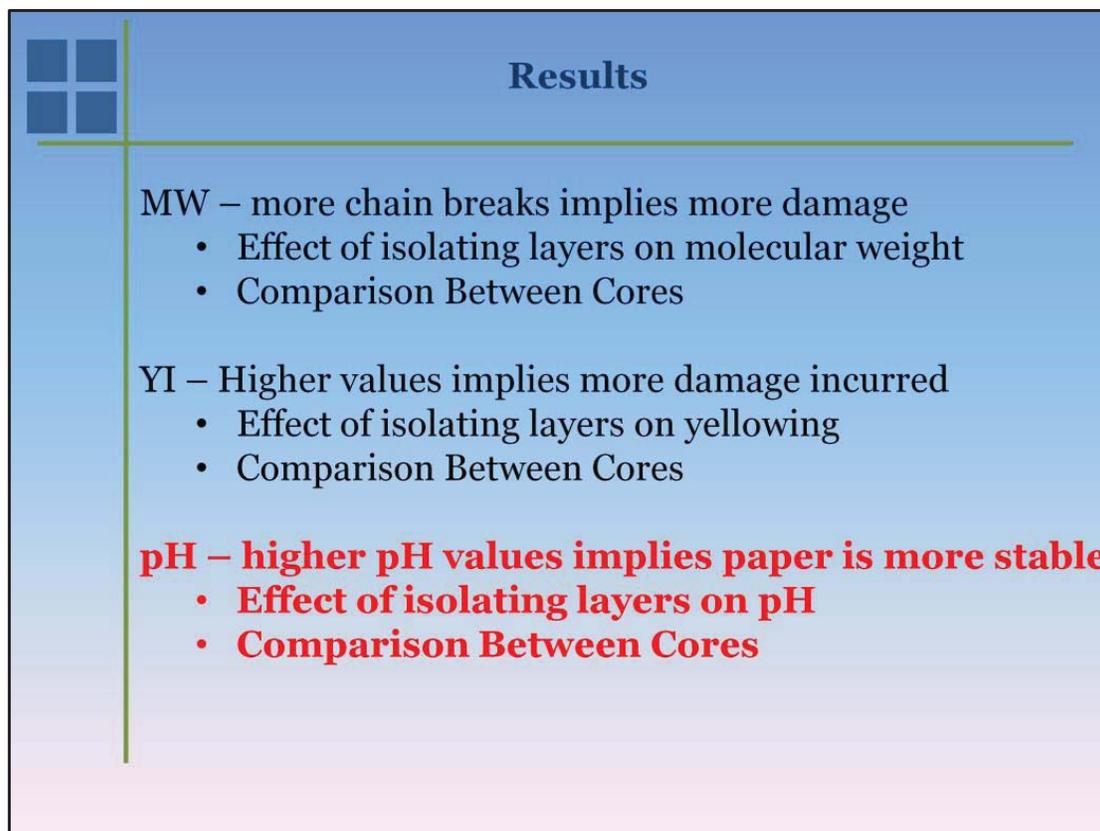


#### Tan Tube and Blue Tube results:

- As we saw with the non-archival tubes, the control Whatman No. 1 “map” (black line) showed the lowest levels of YI with artificial aging.
- The Whatman No. 1 “map” in direct contact with the Tan Tube showed only slightly more yellowing when a “map” was aged by itself.
- The Whatman No. 1 “map” in direct contact with the Blue tube showed slightly higher levels of yellowing than when a “map” was aged in contact with the Tan Tube.
- Similar to the non-archival tubes, the Tyvek and Marvelseal isolating layers both promoted yellowing versus using a different isolating layer or putting a “map” in direct contact with the Tan Tube or Blue Tube.
- The buffered tissue, Mylar, and aluminum foil isolating layers inhibited yellowing of the Whatman No. 1 “maps” compared to direct contact or if a “map” was aged by itself.



- As with the chain breaking results, we saw that with accelerated aging at 90°C and 50% RH, the three best isolating layers for inhibiting yellowing were aluminum foil, the buffered tissue, and the Mylar.
- Unlike with the chain breaking results, the best way to inhibit yellowing was to age a “map” by itself and not on a storage tube.
- See the previous slides for recommendations for use of isolating layer for each type of the four tubes.



## Results

MW – more chain breaks implies more damage

- Effect of isolating layers on molecular weight
- Comparison Between Cores

YI – Higher values implies more damage incurred

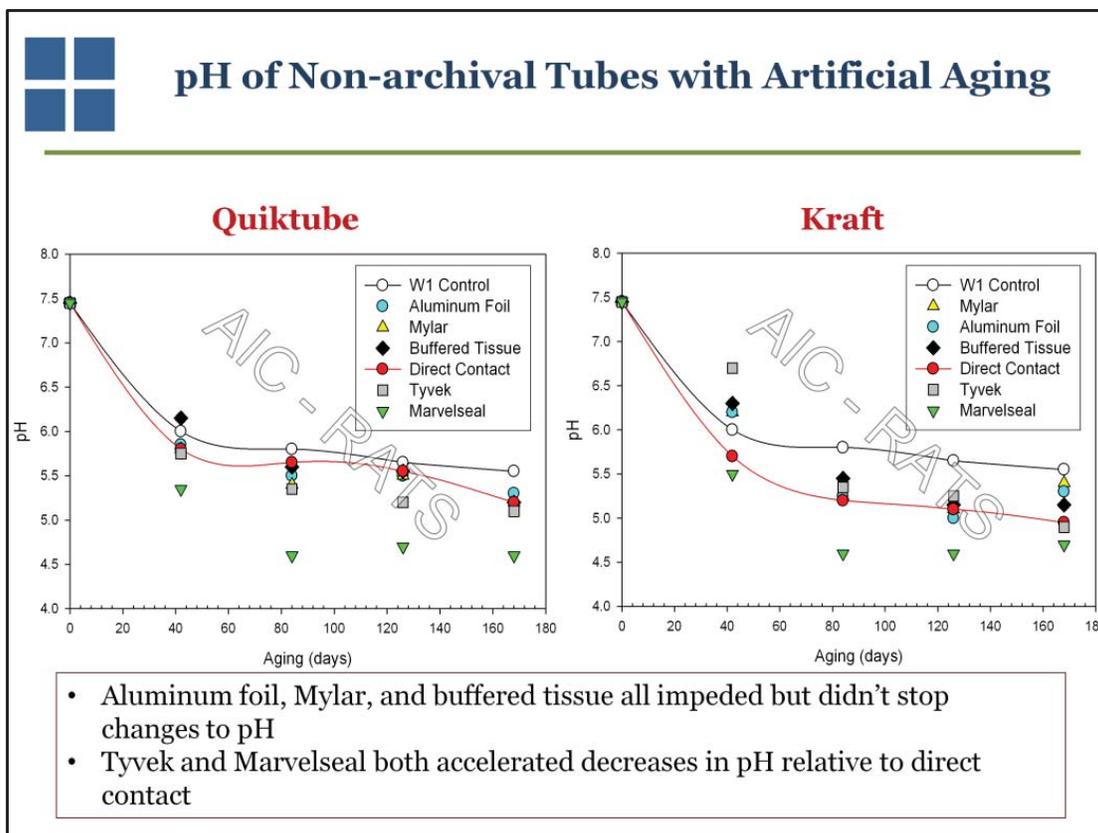
- Effect of isolating layers on yellowing
- Comparison Between Cores

**pH – higher pH values implies paper is more stable**

- **Effect of isolating layers on pH**
- **Comparison Between Cores**

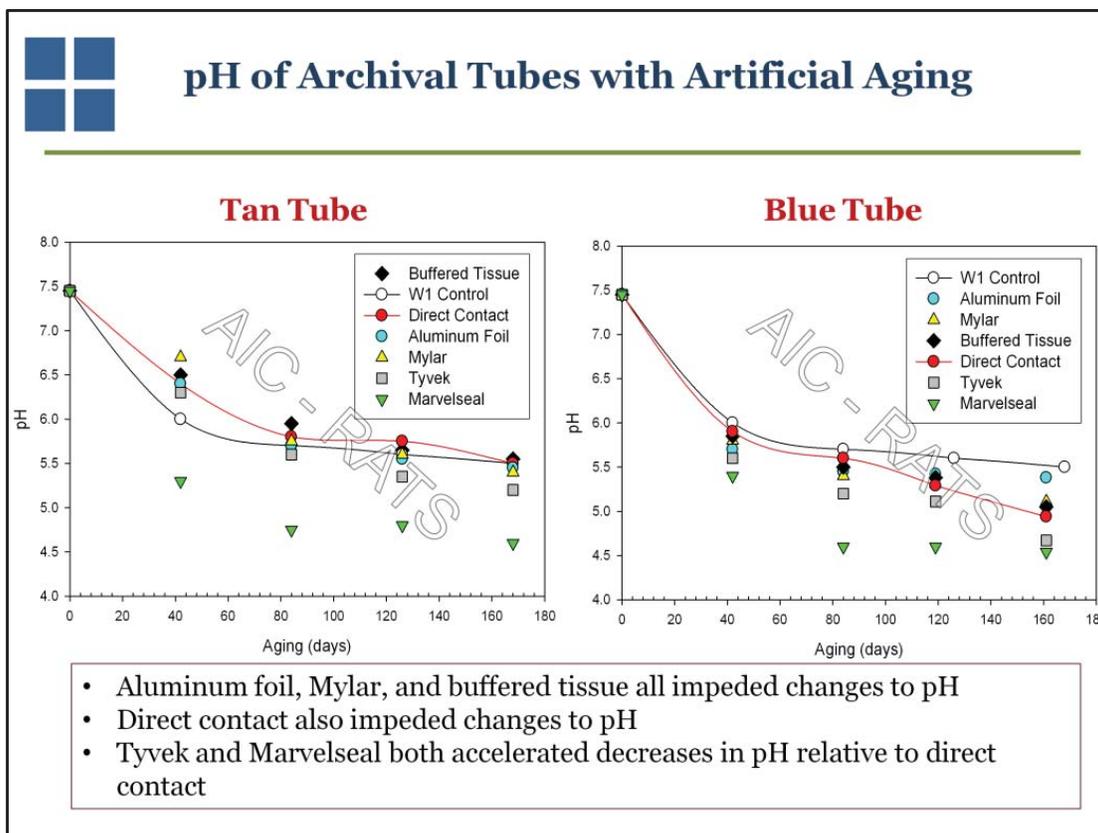
- Finally, lets look at decreases in the pH – or increases in acidity -- of the Whatman No. 1 “maps” after they have been aged at 90°C and 50% RH by themselves, in direct contact with the storage tubes, or when they have been rolled onto tubes with protective isolating layers.
- Reminder: the more acidic a piece of paper is, the faster it will degrade

(*Composition and condition of naturally aged papers* C. H. Stephens, T. Barrett, P. M. Whitmore, J. A. Wade, J. Mazurek, M. Schilling; *Journal of the American Institute for Conservation* **47** 201-215 [2009])



Quiktube and Kraft Tube results:

- The Whatman No. 1 control “map” showed the smallest decrease in pH.
- This implies that the ideal method to prevent changes in the pH is to not put a “map” on a rolled storage tube at all.
- The aluminum foil, Mylar, and buffered tissue rolled onto a Quiktube or Kraft tube did better job protecting the Whatman No. 1 “map” from changes to pH than putting a “map” directly on a Quiktube or a Kraft tube.
- The Tyvek and Marvelseal isolating layers promoted decreases to the pH of the Whatman No. 1 “maps”.

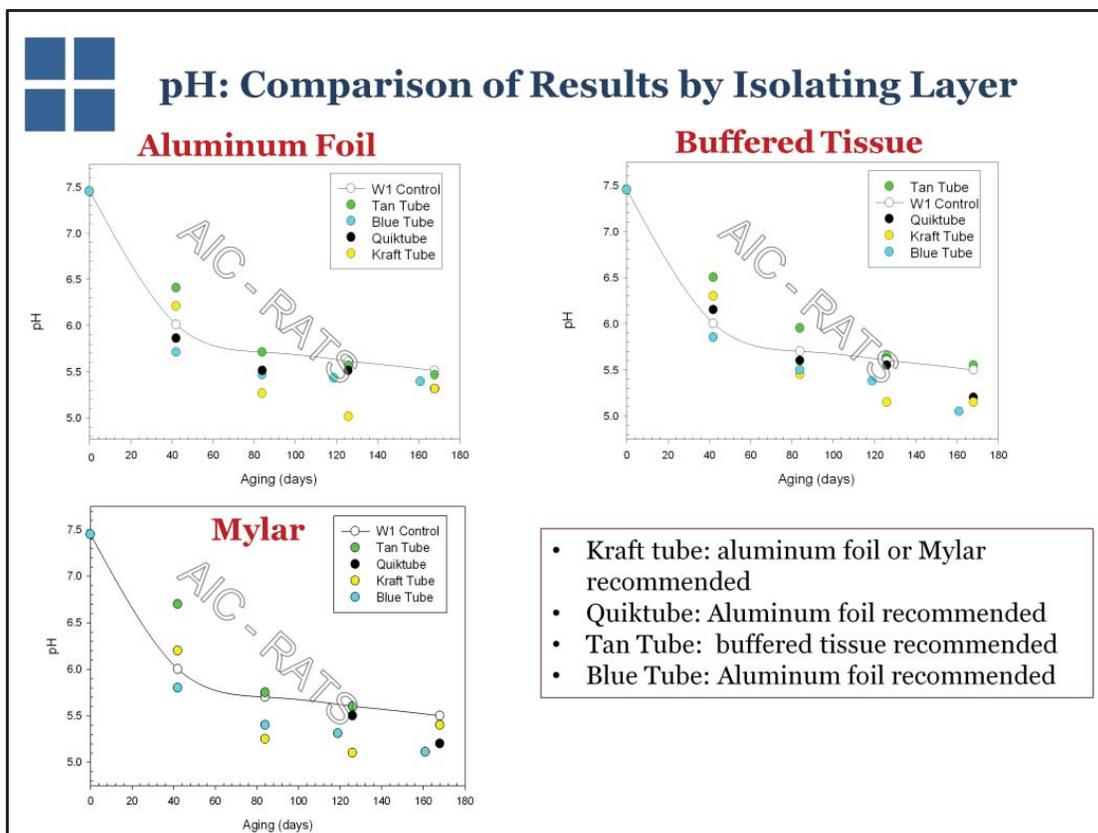


**Tan tube results:**

- The Whatman No. 1 control “map” showed the smallest decrease in pH.
- As we saw with the chain breaking results, the best storage design using the Tan tube was to use buffered tissue as an isolating layer, as it inhibited decreases to the pH slightly more than when a “map” was in direct contact with the Tan tube.
- One again, the Marvelseal and Tyvek isolating layers promoted decreases in the pH of the Whatman No. 1 “maps” (data above the below line).
- Whatman No. 1 “map” in direct contact with the tube proved equal to the Mylar and aluminum foil isolating layers at inhibiting decreases to the pH.

**Blue tube results:**

- The Whatman No. 1 control “map” showed the smallest decrease in pH.
- At these aging conditions, the Marvelseal and Tyvek isolating layers promoted changes to the pH of the Whatman No. 1 “maps” (data below the red line).
- The use of aluminum foil, Mylar, or buffered tissue as isolating layers inhibited decreases to the pH of the Whatman No. 1 “maps” compared to direct contact of a map with the Blue tube.



- As with the chain breaking and YI results, we saw that with accelerated aging at 90°C and 50% RH, the three best isolating layers for inhibiting changes to pH were aluminum foil, the buffered tissue, and the Mylar.
- With the exception of buffered tissue rolled onto the Tan Tube, where the buffered tissue was better at inhibiting changes to the pH than not putting a “map” on a tube at all, the best way to inhibit changes to the pH was to age a “map” by itself and not on a storage tube.
- See the previous slides for recommendations for use of isolating layer for each type of the four tubes.



## Observations From Current Study

- The best isolating layer for:
  - Quiktube® = Heavy duty aluminum foil
  - Kraft Tube = Mylar
  - Tan Tube = Buffered tissue or heavy duty aluminum foil
  - Blue Tube = Heavy duty aluminum foil
- Marvelseal and Tyvek promoted the degradation of the W1 paper at 90°C – more research should be done at lower temperatures
- The glues used to make the tubes are an important component to the usefulness of a support core for long term storage

- Based on our current results, our main conclusions are stated in this slide.
- This is still a work in progress, as we need to understand WHY some of the results came out the way that they did. For instance, we still don't completely understand WHY the blue tube becomes stained and transfer that stain to the "map" and we haven't identified what the brown stain is made of. We do know, however, that the brown stain material is water soluble and can be rinsed off a "map".
- Slides 26 – 28 will show some of our working hypotheses, but they are not "conclusions" in the truest sense of the word. They are observations, ideas, and food for thought.



## Closing Comments

- A goal of this research & presentation is to raise awareness that:
  - Not all paper-based cores perform the same
  - The adhesives used to make a paper core have an effect on performance
  - Isolating layers can have a positive or negative effect on performance



- Our overarching goal was to understand how these different materials perform under artificial aging conditions.
- We weren't and aren't interested in saying anything negative about any particular brand or product.
- Rather, it is up to all of us to make sure we think about the materials we use when we do treatments and sometimes we have to do tests on our own to double check the properties of these materials.
- Vendors can change where they source materials and it's imperative that we test and re-test these materials on an ongoing basis to make sure they perform the way we want.
- Also, we should be able to ask our vendors to take on more responsibility, informing us of changes and asking them to perform tests to make sure they are selling us a consistent product.



## Closing Comments

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- Staining was localized at the seam gaps. Skiving is a solution core manufacturers use when customers request a seamless core.
- The results for the two archival cores in this study are not a reflection of *all* archival tubes. Color of paper does not imply adhesive (i.e. all blue colored tubes are not made with sodium silicate)
- Ask your vendor for information of both the paper and glue components of the core.
- Each situation is unique. There are many possible combinations of cores + isolating layers. Ask yourself what detrimental mechanisms are you addressing with your choice of isolating layer? Could your core or isolating layer choices actually increase degradation, either on their own or by interacting with other materials?

- This slide contains some possible solutions to some of the issues we mentioned as well as some suggestions.
- We haven't found a storage tube that doesn't have a seam gap, however, there is a way to manufacture rolled tubes such that they don't have seam gaps. This process is called skiving. It costs slightly more, but it creates a smooth surface. The possible benefit of this type of tube is two-fold: it would decrease the amount of staining and provide a smooth surface for the art object. Perhaps we could all talk to our vendors about making tubes such as these for conservation/preservation applications.
- Regarding archival tubes, it is our working hypothesis that the paper to used to manufacture archival tubes is great, but that perhaps the glues used to manufacture them are not necessarily great. Hence, the color of an archival tube matters not at all but the adhesive used in the manufacturing of the tube does.
- Which is why we want you to ask about the glues used to make the tubes you use. Based upon some experiments shown on slide 27, we would advise you to consider not using tubes adhered with sodium silicate. Other glues might be acceptable (or not), and we don't have a suggestion for what might be an ideal glue, but we're fairly certain that tubes containing sodium silicate do not offer any benefit for long-term preservation over a tube that is made with a PVA or PVA/PVOH glue mix.



## Acknowledgements

**Amy**  
(AEB59@pitt.edu)

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- Office of Surface Mining Reclamation and Enforcement
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- Lisa Goldberg, Valerie Tomlinson, Berta Blasi & Bill Minter

**Catherine**  
(Catherine.Stephens@yale.edu)

- The Andrew W. Mellon Foundation
- Bob Strauss
- Amy, for coming to me with her great query!

## Why did the Tyvek and Marvelseal 360 Isolating Layers Perform so Terribly During These Experiments?

Both are made with polyethylene,  $T_m \approx 140^\circ\text{C}$

### Tyvek – 100% polyethylene



### Marvelseal 360 – a 4-layer system

Nylon
Polyethylene
Aluminum Foil
Polyethylene



- Hypothesis: at  $90^\circ\text{C}$ , the polyethylene degraded as well as the “maps”
- Isolating layers are not necessarily innocent bystanders
- Experiment should be repeated at lower temperatures to verify danger at room temp

- We performed these experiments at  $90^\circ\text{C}$  and 50% RH. The reason for this is that degradation occurs faster at a higher temperatures. In scientific parlance, we refer to this rate as “laboratory time scale”, because it means experiments may takes days to weeks and not months to years.
- While  $90^\circ\text{C}$  and 50% RH may be an ideal temperature to accelerate the aging of paper “maps”, it may not be the ideal test conditions to test the rest of these materials.
- Specifically, it may not be an ideal condition to age Tyvek and Marvelseal 360, as they are both made from polyethylene, which has a melting temperature of  $\sim 140^\circ\text{C}$ . It’s our hypothesis that at  $90^\circ\text{C}$ , these two materials underwent degradation that they might not undergo at room temperature ( $\sim 23^\circ\text{C}$ ) or natural aging conditions.
- Hence, we would like to do these same experiments with the same materials at  $40^\circ\text{C}$ . This temperature is closer to real temperature aging conditions but will still speed up aging. We did start aging these materials at  $40^\circ\text{C}$ , however, due to circumstances beyond our control, we couldn’t complete these experiments.
- We will say however that Tyvek is not intended to be used as an isolating layer for any application. As you can see in the upper left hand black and white SEM image, Tyvek is designed to be a porous material. Hence, it will allow certain materials to pass through it, perhaps materials we don’t want to get in contact with our artifacts. Further, as you can see in the color image in the to the right of the SEM image, the staining of the “map” was very mottled. This is because the structure of the Tyvek is not uniform, so there will be areas where the sheet is thicker and thinner, making it more difficult or more easy, respectively, for gases to pass through its membrane.
- The images on the right show that the Marvelseal 360 cracked, turned yellow, got gummy, and stained the tubes it was in contact with aging. The tube in the bottom right image started out as a tan tube and ended up looking like an unaged kraft tube due to the staining by the Marvelseal 360!

## Does the Adhesive Used to Make the Tube Matter? (Yes?)

### Polymeric Adhesives

	Cotton paper			Tan Tube		Blue Tube	
	0	3wks	9wks	0	3wks	9wks	0
No glue							
PVA/PVOH							
PVOH							
PVA							

- Synthetic adhesives brown with aging at 90°C, but don't discolor the paper (upper left)
- Sodium silicate reacts with the paper (upper right), turning it brown; doesn't discolor on its own (lower right)
- The discolored sodium silicate/paper product is water soluble

### Sodium Silicate

6 Weeks

Sodium silicate on glass

- This is a busy slide, but it is intended to illustrate several observations we made during our experiments.
- Using MSDS forms as well as through phone calls, we discovered the adhesives different manufacturers used to produce the various tubes we used in our study. We obtained either the exact same glue used by the manufacturer or something that was a close approximation of the adhesive used to make the tubes.
- There are typically two types of glues used to make rolled storage tubes, synthetic polymer glues (polyvinyl acetate [PVA] or polyvinyl alcohol [PVOH] or some combination of both) or sodium silicate ( $\text{Na}_2\text{SiO}_3$ ).
- In the upper left image, you can see that we brushed out some of the synthetic glues onto Whatman No. 1 paper ("cotton paper") as well as the paper used to manufacture the two archival tubes. We aged those samples at 90°C for 9 weeks and took out samples in 3 week increments to monitor qualitatively the response of the glue to those aging conditions. For each sample the "0" represents the appearance of the glues on the paper before they were put into the oven.
- In the upper right hand image, we have an example of a cotton paper brushed with sodium silicate (which starts out clear and colorless) and aged for 6 weeks at 90°C. When you brush sodium silicate onto the paper, it sinks into the paper, becoming part of the paper matrix.
- Still looking at the upper right hand image, above the portion of sample that is very brown in color, you will notice a smaller piece of paper that is not brown. This is a piece of the 6-week aged sample that we rinsed with water, showing that the brown staining that was caused by the contact between the cotton paper and sodium silicate is able to be washed out. Hence, whatever chemical is formed by the contact between paper and sodium silicate is water soluble – possible good news.

## Does the Adhesive Used to Make the Tube Matter? (Yes?)

### Polymeric Adhesives

	Cotton paper	Tan Tube	Blue Tube
No glue	0 3wks 9wks	0 3wks 9wks	0 3 9wks
PVA/PVOH			
PVOH			
PVA			

- Synthetic adhesives brown with aging at 90°C, but don't discolor the paper (upper left)
- Sodium silicate reacts with the paper (upper right), turning it brown; doesn't discolor on its own (lower right)
- The discolored sodium silicate/paper product is water soluble

### Sodium Silicate

6 Weeks

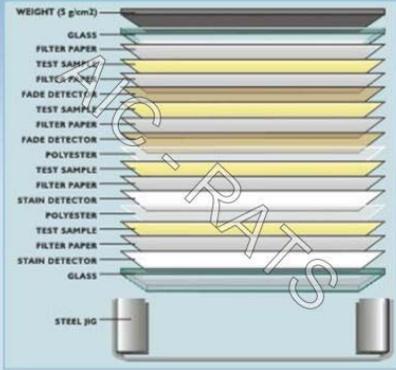
- In the lower right image, we show that when sodium silicate is brushed out onto glass and aged at 90°C, it remains clear and colorless throughout. Hence, the browning observed in the upper right hand image can be inferred to be a chemical reaction that took place between the sodium silicate and the cellulose of the Whatman No. 1 paper. This reaction is perhaps what we observed when we put the “map” in contact with the blue tube during our scouting experiment. We still need to prove this, though.
- By contrast, the brown staining you observe in the upper left hand image is different than the staining between the paper and sodium silicate. The synthetic glues sit on top of the papers after they are brushed on and allowed to dry. When these samples browned with aging, they didn't brown/stain the paper. The glues only browned themselves, internally.

## Photographic Activity Test (PAT): Why we Didn't use it

The PAT evaluates possible chemical interactions between enclosure materials and photographic images, negatives, slides, and motion picture film

Hence, it's a test to see if the silver component of a photograph will fade or be stained by other materials in its vicinity

We aren't sealing with artifacts containing silver hence this test wont give us the information we need about the effectiveness of isolating layers and quality of storage tubes



Schematic from the Image Permanence Institute

- See slide for commentary

'The never ending story of the conservation of modern and contemporary art'



Madeleine Berkhemer

41st Annual Meeting AIC May 29 – June 1 Indianapolis

RATS session Saturday June 1st

Thea van Oosten  
Anna Laganá  
Suzan de Groot

Cultural Heritage Agency of the Netherlands (RCE)

Thea van Oosten<sup>1</sup>, Anna Laganá<sup>2</sup>, and Suzan de Groot<sup>3</sup>

<sup>1</sup>Senior Research Scientist, Cultural Heritage Agency of the Netherlands (RCE)

<sup>2</sup>Freelance conservator/researcher

<sup>3</sup>Researcher, Cultural Heritage Agency of the Netherlands (RCE)

Presented at the RATS session

41st Annual Meeting of

The American Institute for Conservation of Historic and Artistic Works (AIC)

Indianapolis, In, May 29-June 1, 2013

'The never ending story of the conservation of modern and contemporary art'



Madeleine Berkhemer

41st Annual Meeting AIC May 29 – June 1 Indianapolis

RATS session Saturday June 1st

Thea van Oosten  
Anna Laganá  
Suzan de Groot

Cultural Heritage Agency of the Netherlands (RCE)

Contemporary works of art often pose particular practical and ethical concerns when they are made with techniques and materials others than those used traditionally by artists. Using objects in a way that they were not intended to be used may shorten the service life of these objects.

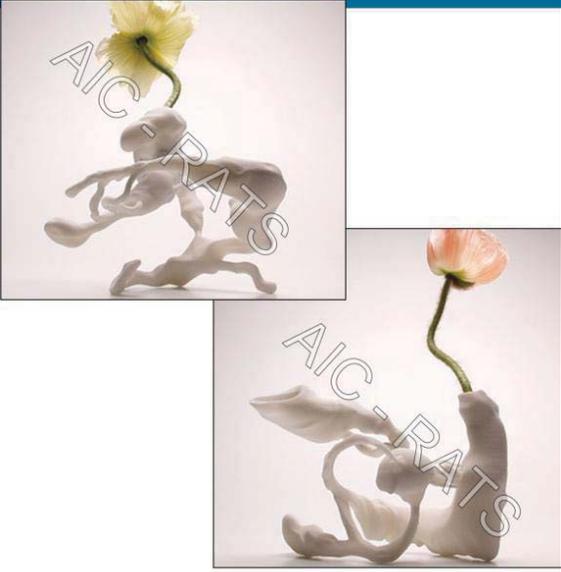
Moreover, in some years new techniques such as 3D rapid prototyping, Selective Laser Sintering (SLS) and Fused Deposit Modeling (FDM) will pose dilemmas to conservators and curators to decide how damaged objects made with these techniques should be restored or remade.

Examples of these new techniques will be presented to illustrate the dilemmas and possible solutions; 'Milly's Maserati', an installation by the Dutch artist Madelene Berkhemer and a series of vases by Marcel Wanders, a Dutch designer.

**Outline presentation**

**NYLON**

- Biobased Nylon
- Rapid prototyping
- Madeleine Berkhemer
- Marcel Wanders/Iris van Herpen
- Cleaning of nylon
- Ongoing research



**Snotty vase (Nylon) Marcel Wanders,**

A question arises whether it is more cost effective to invest time in researching the conservation of these objects or to have the objects remade or restored using 3D techniques

Outline of the presentation:

Nylon and biobased nylon

Madeleine Berkhemer

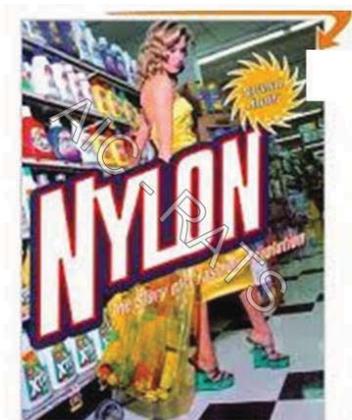
Rapid prototyping

Marcel Wanders/Iris van Herpen

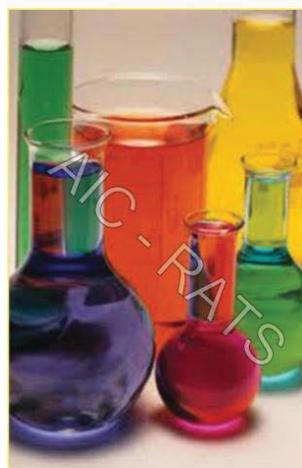
Cleaning of nylon

Ongoing research

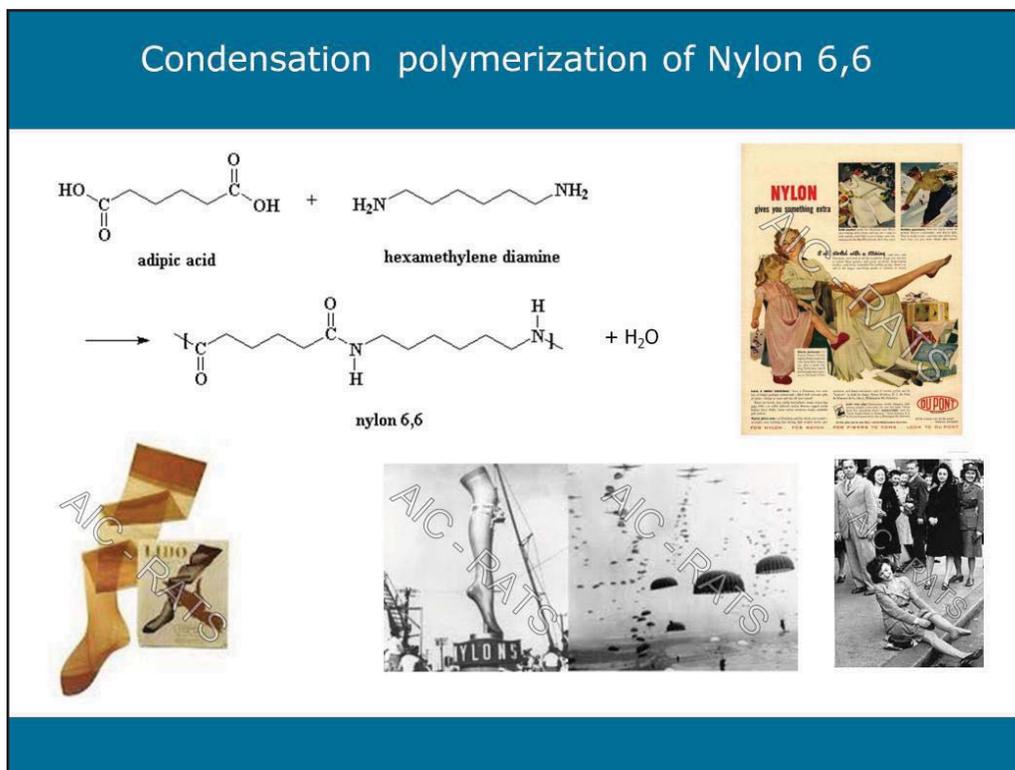
## Nylon , very known by name, but what is it actually?



W.H. Carrothers

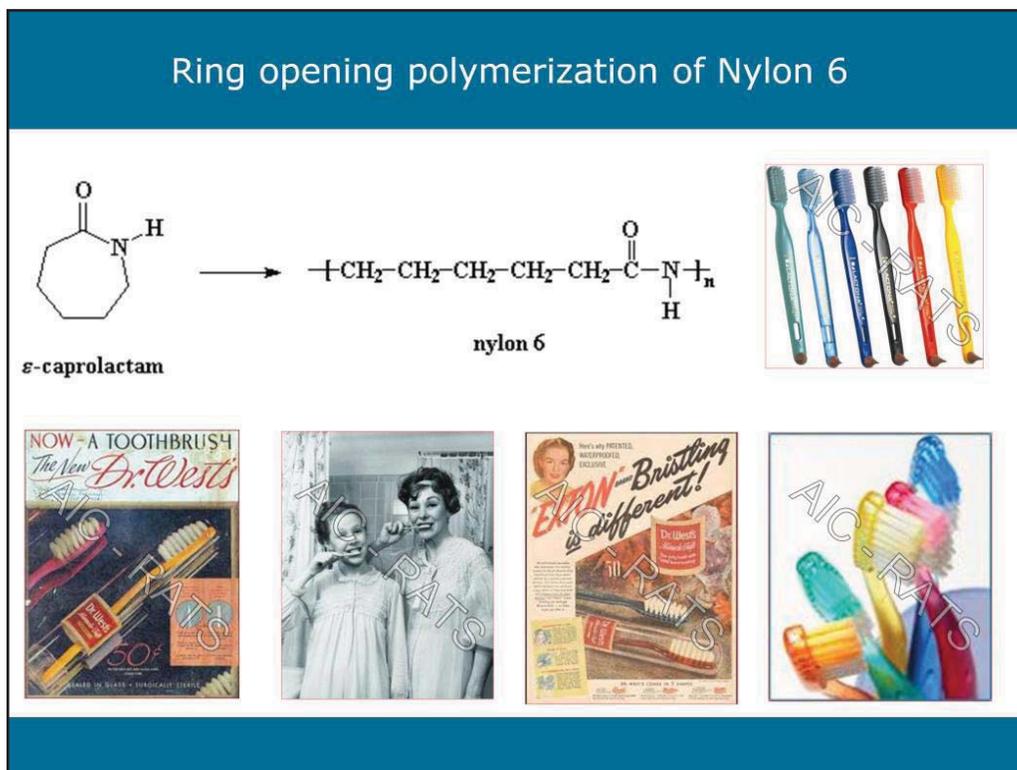


In 1924 Wallace Hume Carothers started with the research into the chemical structure of polymers. In 1928 he had set up the research laboratory “Dupont” for the development of plastics and in 1938 he brought nylon onto the market.



It is impossible to imagine modern society without nylon, It is a component of countless products in all branches of industry, not least the textile industry. Nylon fabrics have a soft sheen and delicate appearance, making it the synthetic alternative to silk. The best-known article of synthetic clothing is the pair of tights, the successor to the nylon stockings, also simply known as nylons.

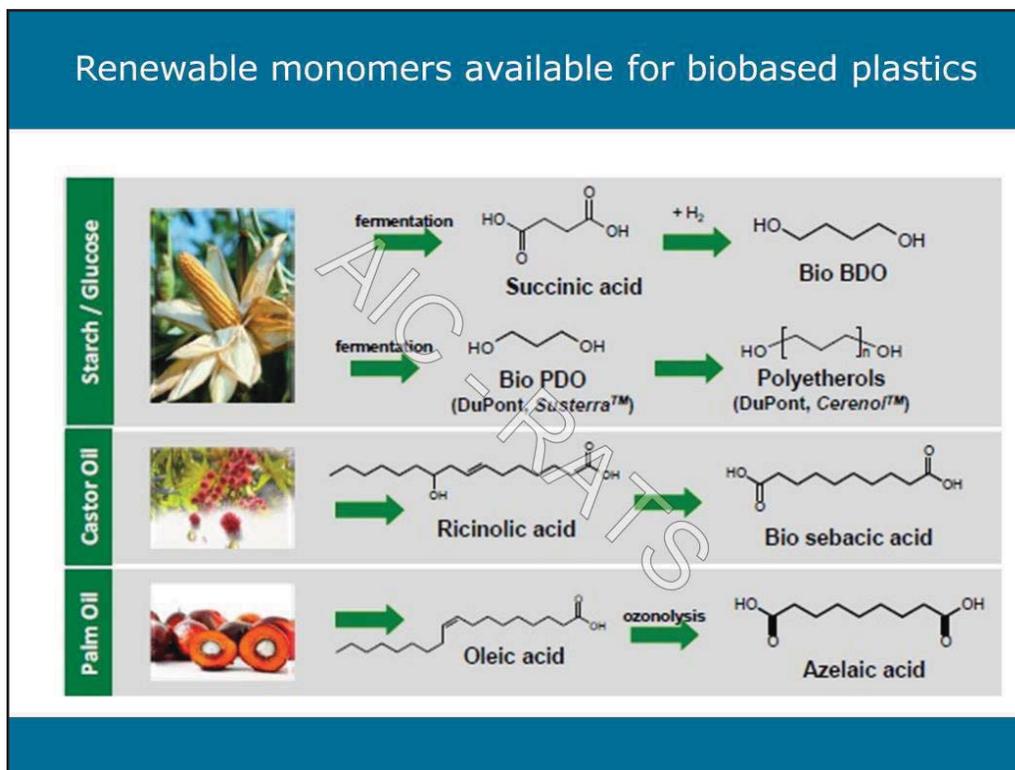
Nylon 6,6, of Dupont Company is made by condensation polymerization of adipic acid and hexamethylenediamine, an organic alkaline component. The formed nylon polymer is manufactured in the form of pellets by the chemical company and made into fibers by the process of melt spinning at the manufacturer. At spinning, fiber length, weight, elasticity and luster are determined. Luster is acquired by adding titanium dioxide (TiO<sub>2</sub>). The result is a very elastic product, which keeps its form, even after several washings and stretching.



Nylon 6 is made by the ring opening polymerization from the monomer caprolactam. Nylon 6 does not behave much differently from nylon 6,6. The only reason both are made is because DuPont patented nylon 6,6, so other companies had to invent nylon 6 in order to get in on the nylon business.

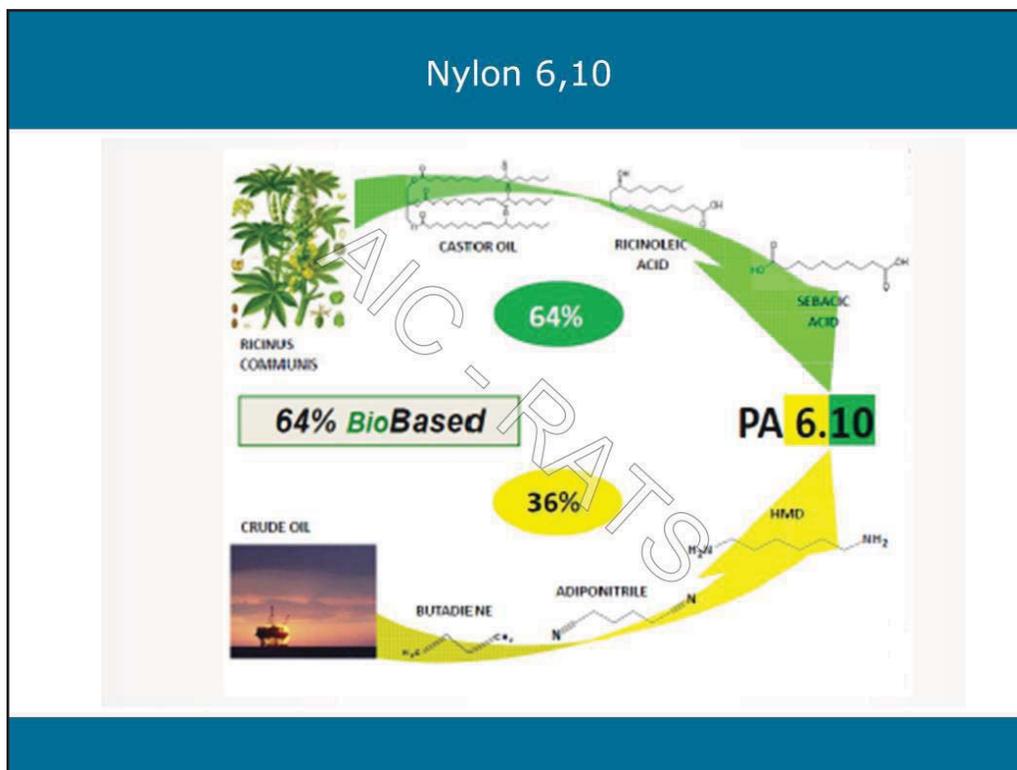
Nylon 6,6 has been used more often in Northern America and nylon 6 is more used in Europe.



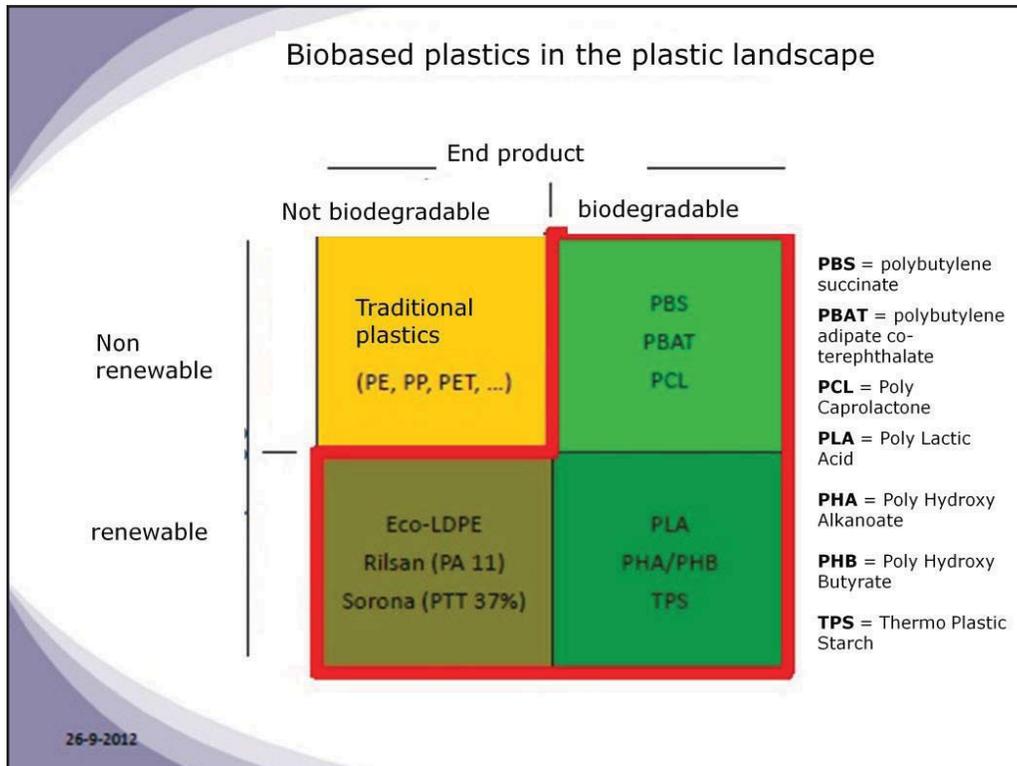


For the past 18 years, some plastics have been made from renewable sources such as corn, other plants, sugar, etc. And since 2008 a few biodegradable plastics have entered the marketplace. These are typically produced by using bacteria to prepare sugars for polymerization. With current technology most biodegradable plastics are made from sugar or starches. However, there are commercial technologies that use carbon dioxide and catalysts to produce biodegradable plastics. Scientists are also working to develop plastics from algae using processes that rely on nanotechnology. It is likely that the next 100 years of plastics will show even greater innovation than the first 100 years.

<http://www.2wplastic.com/>



An example of this is the semi-crystalline polyamide PA 6,10, which is synthesized through the polycondensation of 1,6-hexamathylene diamine and 1,10 decandioic acid (sebacic acid). Sebacic acid is extracted from castor oil: a natural raw material obtained from the seeds of castor oil plant. So for the nylon 6,10 family approximately 60% of raw material comes from renewable sources.



Nowadays monomer feedstock for the production of plastics is derived from renewable feedstock.

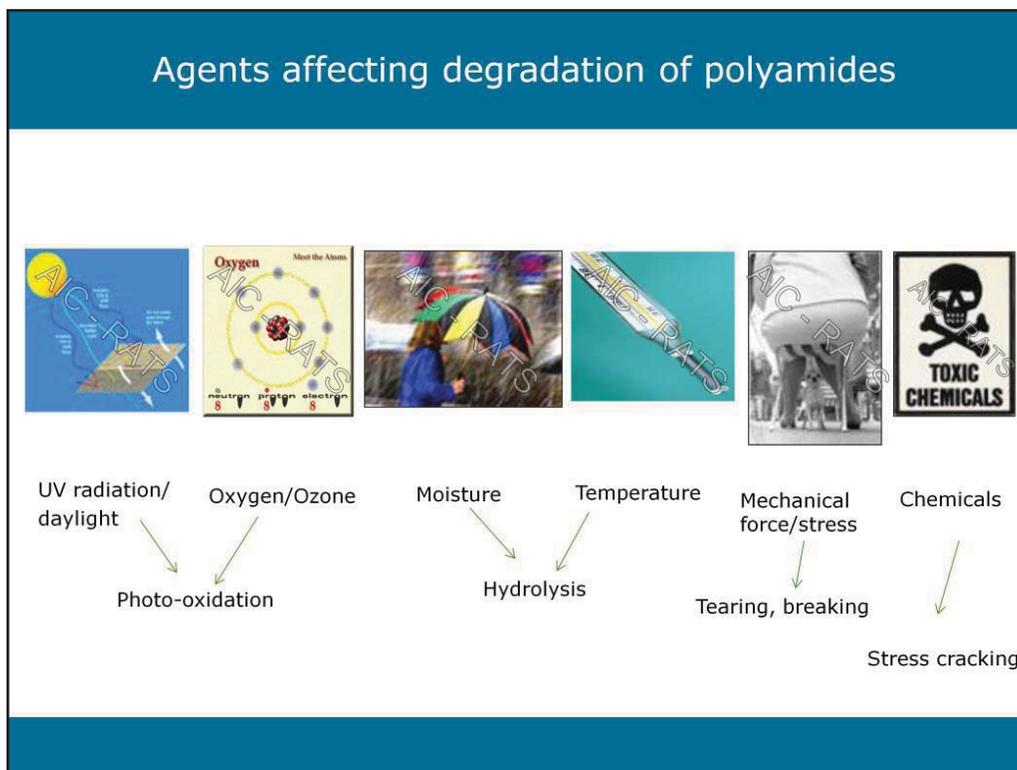
There are many types of nylon such as nylon 6, nylon 66, nylon 6/66, nylon 6/9, nylon 6/10, nylon 6,12, nylon 11 and nylon 12. Some of them (nylon 6, nylon 11 and nylon 12) are synthesized using totally from renewable feedstock. Others, including nylon 6,10, nylon 6,12 etc, are made from partly from renewable feedstock. Most types of nylon are semi-crystalline rigid materials with good thermal properties and chemical resistance. Different types have slightly different properties. Most of the nylon types can be used at elevated temperatures as they have high melting points (Mp). Some examples are: nylon polyamide 6 (polycaprolactam) Mp 220 °C, nylon polyamide 6,6, (polyhexamethylenadipamide) Mp 255 °C, nylon 6,10, (polyhexamethylene sebacamide) Mp 185 °C.

## Biobased plastics



The manufacturing of biobased (renewable) plastic products is the same as for the traditional fuel based plastics

Renewable nylons are easy to process, most processing technologies such as extrusion, extrusion-blow molding, and injection molding that are normally used for processing nylon objects made from petroleum based feedstock can also be used for renewable nylons. The polyamide matrix accommodates countless additives and filling agents, such as plasticizers, stabilizers, colorants, lubricants, impact modifiers, glass fiber, carbon fiber, etc.



Preventive conservation may be defined as activities that limit the rate and extent of degradation of materials by implementing procedures for storage, exhibition, packing and transport. In practice, preventive conservation involves limiting artefacts' exposure to factors which cause degradation including (day) light, UV-radiation, oxygen and ozone, heat, stress imparted in the object, chemicals, solvents, contaminants and additives such as filling materials.

## ‘Milly’s Maserati’ and ‘Garden of Delight’ by Madeleine Berkhemer

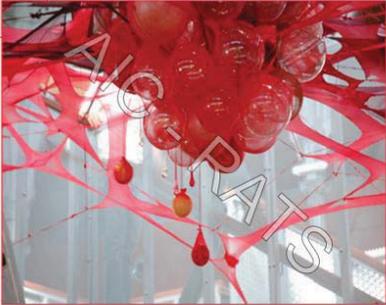
Inventory of problems with nylon objects

State of the art conservation research

Contact industry and artist

Set up research; artificial ageing and consolidation

Fulfill research in collaboration with students of University (conservators)



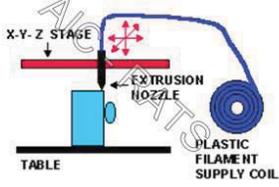
Conservation includes the role and context of an object being treated; in the case of contemporary works of art and design this includes the artist’s and designer’s views on the object and how he or she intended it to look and to behave.

The artist Madeleine Berkhemer lives and works in Rotterdam. She creates erotically charged work, and her sculptures, drawings and performances are defined by the heterogeneity of its materials and styles. They are investigations of the dimensions of time and space and radical examinations of social and economic conditions. The artist’s installations include nylon panty hose tied around objects such as this racing car in ‘Milly’s Maserati’. The stress imparted in the nylon panty hose due to this wrapping might subject the material to accelerated ageing. Moreover, the environment in which the installation is displayed is affecting the museum life of the object. To prolong the lives of these works of art, research into the consolidation possibilities has been set up at RCE, in close collaboration with the artist herself.

The research includes; inventory into problems with nylon, an artist’s interview, obtaining samples of the artist’s materials, contacting the nylon manufacturing industry, heat and light ageing of nylon test samples under stress, the search for protective coatings for nylon, application of the coating on nylon test samples, heat and light ageing of the consolidated test samples and evaluation of results, dissemination of the results.

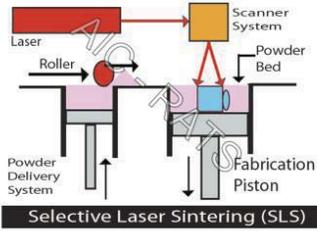
### 3D rapid prototyping

#### Fused Deposition Modeling



The diagram shows a plastic filament supply coil on the right, connected to an extrusion nozzle. The nozzle is mounted on an X-Y-Z stage above a table. The nozzle is extruding a filament that is being deposited onto the table to form a 3D object.

#### Selective Laser Sintering



The diagram shows a laser beam directed at a powder bed. A roller moves the powder bed, and a fabrication piston moves the powder bed up and down. A scanner system is positioned above the powder bed. The process is labeled as Selective Laser Sintering (SLS).

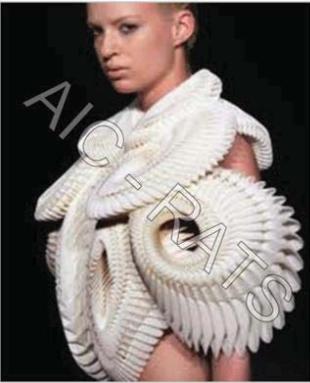


Bracelets: Peggy Bannenberg

Fused Deposition Modelling (FDM) is a production method in which a plastic filament is unwound from a coil to an extrusion nozzle. The nozzle is heated to melt the material and can be moved in both horizontal and vertical directions by a numerically controlled mechanism, directly controlled by a computer-aided manufacturing (CAM) software package.

Selective Laser Sintering (SLS) is a production method in which small particles of solid material (nylon 12) are melted together by a laser in any desired shape (3D).

## Iris van Herpen



[http://www.youtube.com/watch?v=HEdQpWk5qmw&list=UUAckDMoOuEM9\\_Ur0RrAvIkQ](http://www.youtube.com/watch?v=HEdQpWk5qmw&list=UUAckDMoOuEM9_Ur0RrAvIkQ)

Iris van Herpen, A Dutch designer creates dresses using 3D rapid prototyping. On the screen are dresses of the collection Escapism, Look 11 from 2011. Polyamide 12 was used and the technique is laser sintering using 3D rapid prototyping by the Company Materialise in Belgium.



Nowadays more and more polyamide (nylon) objects are be designed and created using 3D rapid prototyping. Jewellery, vases and other design objects made by these rapid prototyping techniques such as the snotty vases of Marcel Wanders are currently highly collectible.

Coryza, Influenza, Ozaena, Pollinos and Sinusitus consist of a collection of 5 different vases (15 x 15 x 15 cm). The designs are based on 3D scans of airborne snot and produced using a digital prototyping technology. The collection of 5 airborne snotty vases has recently been purchased by the Stedelijk Museum in Amsterdam. Moreover, the Arts Institute of Chicago and SF MOMA also have these snotty vases.

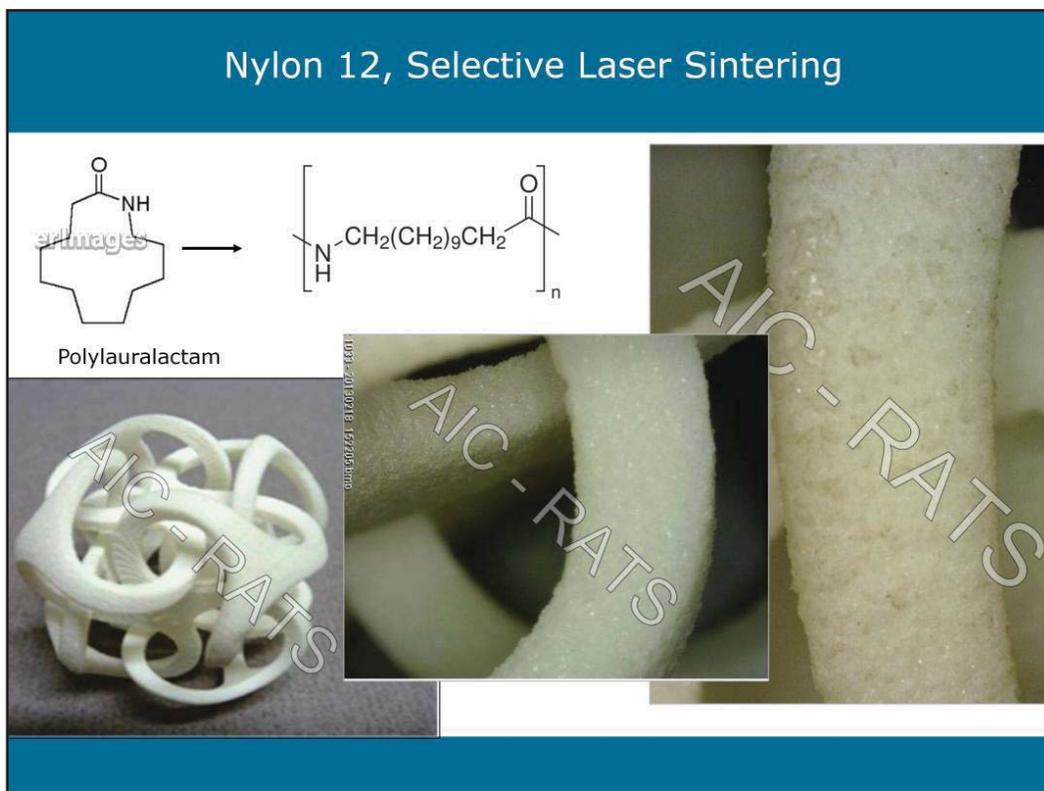
Protocols for the conservation of these objects are have not been established and therefore, the conservation treatment of broken 3D rapid prototyped nylon snotty vase by Marcel Wanders proved to be a challenge

Read more: <http://www.dwell.com/articles/profiles-marcel-wanders.html#ixzz25xOwMLev>  
<http://www.youtube.com/watch?v=FJ8TCLHAv90>



Making and remaking objects using SLS requires quality control of materials and processes. The properties such as density and crystallinity of a material should be controlled and the same for all batches used. These properties depend upon the geometry of the object, the sinter location, the sinter orientation and the powder used (nylon).

‘If you do the same, you get the same (if you know what you do) ‘is the Statement of Materialise Company.



At RCE, investigations have been made to observe the behavior of some 3D rapid prototyped nylon objects under the influence of changes in light, RH and temperature in order to set up guidelines for the care and preventive conservation of nylon 3D rapid prototyped objects. Cleaning nylon objects is also part of the research. Cleaning a plastic object requires consideration of the highly specific nature of synthetic and semi-synthetic materials, and particularly their degradation pathways. When plastics degrades one deals with highly perishable materials that often display signs of ageing in the form of structural deformations, stiffening of the material and chromatic alterations.



From surveys in various countries it appeared that approximately 75% of collections require cleaning. Dirt on plastics most frequently comprises oily materials from handling and use prior to collection and particulates from air. Because plastics are good electrical insulators, they hold dust via static electricity. In addition, soiling may be present at surfaces as a result of degradation processes. Phthalate plasticisers migrate to surfaces of PVC with time and hydrolyse slowly to produce white crystals of phthalic acid or anhydride. If not removed, these can contaminate other objects or packing materials. Cleaning is also necessary to remove stains, spots and residues, whether they are degradation products or arise from an external cause ([www.popart.mnhn.fr](http://www.popart.mnhn.fr) and [www.popart-highlights.mnhn.fr](http://www.popart-highlights.mnhn.fr))

Cleaning involves the removal of every substance located at the substrate-environment interface of an object, which causes damage to its materiality or meaning, and which has neither been applied intentionally by its creator nor is a sign of its historical use (Bollard 2007, 2008). Cleaning techniques can be divided into mechanical and chemical. Mechanical cleaning comprises the use of cloths, brushes, sponges, pressurised gas or particles to physically push or suck dirt away from surfaces. Mechanical cleaning of plastics is problematic as most exhibit poor resistance to abrasion.



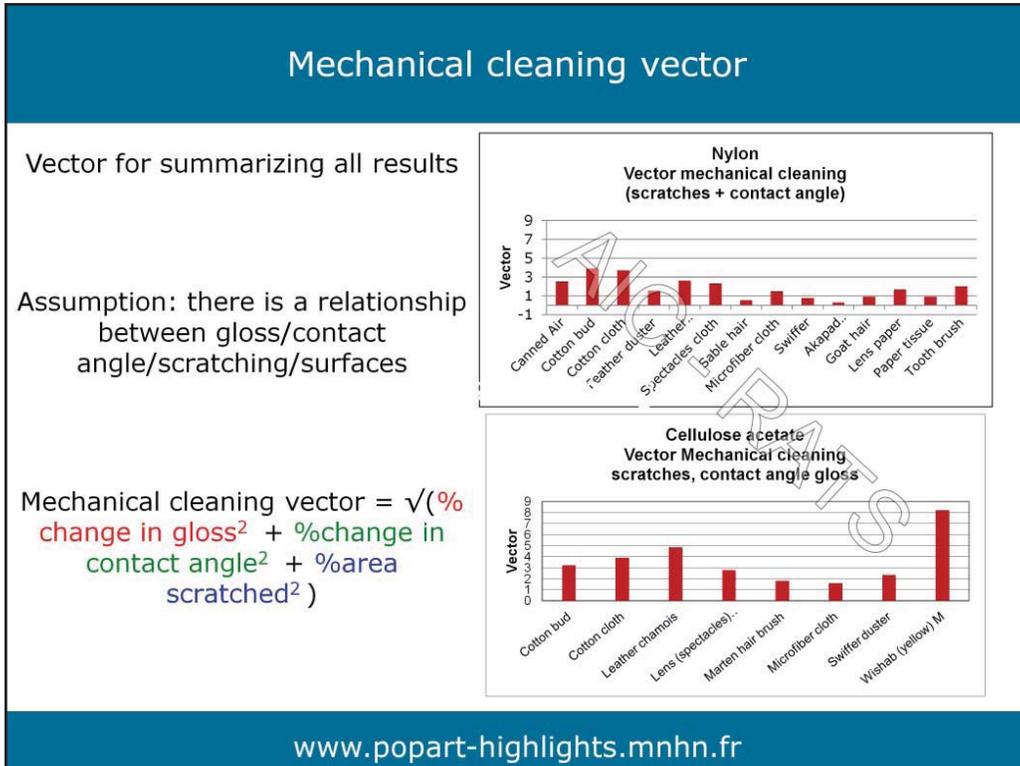
Scratches are areas with higher reactivity than their surroundings and are therefore more vulnerable to chain scission, reduction in tensile strength and permanent damage. In addition to a loss of physical properties, the presence of scratches changes the light reflecting properties of surfaces, resulting in a loss of gloss.

The percentage of area covered with scratches was calculated for each type of plastic and cleaning procedure. Photomicrographs of surfaces at 25x magnification were examined for scratches and coloured falsely using the image manipulation program Adobe Photoshop® at a line width of two units. Images were converted to black and white with Image-J free computer software ([www.rsbweb.nih.gov/ij](http://www.rsbweb.nih.gov/ij)) and the binary threshold feature used to calculate the percentage area scratched. The process was repeated in two areas and an average value calculated.

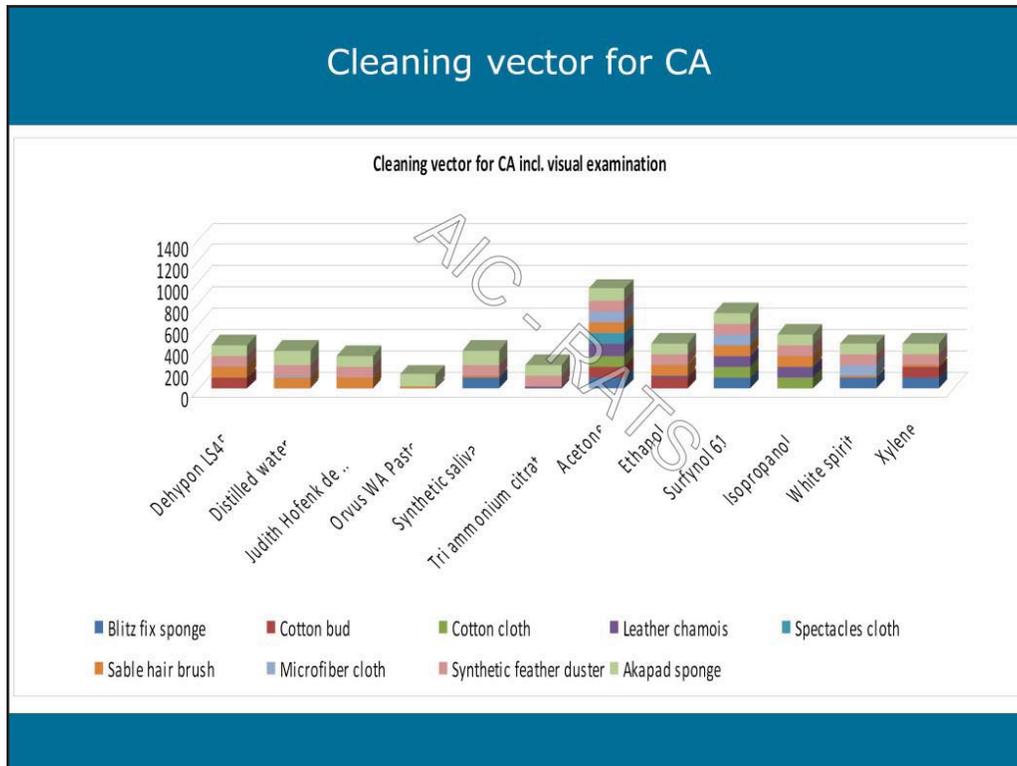
Contact angles give information about the surface energy (tension) and the polarity of a material. Surface tension is defined as the force per unit length exerted by a surface. The contact angle is the angle a drop of liquid makes with a solid surface. The contact angle is specific for any given system. If the liquid is very strongly attracted to the solid surface (for example water on a strongly hydrophilic solid such as paper) the droplet will completely spread across the solid surface and the contact angle will be close to  $0^\circ$ . Less strongly hydrophilic solids will have a contact angle up to  $90^\circ$ . If the solid surface is hydrophobic, the contact angle will be greater than  $90^\circ$ . Changes in surface energies of model plastics induced by cleaning were likely to be caused either by contamination from residues of cleaning agents or by surface.

Contact angles were made in triplicate and the mean angle calculated.

Gloss of test substrates before and after cleaning was determined using a Minolta multi-gloss 268 reflectometer.



Vector M does not take into account the results of visual examination.



The cleaning of cellulose acetate (CA) was performed by RCE for the POPART project and the results are to be seen on the screen. For nylon this cleaning vector has to be calculated, as the Gloss meter broke and the results are not fully available yet.

## Ongoing research

All cleaning actions and visual observations after cleaning will result in a fact sheet for the mechanical cleaning tools and aqueous- and solvent cleaning for nylon.

Nylon 3 D rapid prototyped objects will serve as dummies for the best tools and solvents (best cleaning treatment)

Research into the effectiveness of a protective coating for nylon objects under stress will be presented in San Francisco (NATCC2013)



The ongoing research will include the fact sheet of how to clean nylon. Moreover, future work will focus on the protection of nylon objects, such as the party hose in the work of Madeleine Berkhemer, and several consolidants containing anti-oxidants will be investigated.

## Acknowledgements

The Samuel H. Kress Foundation

Madeleine Berkhemer, Rotterdam, [www.madeleineberkhemer.com](http://www.madeleineberkhemer.com)

Materialise, Dr. T. Roels, Leuven, Belgium, [www.materialise.com](http://www.materialise.com)

Peggy Bannenberg, Amsterdam [www.peggybannenberg.nl](http://www.peggybannenberg.nl)

Sandra Weerdenburg/Netta Krumperman, Stedelijk Museum Amsterdam



*Thank you for your attention*

The following people are thanked:

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Madeleine Berkhemer, Rotterdam, [www.madeleineberkhemer.com](http://www.madeleineberkhemer.com)

Materialise, Dr. T. Roels, Leuven, Belgium, [www.materialise.com](http://www.materialise.com)

Peggy Bannenberg, Amsterdam [www.peggybannenberg.nl](http://www.peggybannenberg.nl)

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# Non-destructive Identification of Polymeric Binder Degradation in Audio and Video Tapes

[Eric M. Breitung](#)<sup>1</sup>, Samantha Skelton<sup>1,2</sup>, Juan Rodriguez<sup>1</sup>, Lu Zhang<sup>2</sup>, Brianna Cassidy<sup>2</sup>,  
Peter Alyea<sup>1</sup>, and Stephen L. Morgan<sup>2</sup>

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1 June 2013



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Presented at the RATS session

41st Annual Meeting of

The American Institute for Conservation of Historic and Artistic Works (AIC)

Indianapolis, In, May 29-June 1, 2013



# Non-destructive Identification of Polymeric Binder Degradation in Audio and Video Tapes

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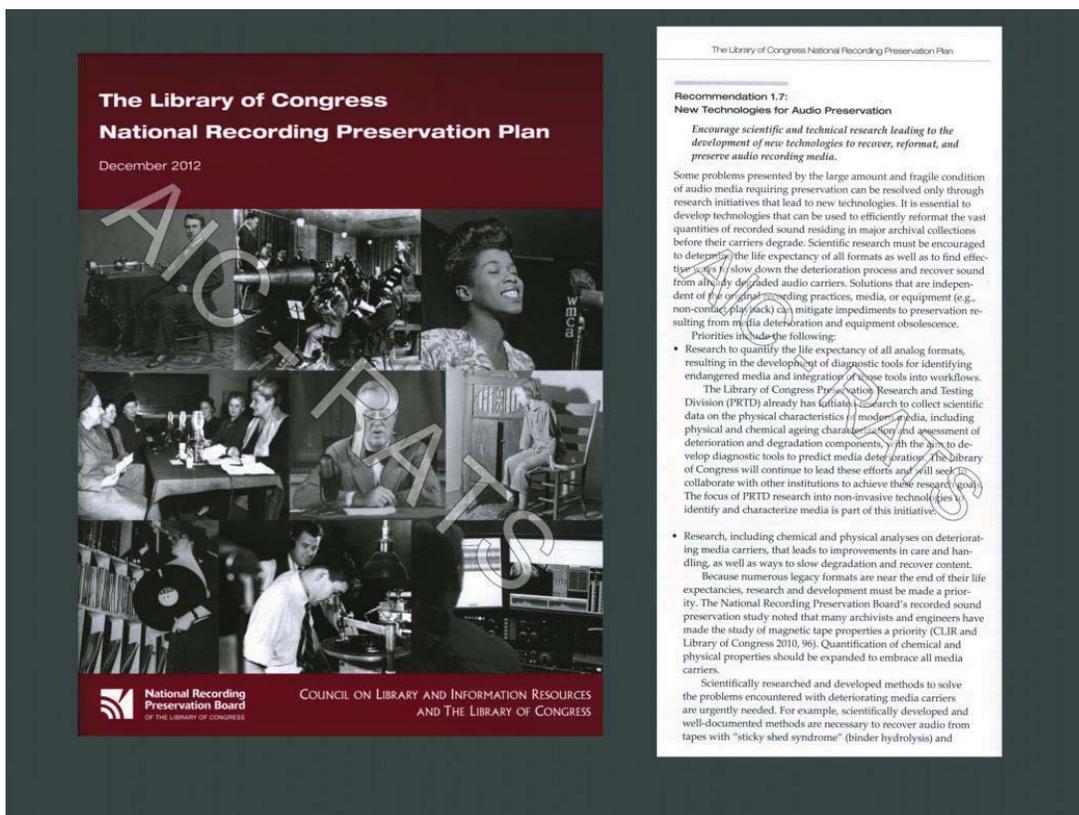
<sup>1</sup>Preservation Research and Testing Division, Library of Congress  
Washington, DC, 20540, [ebre@loc.gov](mailto:ebre@loc.gov)

<sup>2</sup>Department of Chemistry and Biochemistry, University of South Carolina  
Columbia, SC 29208, [morgansl@mailbox.sc.edu](mailto:morgansl@mailbox.sc.edu)

1 June 2013



Eric Breitung reports on an Institute of Museum and Library Services (IMLS) funded project that is a collaborative effort between the Library of Congress and the University of South Carolina. This presentation is an update to the work presented at the 2012 AIC annual meeting.



The Library of Congress recently published a report along with the Council on Library and Information Resources that discusses a broad plan suggesting needed action for the preservation of both audio and video recordings.

## THE NEED

### Cultural Heritage Index (U.S.)

- 46 million tapes  
(reel to reel, VHS, DAT, cassette, etc.)
- >40% in unknown condition

### Current evaluation methods:

- Visual inspection
- Playing (potentially destructive)
- If the tape squeals, flakes, breaks, or sticks to playback equipment, it is removed and treated. This process may render the playback device unusable until it is cleaned and can permanently damage the tape, which leads to loss of data.



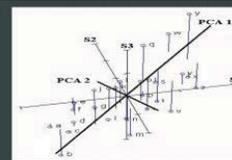
A reliable, non-destructive identification system is not available

The Cultural Heritage Index is a survey of U.S.-based cultural heritage institutions. This report indicated that the number of magnetic tapes held in the U.S. is about 46 million and that greater than 40% of them are in unknown condition. While many institutions are working to digitize their magnetic tape recordings, the process is hampered by degraded tapes, which tend to foul recording equipment with sometimes sticky polymeric material. This slows the digitization process, as the playback equipment must be cleaned thoroughly before another tape can be transferred. It also has the potential to permanently damage the tape through the removal of magnetic material onto the guides and heads of the player (image on slide). Because of these issues, a reliable, non-destructive identification system is needed to triage tapes prior to mounting and playback. This will increase efficiency and limit the loss of often unique recordings.

We propose the use of attenuated total reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) along with multivariate statistical analysis as a non-destructive and fast method for the assessment of magnetic tape.



## RESEARCH GOALS



Can infrared spectroscopy, combined with decision-making algorithms based on multivariate statistical analysis, predict the degradation state of magnetic tapes?

Can appropriate IR measurements be performed non-destructively and harmlessly on magnetic tapes without requiring extensive specialized training or expertise?

Is the test system applicable to audio and visual materials with equal success?

## Is ATR SAMPLING NON-DESTRUCTIVE?

**FTIR-ATR crystals tested include:**  
Germanium (Spectra Tech. - STI Thunderdome)  
Zinc-selenide (Harrick Sci. Prod. Inc. - Fast IR)  
Diamond (Thermo Electron Corp. - Smart Orbit, Pike Tech. - Gladiator)

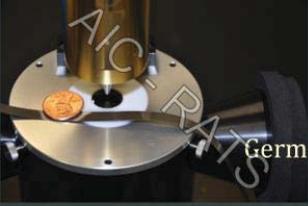
**Compression methods tested:**  
Weights (1 kg, 500 g, 200 g)  
Various clutch systems  
Plate system

- Aluminum & Stainless Steel
- Various thicknesses
- 1-3 stacked plates

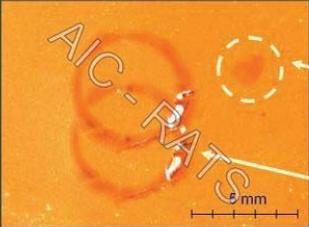
Larger crystals were the least invasive



Diamond



Germanium

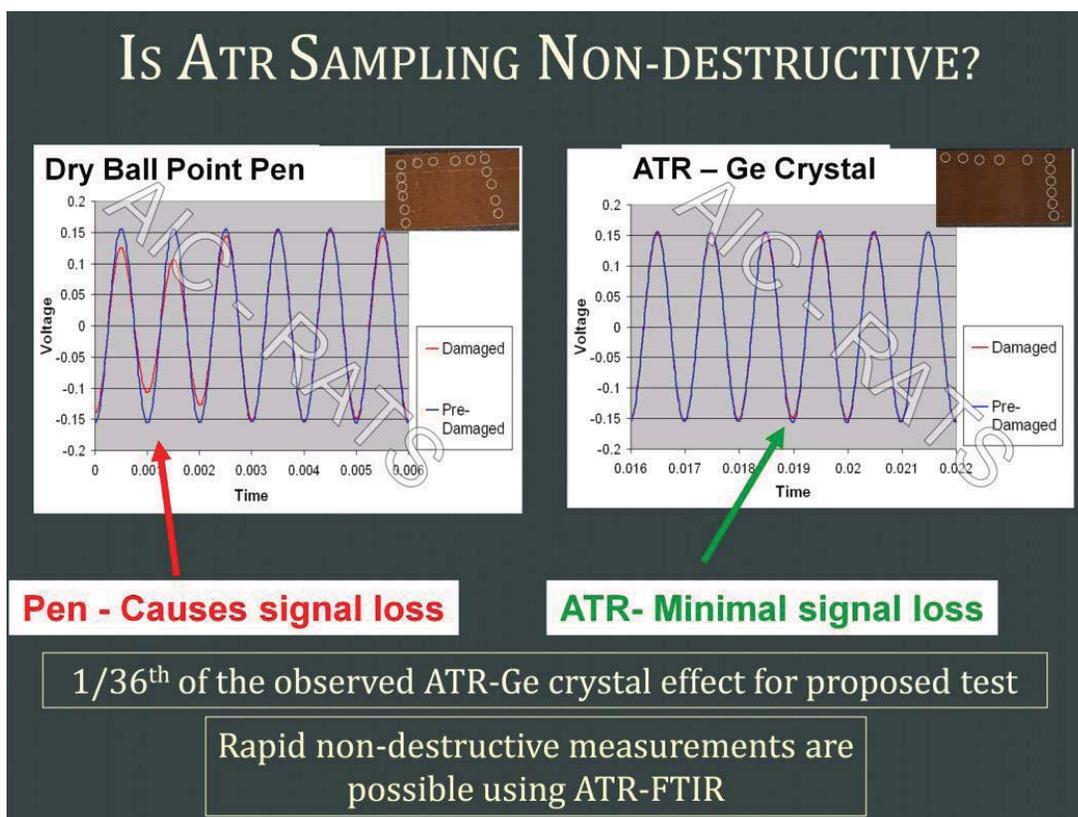


Germanium (steel, Mylar)

Diamond (no plates)

Four ATR accessories were tested for their ability to produce reproducible spectra and minimize damage to the tape being tested.

We found that the larger crystals (ZnSe and Ge), because the area in contact was flat and did not have a transition from crystal to metal plate (as the diamond does) were the least destructive. The picture in the bottom right are extreme versions of the test, where the diamond was used bare – with no plates to diffuse the force from the compression pin. Less damage is possible when using diamond, however, a dent from the transition gap between the diamond and metal plate that surrounds was unavoidable. The larger crystals did not dent the tape, and the smudge left when using a steel plate over a piece of Mylar™ above the tape to diffuse the force from the compression pin was less than 2 mm in diameter and often removable with isopropanol and a cotton swab..



Fidelity testing was completed by Juan Jimenez and Peter Alyea to determine whether the ATR method would result in loss of signal or distortion. A test tone was pre-recorded on a piece of new ¼" magnetic tape. A small area was indented using the tip of a dry ball point pen making a 5x6 grid over the full width of the tape. Similarly, the ATR was pressed on the tape using the steel and mylar pressure dispersion method also in a 5x6 grid over the full width of the tape. The tape was played back using the same machine that recorded it, and the signal was digitized. The chart shows the output signal over the damaged area. Note that this area is 29 times larger than the area needed to assess a tape as degraded or not. We increased the number of contact points from 1 to 30 to make it possible to detect changes to the signal. Note also that the amount of time covered in the chart is 0.006 seconds, and the damage effects a fraction of that.

The ball point pen demonstrates severe damage, where divots are formed in the tape, which should lead to an increase in the distance between the tape and the read head and a loss of signal intensity (loudness). This is shown in the upper left plot. The ATR shows a non-perfect overlay of the pre and post-damaged areas, however, the effect on the output signal is minimal and would be  $1/30^{\text{th}}$  of that shown for a single FTIR measurement. Based on these and the ATR test results, the ATR system does not damage the tape significantly.

## POLYESTER-URETHANE BINDER CHEMISTRY:

1970-1990's

- Polyester-urethane (PEU) main binder
- More than 20 others known
- Variety of other components
  - Lubricants, additives, plasticizers...

PEU is known to degrade at ester linkage

Degraded tapes often contain lower MM polymers chains than non-degraded

$$\begin{array}{c} \text{O} \\ \parallel \\ \sim\text{-C-OH} \end{array} + \text{HO-}\sim \rightleftharpoons \begin{array}{c} \text{O} \\ \parallel \\ \sim\text{-C-O-}\sim \end{array} + \text{water}$$

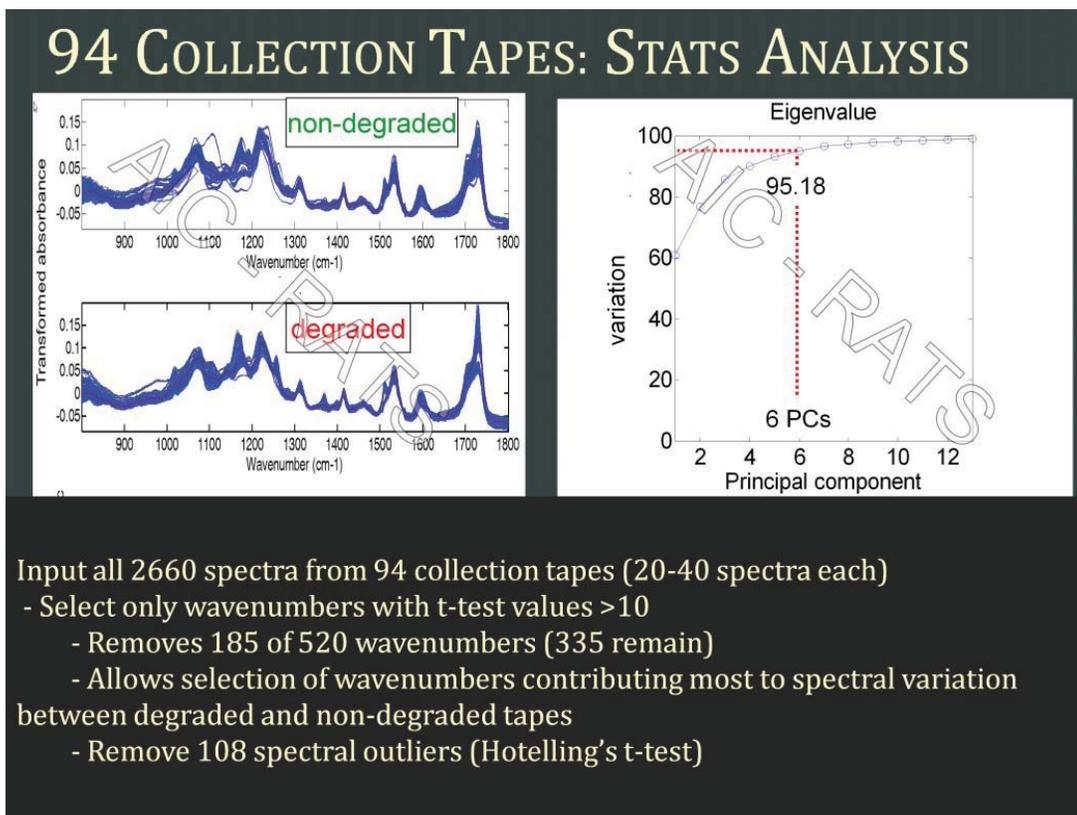
Carboxylic Acid      Alcohol      Ester

Degraded      Non-degraded

Organic binder breakdown believed to be main degradation pathway

Most tapes from the 1970-1990's contain polyester-urethane (PEU) binders. This study focuses on PEU binder containing tapes.

Degradation at the ester linkage is reversible, though cross-linking integrity is not guaranteed after a link is broken. Storage conditions that theoretically equalized the forward and reverse reaction were proposed in the 1970's, but tapes stored under those conditions were also found to degrade. The gel permeation chromatography data shown at the bottom of the slide shows a significant change in molar mass distribution of the binder between degraded and non-degraded, where lower molecular masses are present in the degraded tapes.



To assess our system, Samantha Morgan, now at the University of Delaware's conservation program collected, 2660 ATR-FTIR spectra from 94 PEU tapes. Multivariate statistical analysis included the following processes: spectral preprocessing using standard normal variate transform, mean centering, and feature selection after T-test assessment, and evaluation using principal component analysis (PCA) followed by linear discriminate analysis (LDA). In the case shown above, the data was grouped by the tape's degradation state, which is not accounted for during PCA and is used to improve separation of the groups during LDA.

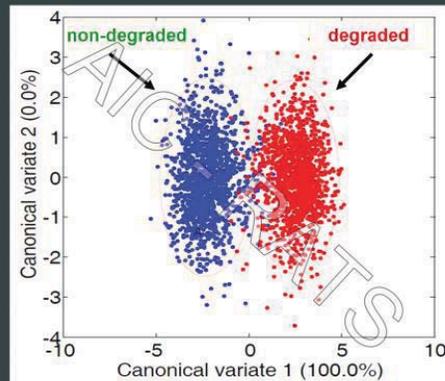
**REMOVING SPECTRA:** Hotelling's  $T^2$  values or Mahalanobis distances (the generalization of distance in multivariate data) measured for single samples from the center of group of samples can be employed diagnostically to recognize unusual samples (outliers) that deviate from the behavior of the remaining samples.

**REMOVING WAVELENGTHS:** Variables contributing to group separation can be identified by examining Student's  $t$ -tests for single variables at a time. These statistics measure the ability of each variable by itself to discriminate among the two groups.

A threshold value of  $t = 10$  (well above the Bonferroni-corrected critical  $t$  statistic) was used identify discriminating variables.

Deleting absorbance/wavenumber data having calculated  $t$ -values less than 10 resulted in removal of 185 wavenumbers and reduced the number of employed from 520 to 335.

## LDA CLASSIFICATION:



### Classification accuracy

2348/2552 = 92 %

### Classification error

204/2552 = 8 %

The blue cluster represents non-degraded tapes and the red cluster represents degraded tapes, as determined by sound engineer playback. The statistical analysis shows that these two clusters are not 100% separated – some overlap is observed, however, the number of spectra in the overlap region is dwarfed by the number of tapes represented by the non-overlapping regions. Using a leave one tape out analysis to assess the model, 92% of the 94 tapes correctly classify as degraded and non-degraded!

## IS THE DATASET BIASED TO THE LC COLLECTION?

### Select and evaluate tapes from other institutions

- Archives
  - National Public Radio (NPR)
  - New York University (NYU)
    - Moving Images Archiving and Preservation Program
- Libraries
  - Moving Image Research Center (MIRC)
    - University of South Carolina
  - Library of Congress (LC)
- Museums
  - Museum of Modern Art (MoMA)

NPR and two separate collections from LC  
to be assessed this summer

Because the 94 tapes were selected from the Library of Congress's collection, it is unclear whether the tape identification system will apply to other institution's collections. The LC holds many tapes that are transfer copies of other degraded media such as lacquered discs and wax rolls. We are establishing connections with other institutions and offered to assess their tapes to determine whether the model shown in the last slide is widely applicable.

## HOW REPRESENTATIVE IS THE DATASET?

### 40 Formulations reported to degrade

Agfa PEM-468, 469, 526
Ampex 373, 406, 407, 456, 457, 499, 2020
Audiotape/Capitol Q15
EMTEC SM911
Melody 169
Scotch/3M Classic, Master-XS, 175, 201, 250, 806-9, 908, 966, 967, Pro-206, 207, 226, 227, 808, 986
Sony - PR-150, FeCr, SLH, ULH-72-370-BL
TDK 150H

### Many others produced...

Likely both degraded and non-degraded

### 34 New Old Stock Makes/Models tested against 94 LC collection tapes

- 40 formulations reported to degrade
- 10 of 40 available from 'reported to degrade' list
- 10 of 10 tested by playing
- 8 of 10 of these determined to be 'degraded' by playing

Limited to donations of new old stock

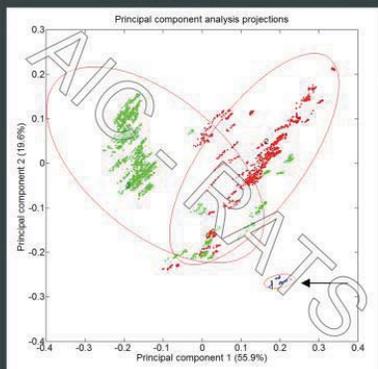
Because access to other institution's collections requires a portable spectrometer and coordination with collection managers, which we are in the process of acquiring, we began assessing the universality of the 94 tape database using non-recorded reference tapes. The Preservation Research and Testing Division of the LC holds 34 new old stock 1/4" tape types. These were evaluated using ATR-FTIR and playback on a vintage Scully 'winder', which is a Scully player with the play head removed. The 'reported to degrade' list shown is a collection of makes and models accumulated from web discussions and literature. Ten of the 34 tapes investigated were on the 'reported to degrade' list and 8 of these were categorized as degraded using the playback method.

## HOW REPRESENTATIVE IS THE DATASET?

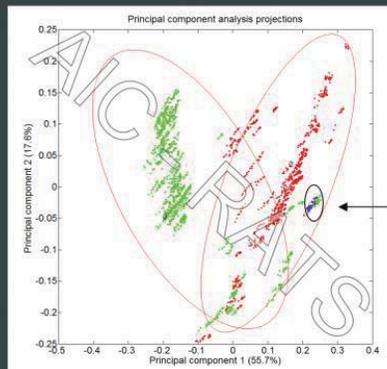
- 10 of 34 NOS types classify well to the 94 LC collection tapes

Ampex 406, Ampex 478, Ampex 632,  
Scotch 209, Scotch 227, Quantegy 632,  
Scotch 214, Scotch 208, Scotch 175, Scotch 212

**Does not Categorize with  
Collection**



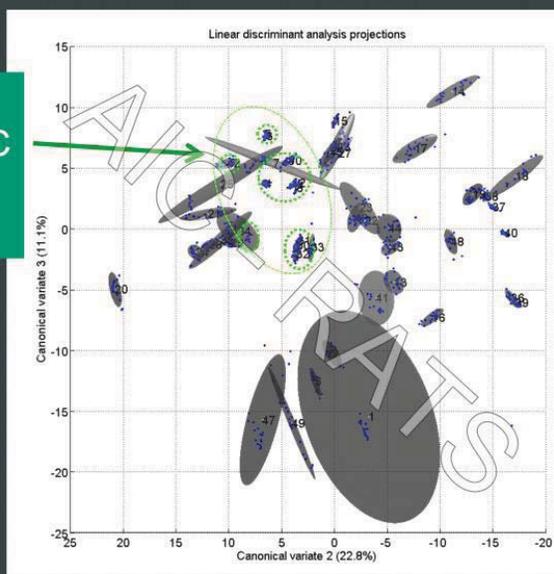
**Categorizes with Collection**



The 34 new old stock (NOS) tapes were individually assessed against the 94 collection tapes discussed in previous slides to determine how many of them might represent makes and models that are present in the LC dataset. The results indicated that 10 of the 34 NOS tapes classify well using PCA to the LC collection.

## HOW REPRESENTATIVE IS THE DATASET?

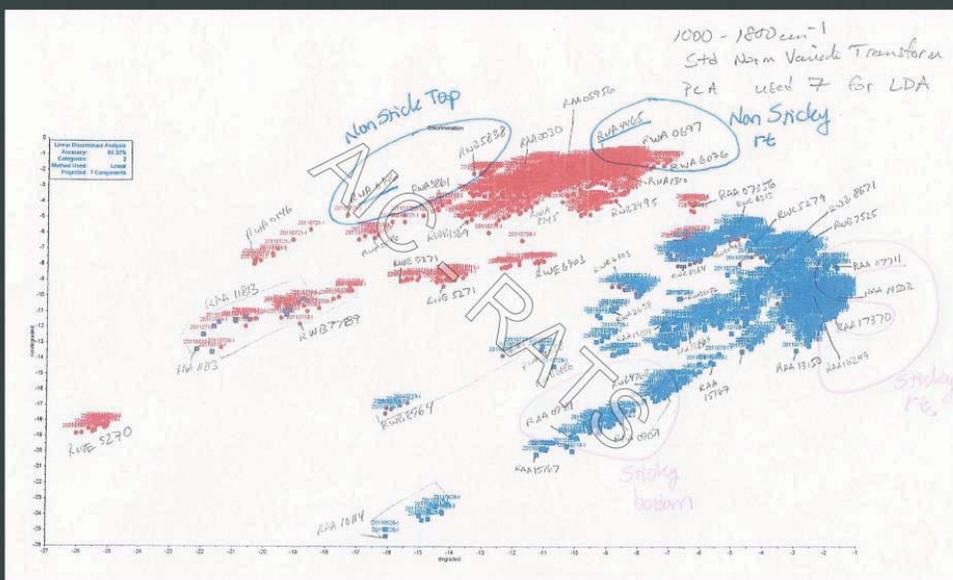
These correlate to LC collection tapes



The LC collection tape based dataset correlates well with ~30% of the on-hand reference makes & models.

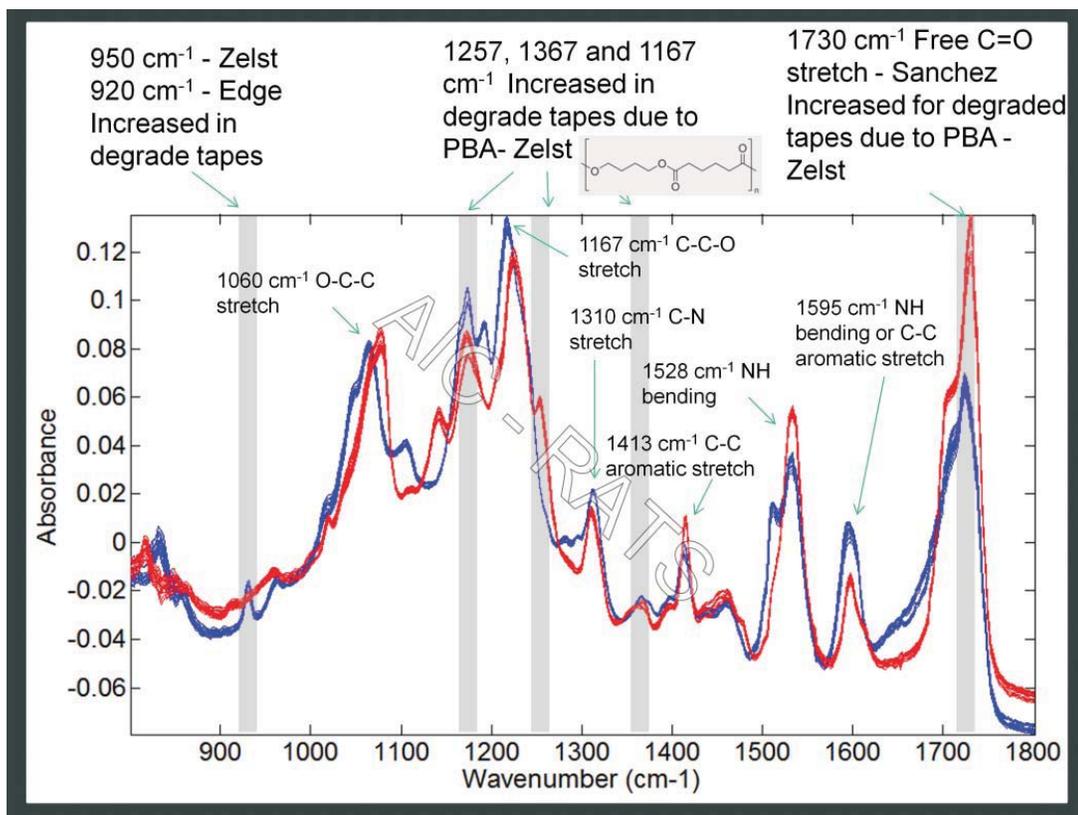
Comparing all 34 NOS tapes with each other, we observe significant variation. If there was little variation, all of the data would overlay in a small region. The ten tapes that correlate well with the LC collection tapes were shown to cluster in the small area in the upper left of the LDA plot. As time permits, we will investigate the chemical differences between the tapes that do and do not classify well with the LC collection.

## IDENTIFYING CHEMICAL DIFFERENCES:



- Can we correlate IR spectral differences to chemical changes?

Understanding the chemical differences between the degraded and non-degraded tapes within the LC collection will inform what IR wavelengths to focus on for differentiating and possibly improve our ability to safely store these materials. The plot shows a PCA analysis of the 94 collection tapes using the Unscrambler program, as our home grown software is unable to easily identify which data point is represented by a particular tape. The labels are tape names, and the circled areas are those tapes chosen for further chemical analysis. The axis are x, degraded, and y, non-degraded.

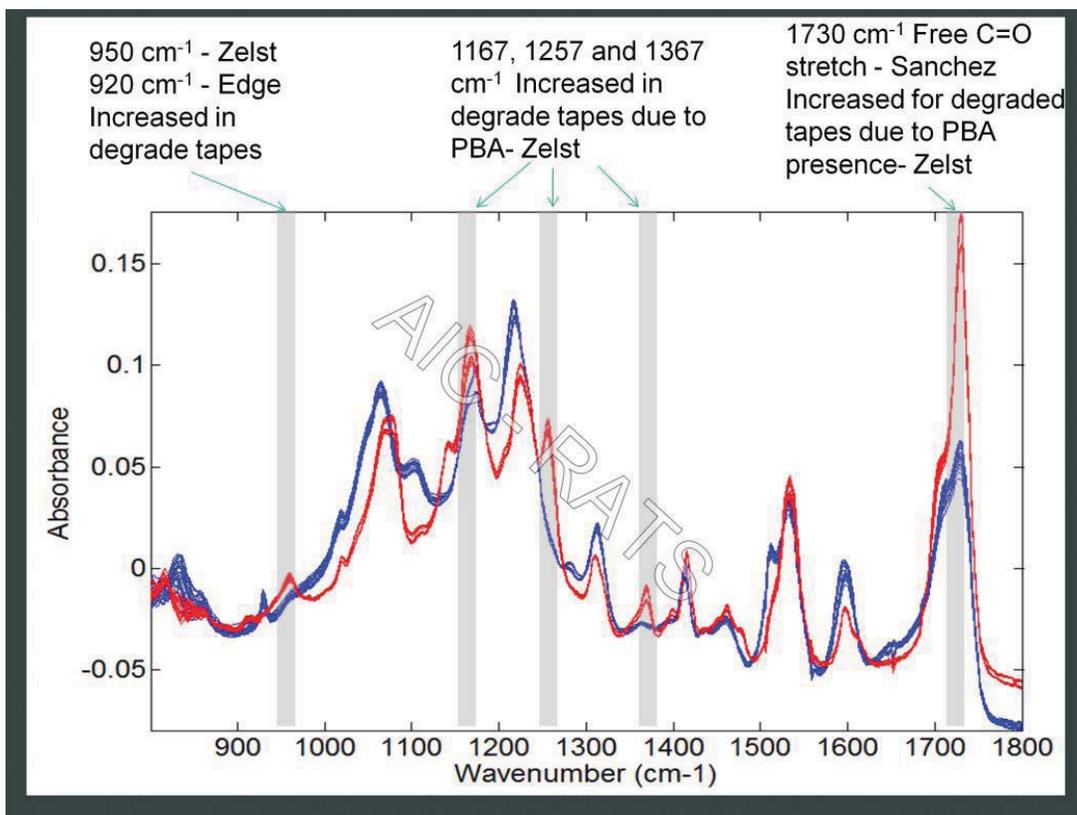


Assessment of degraded and non-degraded tapes comparing the circled areas from the PCA/LDA analysis on the previous slide shows that there are differences, however, because IR does not provide molecular information, it is difficult to suggest with certainty the chemical differences between degraded and non-degraded tapes, though some of the noted changes correlate well to the theory that hydrolysis is causing binder degradation.

Red are spectra from a degraded tape (RAA07711 – bottom right of slide 14’s plot).

Blue are spectra from non-degraded tape (RWA0146 – top left of slide 14’s plot).

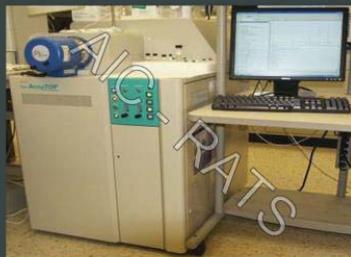
(Note there is an unintentional color mis-match between slide 14 and slides 15 and 16, where red does not always represent ‘degraded tape’ as it should.)



Red is RAA09071, a degraded tape from the bottom left of the plot in slide 14..

Blue is RWA4465, and non-degraded tape from the top right of the plot in slide 14.

## IDENTIFYING CHEMICAL DIFFERENCES:



IonSense DART-MS

- Neg. & pos. ion
- 275C ionized helium
- Time of flight detector
- Magnetic side of tape exposed to heat/ions



pyrolysis-GC/MS

- CDS 5150 pyroprobe
- 275C with helium
- UI-DB5 column
- quadrupole detector
- Magnetic side of tape only + TMAH

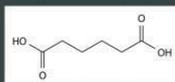
Both direct analysis in real time, time of flight mass spectrometry (DART-TOF-MS) and pyrolysis gas chromatography mass spectrometry (py-GC/MS) were used to assess tapes.

## IDENTIFYING CHEMICAL DIFFERENCES: DART-MS

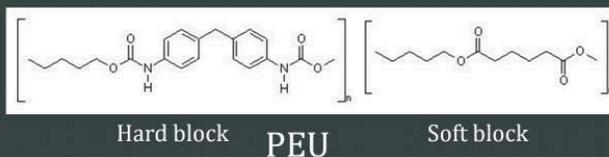
Make/model	Condition	Adipic	Azelaic	Lauric	Myristic	Palmitic
Scotch 227	Degraded	X		X		
Ampex 407	Degraded	X			X	X
Ampex 406	Non-degraded			X		X
Scotch 208	Non-degraded		X			

- Adipic acid associated with PEU break down (Theibaut, et al.)
- Azelaic acid, also a di-acid. Likely PEU break down
- Mono-acids are likely break down products of lubricants

Adipic



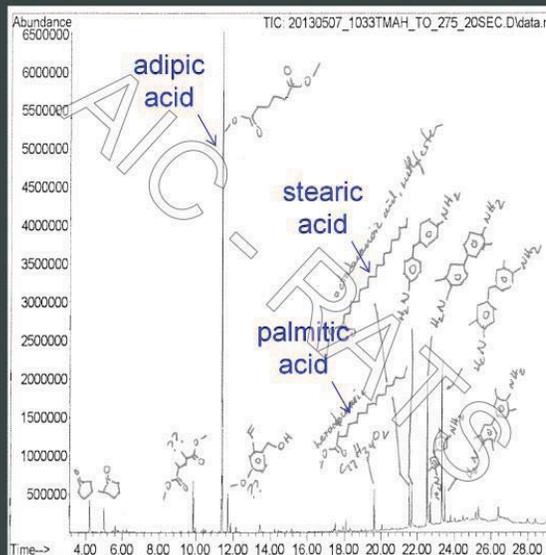
Azelaic



Preliminary DART-MS results indicate that PEU polymer break down products from degradation of the soft block are present only in the degraded tapes. Further assessment of other degraded and non-degraded tapes is necessary to confirm that other makes and models show similar chemical compositions.

## CHEMICAL COMPOSITION ( 1/4" ): PY-GC-MS

- Ampex 407
  - Sample 1033
  - Degraded
  - Adipic, myristic, palmitic acids found via DART-MS



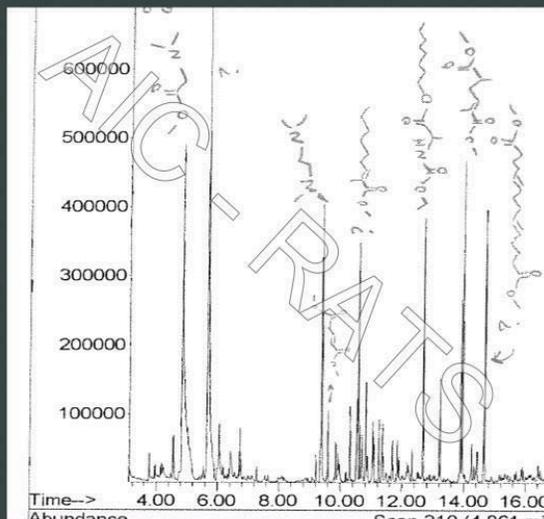
Mono- and di-acids confirmed

Pyrolysis GC/MS assessment, interestingly, shows both mono and di-acids in the degraded tapes. It also shows possible hard-block degradation as multiple di-amines are observed.

## CHEMICAL COMPOSITION ( 1/4" ): PY-GCMS

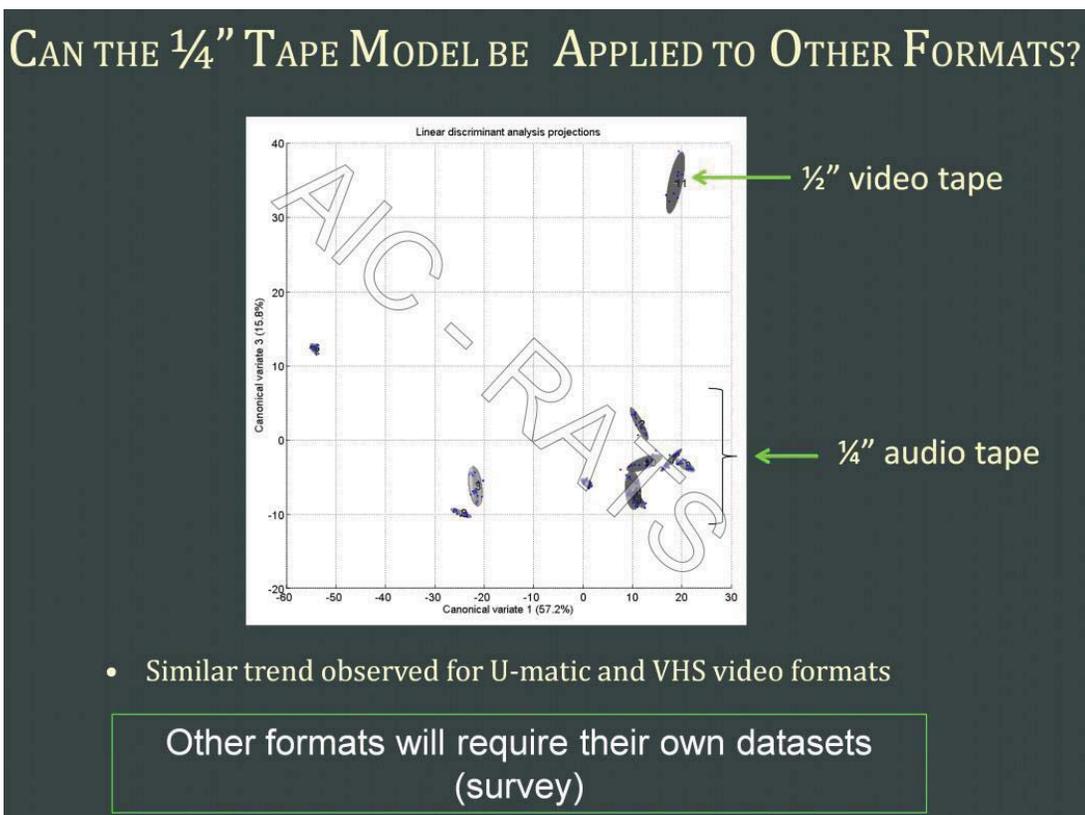
### ■ Scotch 227

- Sample 1184
- Degraded
- Adipic and Lauric acids found via DART-MS



**Adipic and lauric acids not found via py-GCMS**  
**Unsaturated di-acids identified via py-GCMS**

Interestingly, the DART-MS and pyrolysis data are not consistent. Further assessment of both methods is underway to understand the source of the issue. Preliminary data suggests that the transfer line in our CDS-pyroprobe pyrolizer is no longer inert, which is causing strong signals from unlikely small organic molecules such as the bis-dimethyl amine shown at 9 minutes in the chart above.



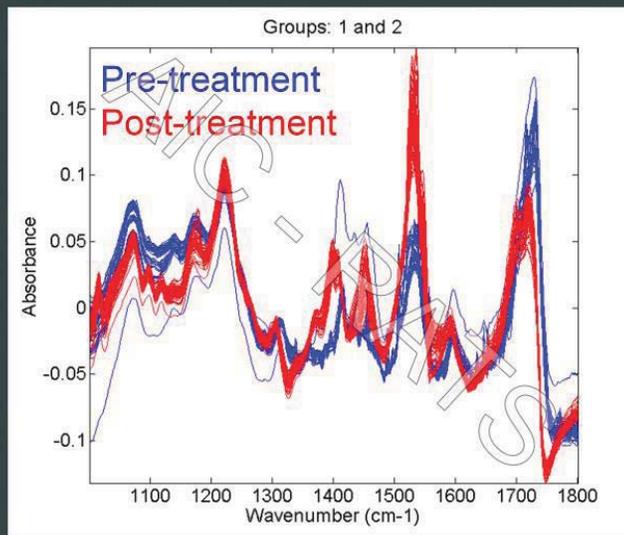
Several video formats were assessed and compared using multivariate statistical analysis with a small subset (10) of the audio tape's IR data. As the plot shows, the video tape data does not overlay or classify with the audio tape data. This may be due to differences in physical structure of the tapes (thickness, magnetic particle size...), which can significantly effect the FTIR baseline. Non-classification may also be due to chemical differences between audio and video tapes. Further investigation of video tape is underway to determine whether the system that allows classification of audio tapes can be applied to video if a full dataset of video infrared spectra is available.

An online survey is available for those interested in influencing what audio and video formats are the focus of our next rounds of testing. Please contact Eric Breitung to participate.

Eric Breitung's contact information: Library of Congress, Preservation Research and Testing Division, ebre@loc.gov , 202-707-3699

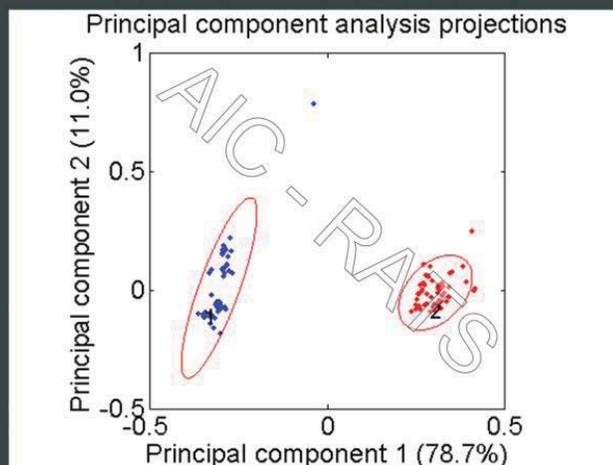
## HALF INCH VIDEO (1/2") : TREATED

- Sony 1/2" open reel
  - W. Forsberg (NYU)
  - M. Jimenez (NYU)
- 6 tapes
  - IR before treatment
    - 3 non-degraded
    - 3 degraded
  - IR after several weeks with silica gel desiccant



With colleagues from NYU, we also investigated how desiccation of 1/2" open reel video affects playback as well as whether the treatment is detectable by infrared spectroscopy.

## DESSICATED VIDEO (1/2") : ANALYSIS



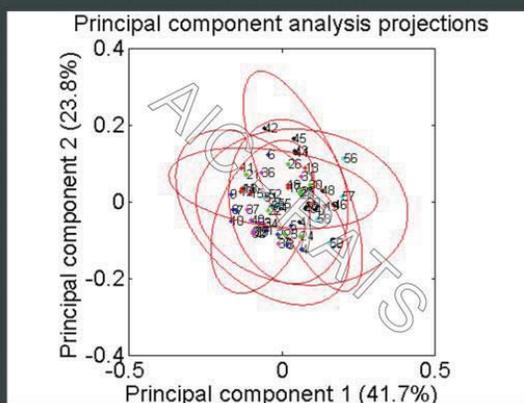
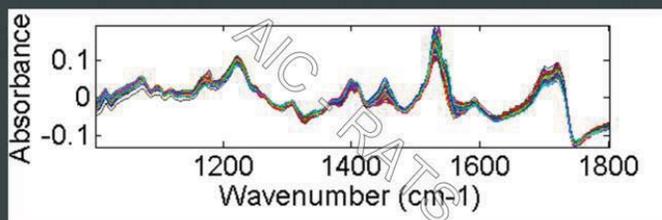
Post-treatment tapes do not correlate with pre-treatment tapes

The data showed that pre-treated tapes, regardless of degradation state, grouped together (blue), and the post-treated tapes grouped together or had similar IR spectra (red) regardless of degradation state.

## DESSICATED VIDEO (1/2") : ANALYSIS

- Sony 1/2" open reel
  - W. Forsberg (NYU)
  - M. Jimenez (NYU)
- 6 tapes
  - IR before treatment
    - 3 non-degraded
    - 3 degraded
  - IR after several weeks with silica gel desiccant
    - 1 remained degraded

No IR differentiation between degraded and non-degraded after treatment



With the current data pre-processing and multivariate statistical analysis, we were also unable to differentiate degraded and non-degraded tapes when looking at only pre-treated or only post-treated tapes. Further work is underway to understand whether the pre-play identification system is only valid for 1/4" audio tapes or whether different pre-processing and/or statistical analysis is necessary to differentiate the degraded and non-degraded tapes.

## FUTURE DIRECTIONS:

- Address other tape formats
  - Prioritize efforts by *surveying* other institutions (Help!!)
  - VHS, DAT, U-matic, etc.
- Correlate main spectroscopic differences to chemical changes within tape
  - More py-GCMS and DART-MS
- Increase reference tape collection
  - May be able to correlate tape brand to unknowns
- Automate software
  - Provide online database and automated software for public use
    - User uploads spectra and categorizes relative to PRTD database

## ACKNOWLEDGEMENTS:

### National Audio Video Conservation Center (LC)

Rebecca Jones

Larry Miller

William Halley

Mike Mashon

Gene Deanna

### NYU

Walter Forsberg

Mona Jimenez

### Audiophile Community

Many generous donors!

### Support

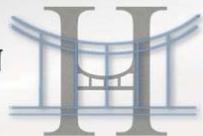
IMLS

LC





HERITAGE SCIENCE FOR CONSERVATION  
Building Bridges with Science & Industry for Heritage Collections



The Role of Polyester Film Encapsulation  
—With and Without Prior Deacidification—  
A Study Using  
Long-Term, Low-Temperature Accelerated Aging



Funded by The Andrew W. Mellon Foundation

William Minter<sup>1</sup> and John Baty<sup>2</sup>

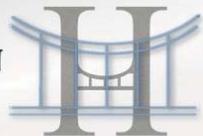
<sup>1</sup>Book Conservator in Private Practice, Woodbury, Pennsylvania, USA  
Former Senior Project Conservator, Heritage Science for Conservation program  
Johns Hopkins University

<sup>2</sup>Assistant Research Professor and Heritage Science for Conservation Scientist  
Departments of Materials Science and Engineering—Whiting School of Engineering  
and Conservation and Preservation—Sheridan Libraries and University Museums  
Johns Hopkins University

Presented at the RATS session  
41st Annual Meeting of  
The American Institute for Conservation of Historic and Artistic Works (AIC)  
Indianapolis, Indiana, USA, May 29–June 1, 2012



HERITAGE SCIENCE FOR CONSERVATION  
Building Bridges with Science & Industry for Heritage Collections



## The Role of Polyester Film Encapsulation —With and Without Prior Deacidification— A Study Using Long-Term, Low-Temperature Accelerated Aging

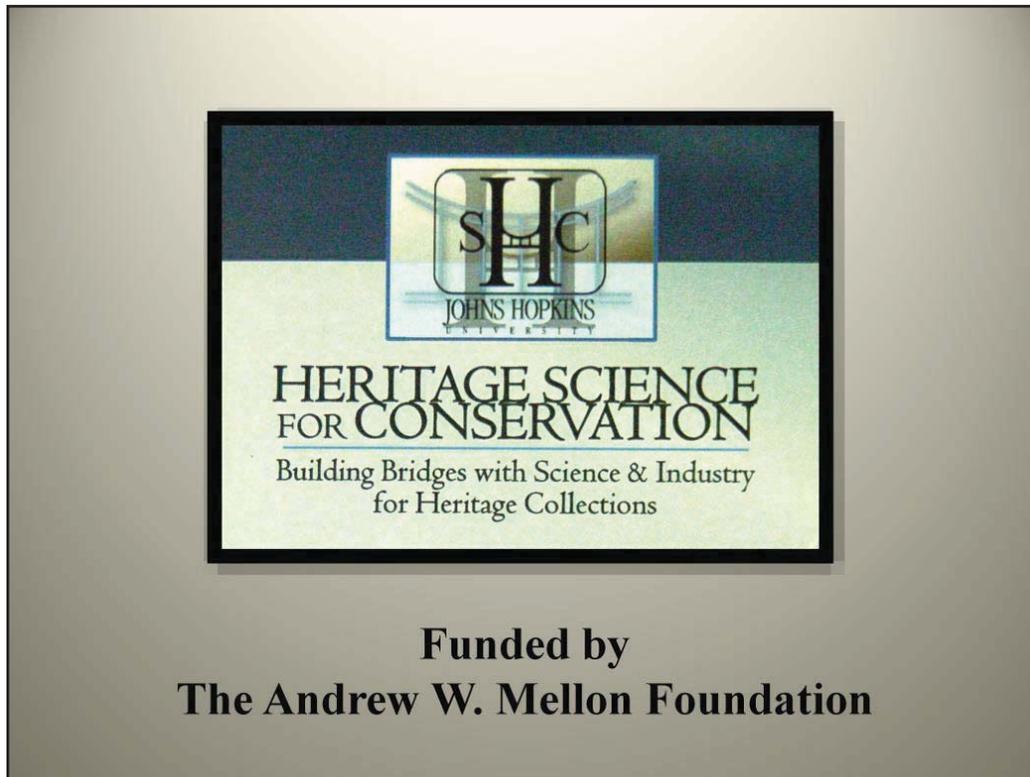


Funded by The Andrew W. Mellon Foundation



**Bill Minter, Conservator in Private Practice,  
former Senior Project Conservator, Heritage  
Science for Conservation, takes the lectern.**

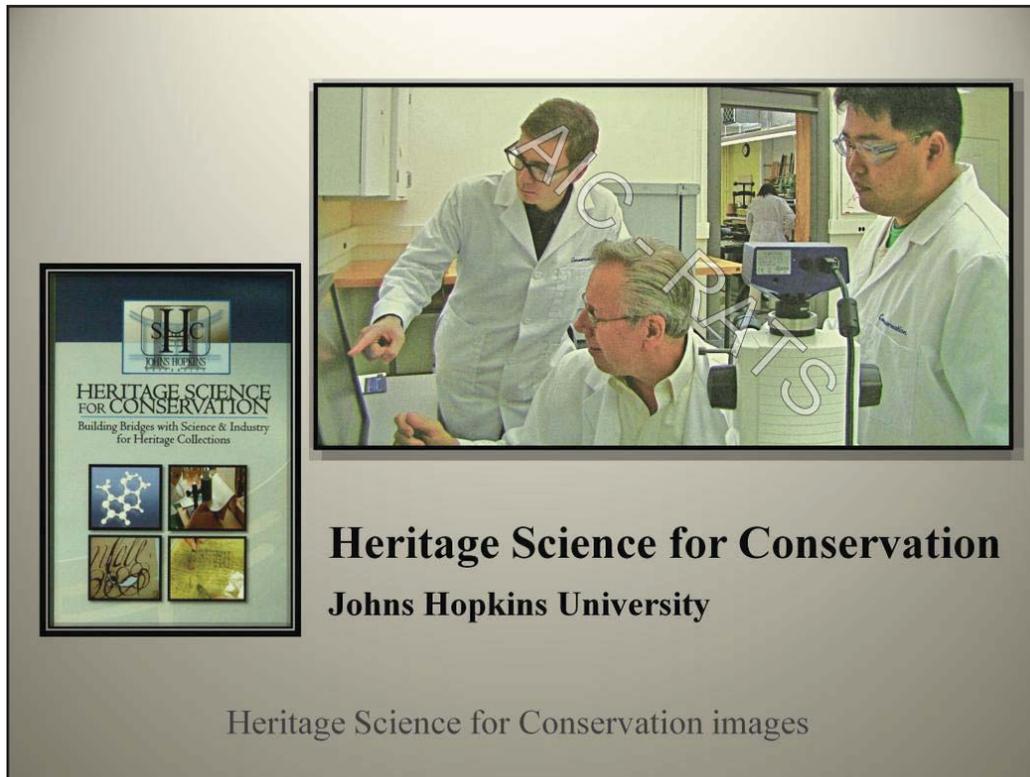
Bill Minter takes the lectern and begins with a statement: As a book conservator, the Heritage Science for Conservation project was a wonderful opportunity for me to work with great group of people in a unique setting of conservation and science.



In 2009, The Andrew W. Mellon Foundation provided funding for a three-year pilot project to bring conservation scientists and conservators together within the same working environment. The project was entitled Heritage Science for Conservation.

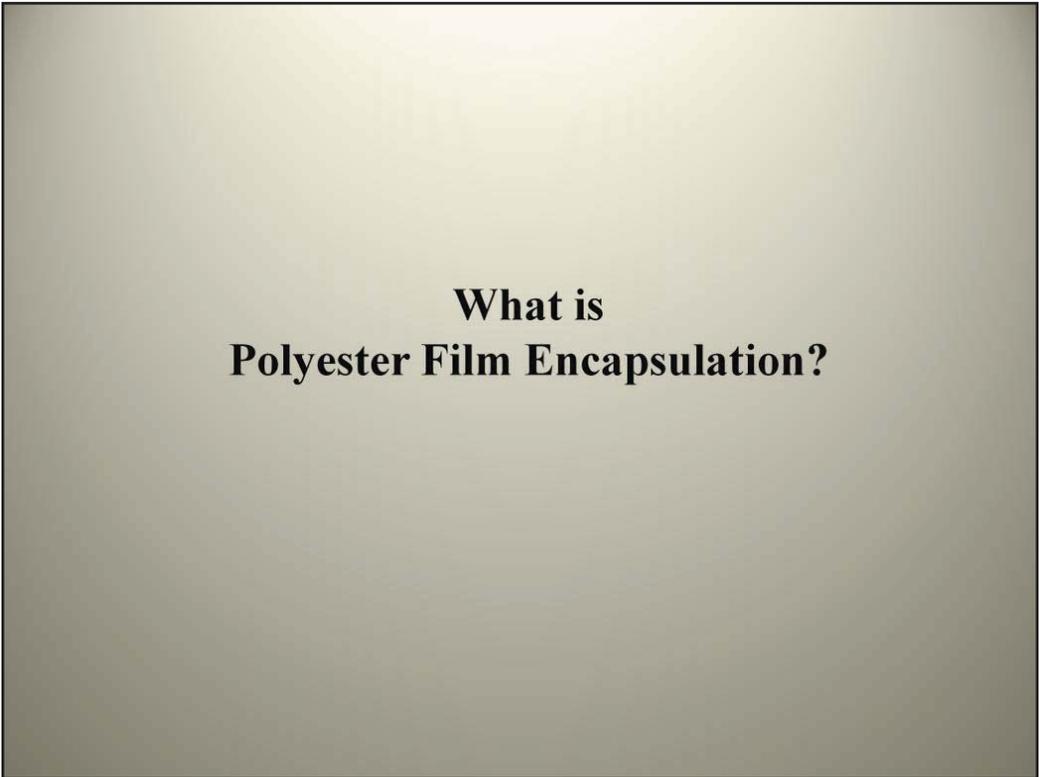
This slide shows the logo that we designed utilizing the “H” to form a bridge symbolizing the unique objectives of this project where we were building a bridge of understanding between our respective fields.

A lab was built from nothing where some basic equipment was purchased and other items were fabricated to meet our needs.



With two postdocs and a senior project conservator, we had a great team! The close working environment provided a wonderful opportunity to exchange a basic understanding of our respective fields.

The pilot project ended in 2011, but fortunately the project was renewed for another five years with new funding from The Mellon Foundation. In 2012, the project moved along with the whole Conservation and Preservation Department to a new space that now includes a TAPPI room for a climate controlled testing environment.



**What is  
Polyester Film Encapsulation?**

For those of you who may be unfamiliar with polyester film encapsulation as used in libraries and archives. . .

**Clear plastic envelope,  
sealed on one or more edges  
to support and protect  
a fragile and/or rare  
document.**

**Replaces Lamination!**

. . . polyester film encapsulation replaces lamination that had been a standard method for protecting paper in libraries and archives. Lamination was unacceptable due to potential problems from the adhesives and the future need to reverse that treatment.

## **Brittle Book Paper 1895 Encapsulated**

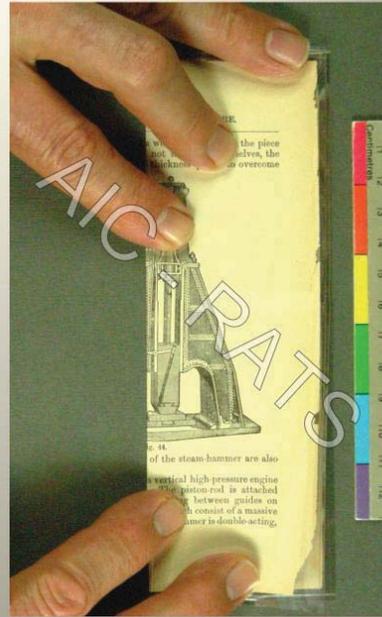
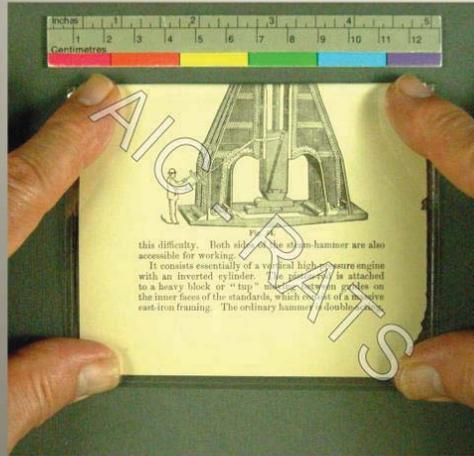
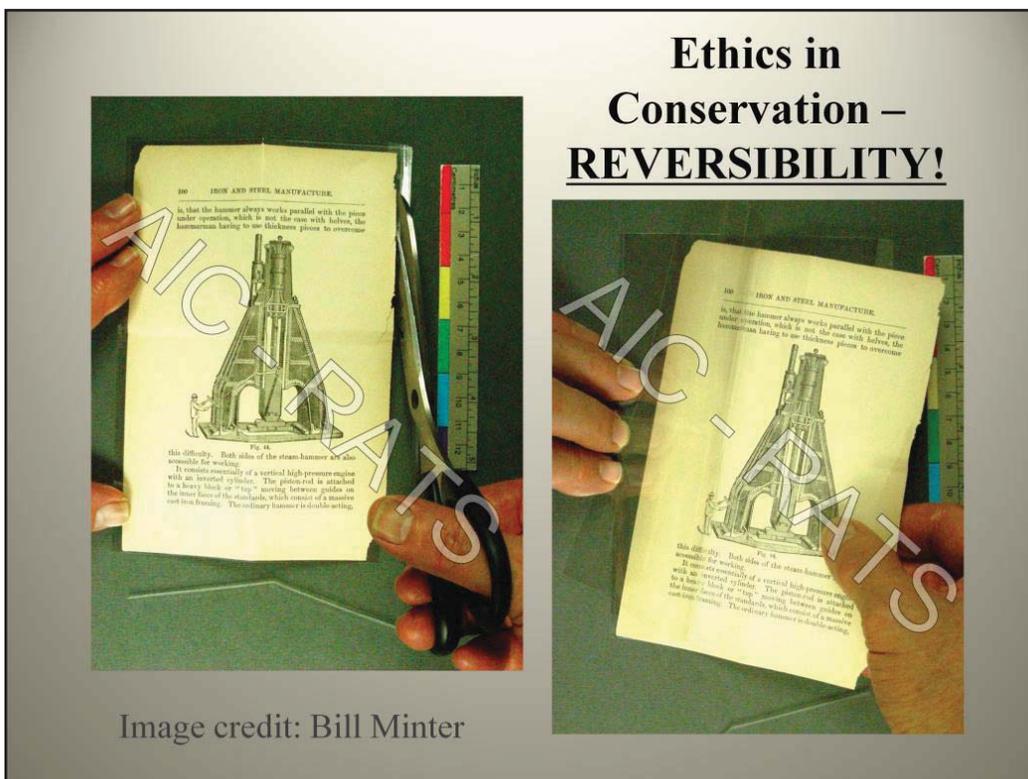
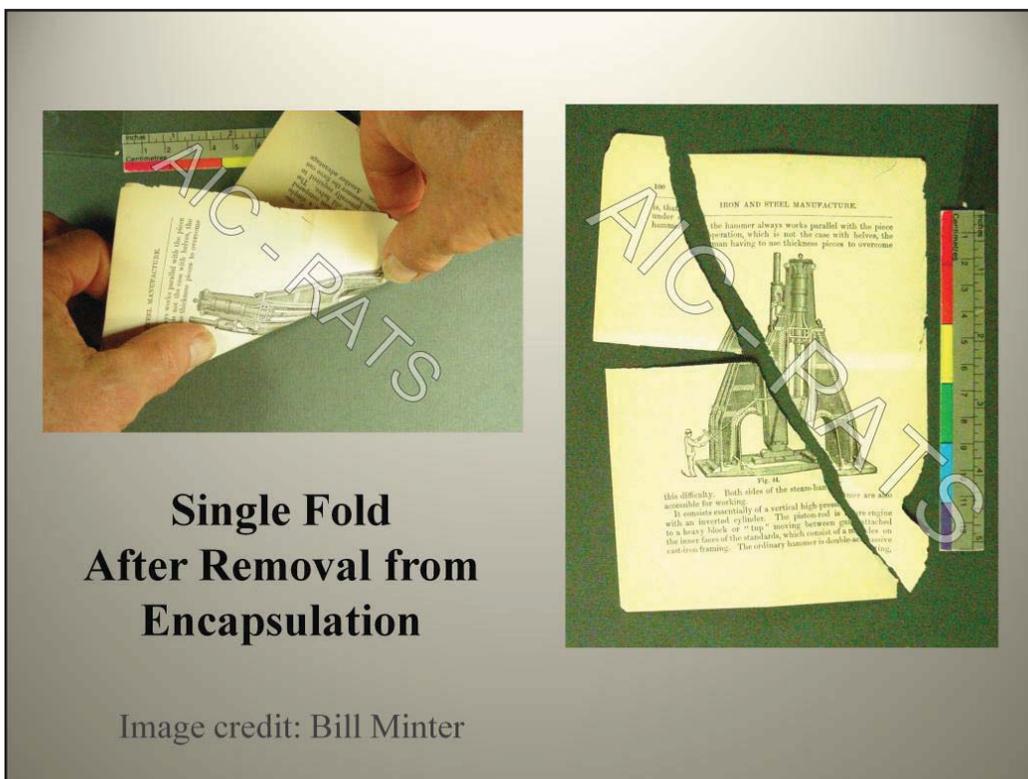


Image credit: Bill Minter

To illustrate the benefit of encapsulation, this sample of brittle paper has been placed between two sheets of polyester film where the four edges have been sealed. The paper is being folded in each image.



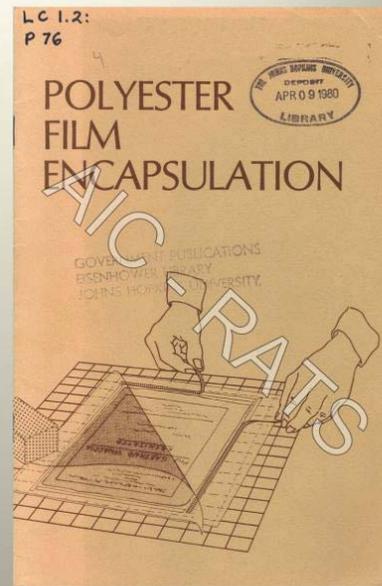
The true beauty of encapsulation is that the seal can be cut and the paper is easily removed, much like taking a letter from an envelope. This is a very good example of reversibility as desired in ethics of conservation.



In the image at left, the same brittle sheet of paper has been removed from the polyester film and is being folded once. The image at the right is the result of that single fold. Note that when the same brittle paper was encapsulated in polyester film it did not break, thus showing another benefit of encapsulation.

**Research by  
The Library of Congress:**

- **Deacidify paper  
before encapsulation**
- **IF NOT, the paper will  
deteriorate faster**



Library of Congress. Preservation Office, & Brown, M. R. (1980).  
*Polyester film encapsulation*. Washington: Library of Congress : for sale  
by the Supt. of Docs., U.S. Govt. Print. Off.

When encapsulation was developed in the 1970s by The Library of Congress, their research showed that paper should be deacidified prior to encapsulation. (Their 1980 summary pamphlet is depicted in this slide.) In subsequent work at Library of Congress conducted by Chandru Shahani on Springhill offset paper (an alum rosin sized bleached kraft book paper), it was suggested that encapsulation alone may accelerate the degradation of acidic paper, all else being equal. This full citation of this article is:

Shahani, C. J. "Accelerated Aging of Paper: Can It Really Foretell the Permanence of Paper." Preservation Research and Testing Series: no. 9503. Washington, DC: Preservation Directorate, Library of Congress, 2005. [Online]  
<http://www.loc.gov/preservation/resources/rt/AcceleratedAging.pdf>. Accessed 15 July 2013.

**Many institutions do not deacidify  
before encapsulation!**

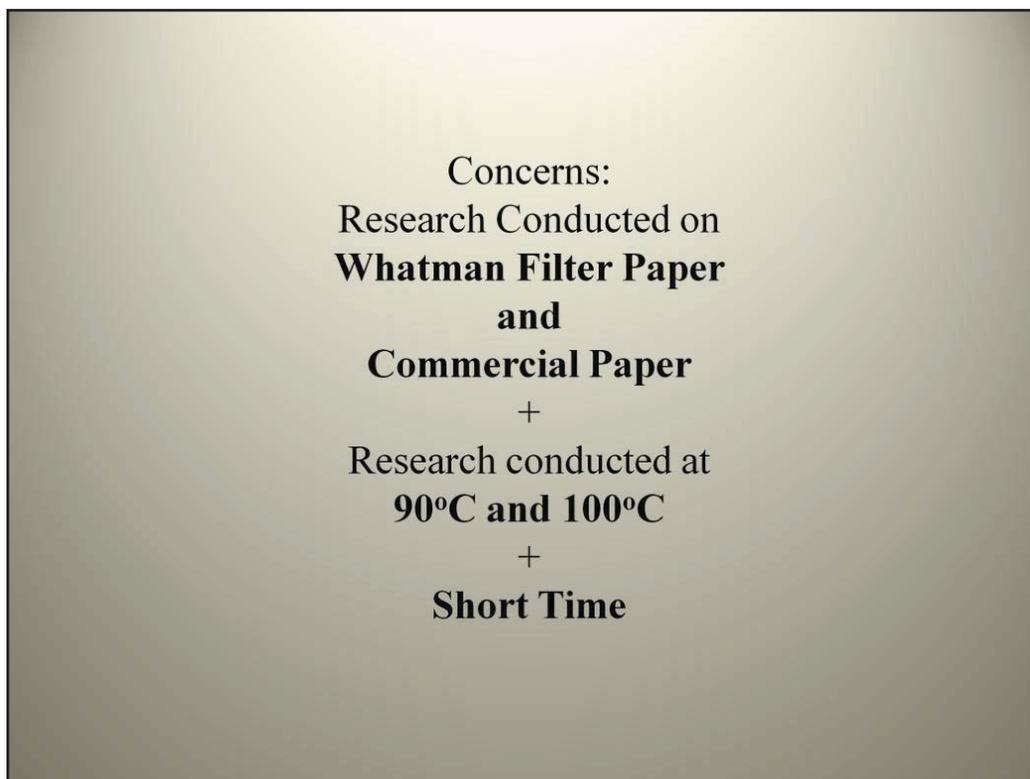
**If historic paper is not deacidified  
and is then encapsulated, how fast  
will it deteriorate?**

**2X, 4X, 10Xs???**

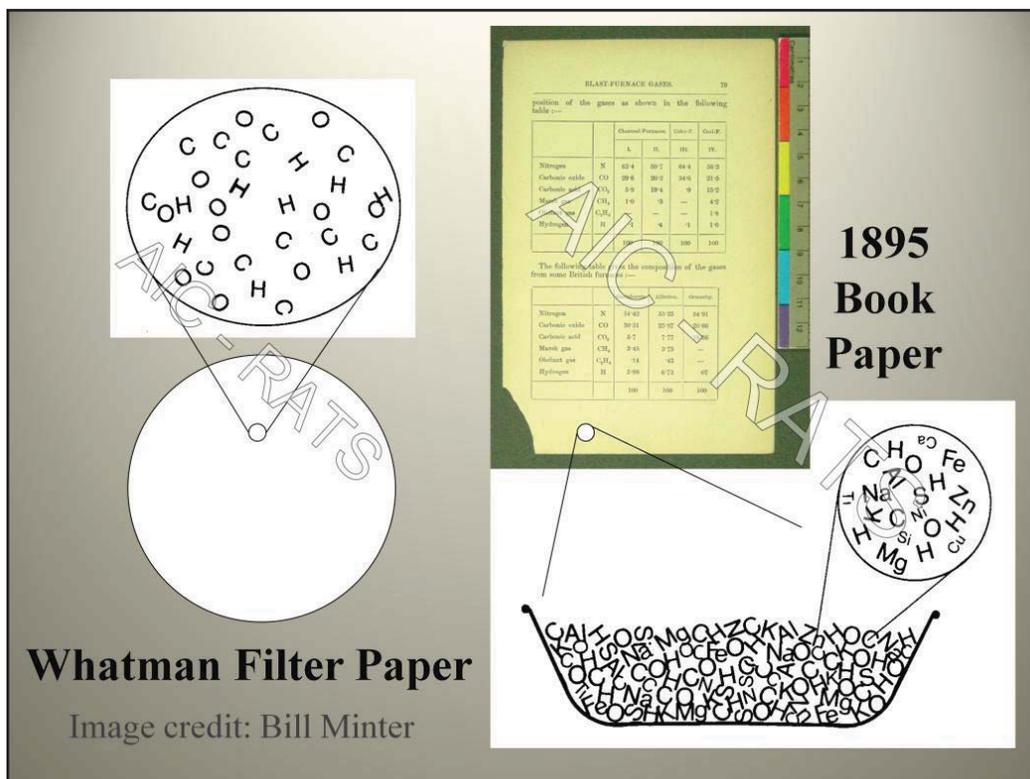
Unfortunately, many institutions do not deacidify because of a lack of the proper facilities, or in some instances because of institutional policy.

If documents are not deacidified, what are the potential problems?

This was a motivation for our research.



From a conservator's perspective, there are two concerns with previous research on paper aging: One concern is that Whatman filter paper has been used for most research. In the case of the work done by the Library of Congress cited above, the research was conducted on a relatively new commercial paper. Unfortunately, these samples do not represent the typical papers found in most libraries and archives. A second concern is that the samples were aged at relatively high temperatures for a very short period of time.



As a conservator, I fully understand the reasons for testing with Whatman Filter Paper. That paper has been well characterized, but nonetheless it is a cellulose paper made from just carbon, hydrogen and oxygen. However, in a typical library, conservators have to deal with a paper “soup” that is not only cellulose, but there are also varying amounts of other elements, including aluminum, iron, sulfur, potassium, and many others. As paper conservators, we need to understand the implications of our treatment on all of these various paper “soup” mixtures.

**What about Testing Vintage Papers  
at Lower Temperatures  
for a Longer Time?**

**And The Researchers Said ....**

**T/H Ovens – Cost**

As a book conservator, I have had a number of opportunities to speak with researchers about using vintage papers and aging the encapsulations at lower temperatures for longer time. One interesting reply was that: “longer aging cycles would tie up an aging oven for too long,” to which I replied “So what?”

From a conservator’s perspective, we assume that lower temperatures would allow for possibly a more realistic result. We do not need test results in one month. We would gladly wait for years if the results from using lower temperatures during a longer test would be more reliable.

At HSC, we purchased a high quality, temperature and humidity controlled oven at a cost of more than \$10,000. For this encapsulation study, we developed a special oven that will be described shortly. The cost was less than \$900.

## Four Vintage Papers – Made Before 1970

- Tested Positive for Alum
- Negative for Groundwood

**Onion Skin**

**L Rollins**

**M Sharp:**  
1970s; 25% Cotton

**Canadian Ledger:**  
1950s, ruled

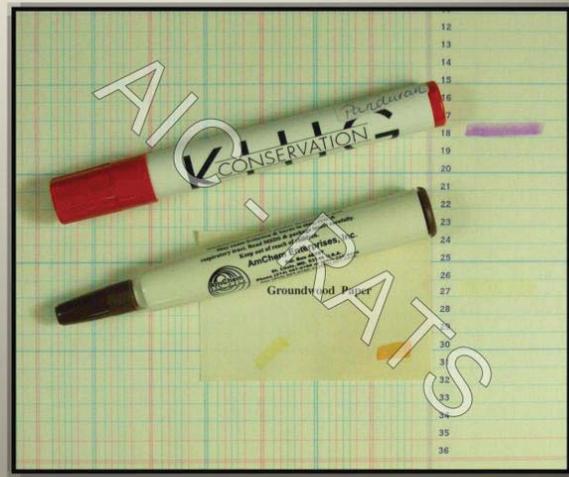


Image credit: Bill Minter

For our study we located four vintage papers that tested positive for alum. Alum is a common ingredient in most paper made from about 1850 until about 1970 and it is most likely responsible for most of the brittle paper found in libraries and archives.

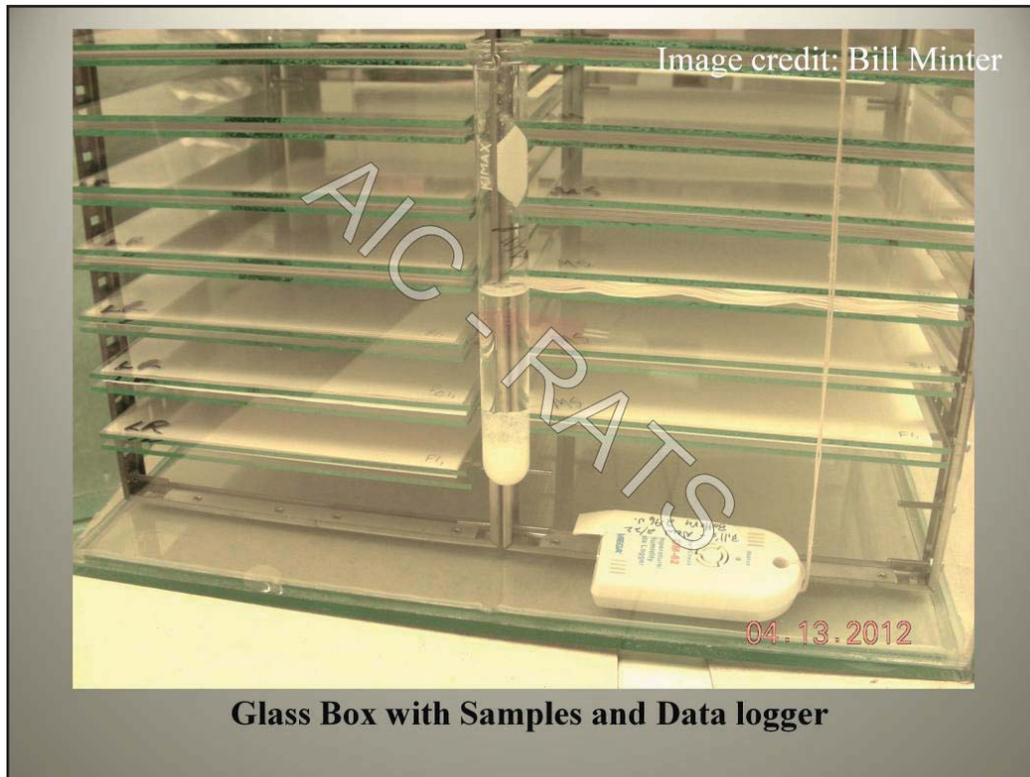
Unfortunately, these papers did not contain groundwood, though it would have been good to have tested a sample with groundwood.



While some of the paper was not treated and used as a control, a certain number of samples were washed and deacidified aqueously in a manner typical of many conservation labs.



Other samples of the similar paper were spray deacidified with the Bookkeeper solution --- a non-aqueous method. This is also a common method of deacidification found in many conservation labs.



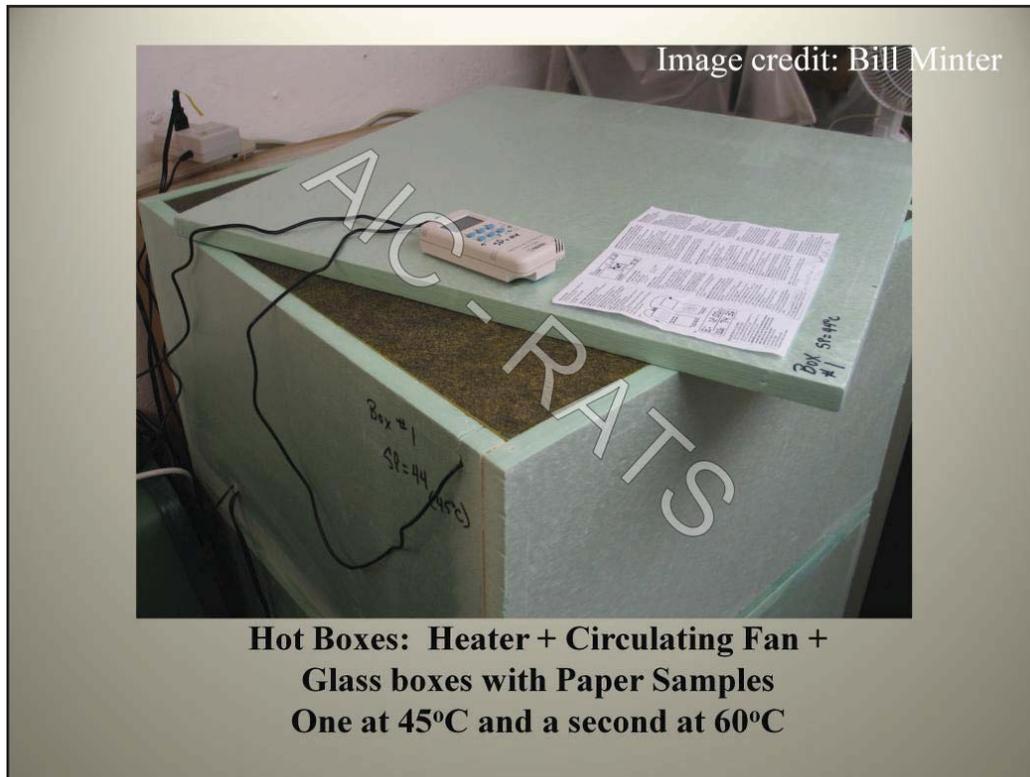
The various paper samples --- deacidified or not, encapsulated or not --- were stacked in a typical book format, between sheets of glass to avoid the influence of binder board and adhesives. The samples were placed in a sealed glass box that included a data logger.



To control the humidity inside the sealed glass box, there was a test tube filled with a saturated aqueous solution of sodium bromide --- 15g sodium bromide in 10 mL deionized water. Thus relative humidity was controlled in the box by the same technology that is often used to calibrate hygrometers.



The sealed glass boxes with samples were placed in custom-built, double-wall insulated “hot boxes.” In the space at the lower right is a heating element that was controlled by a thermostat. An additional small fan circulated the heat throughout the box to maintain a very stable temperature of 45°C in one box (at which the sodium bromide solution equilibrated the atmosphere to 51% RH) and 60°C in the other (which equilibrated to 50% RH).



One of two hot boxes with temperature controller.

---

**Temperature and Relative  
Humidity inside Glass Boxes  
Was Very Stable**

---

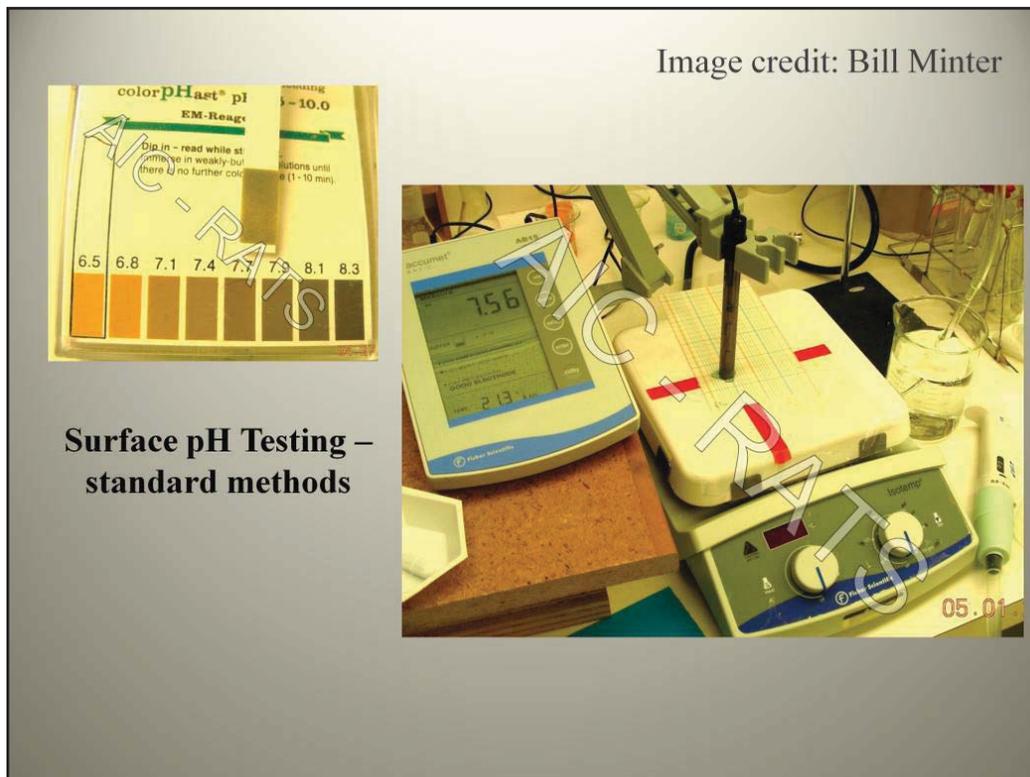
**Time:  
11 Weeks  
22 Weeks  
33 Weeks**

**Longer Time?**

The temperature and the relative humidity within the hot boxes were very stable during the time of the study. Samples were pulled at various times throughout the study. Ideally, we would have liked to have conducted the test for a longer period of time. Note, however, that because we are using historic specimens that have already undergone decades of aging, any significant results we obtain in the near term at lower temperature accelerated aging are useful because they describe aging a relevant point in the artifact's life.

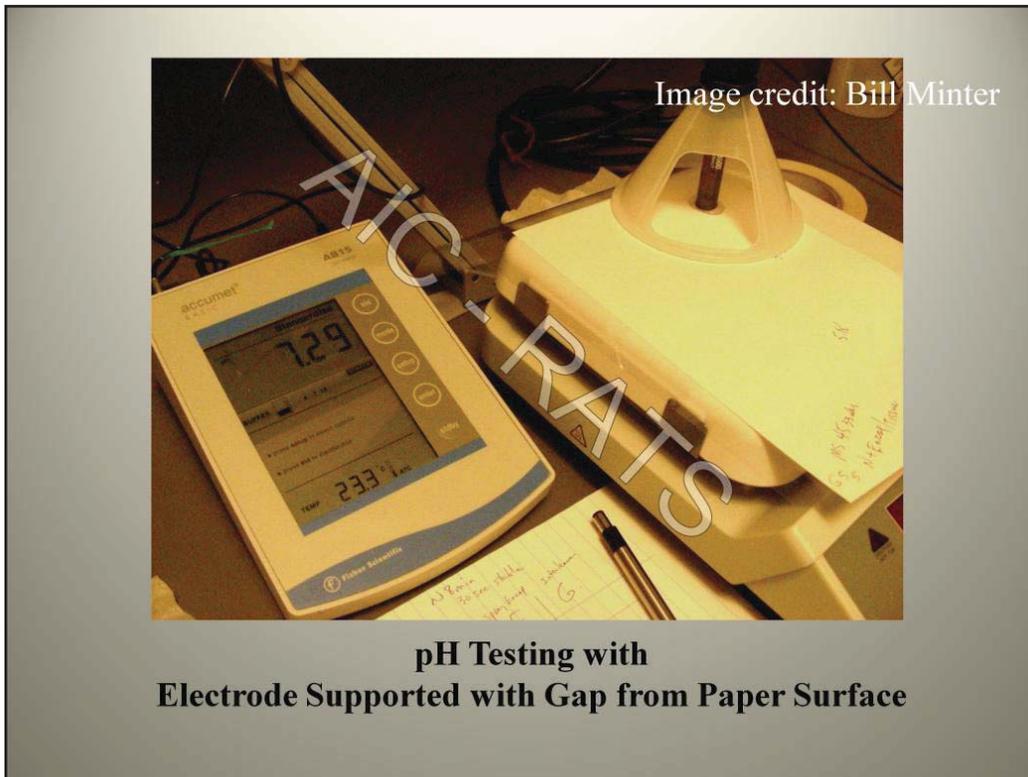


Following the accelerated aging, a number of tests were conducted. One test was folding endurance.



Most book and paper conservation labs utilize the popular pH test strips for most daily work. For this study, it was important to obtain accurate readings, thus the use of a pH meter.

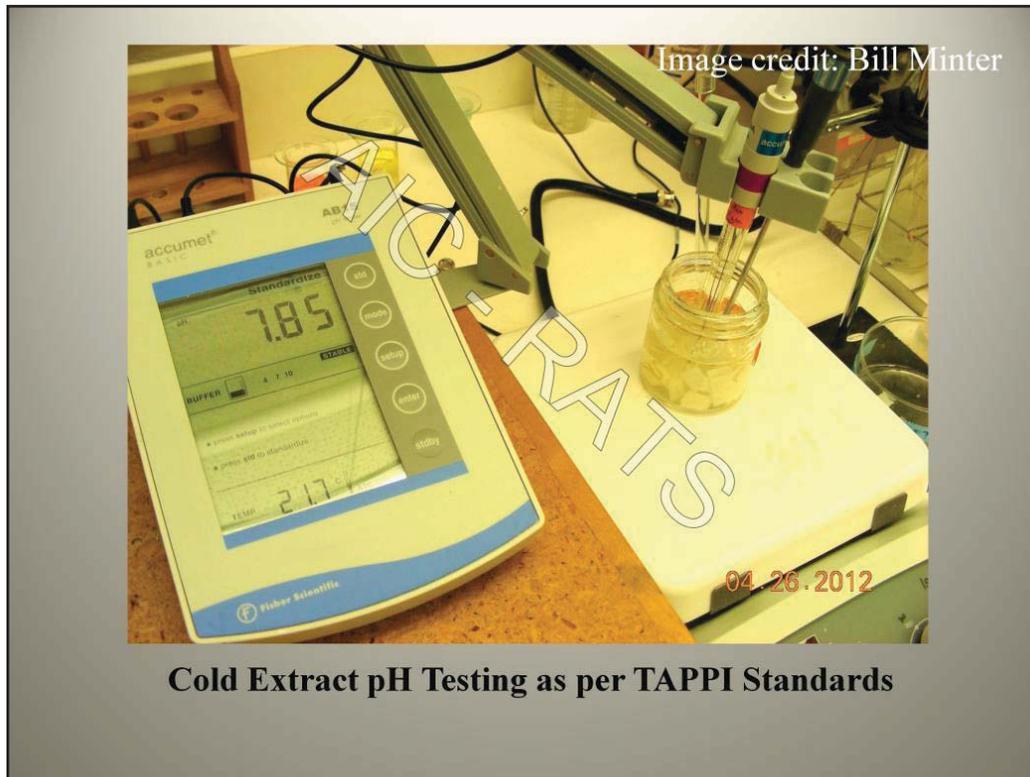
Upon reading the research from the Canadian Conservation Institute, we learned that the flat-head electrode should, ideally, not touch the paper sample, otherwise errors in reading could occur. With that concern in mind, we developed . . .



... a very simple method of holding the pH electrode at a specific distance away from the sample, thus reading the water droplet. In this case, we are utilizing a specially converted funnel to hold the electrode 0.005" away from the paper.



Surface pH of paper has certain variables that are undesirable for research purposes, thus the best method is to use “Cold-Extract pH Testing” a method that is a TAPPI Standard. TAPPI is the Technical Association of the Pulp and Paper Industry that has established standards that are widely accepted in all paper research.



John Baty will now present further tests, results, and conclusions.



John Baty, Assistant Research Professor and  
Heritage Science for Conservation (HSC)  
Scientist, takes the lectern.

Good afternoon. I want to move from Bill's excellent description of our materials and methods to results and discussion.

But I want to start with a rigorous statement of our hypotheses. First so that we are on exactly the same page when I give our conclusions, and second to show that the clarification of hypotheses is a critical component of the collaboration between conservator and scientist—identifying the best, most relevant questions and testing them rigorously and reproducibly.

## 1. The “*stewing in its own juices*” question

It was a privilege to work with Bill on some of the most pressing preservation questions on polyester film encapsulation, beginning with the “stewing in its own juices” question . . .

1. We hypothesize that encapsulated acidic sheets will degrade faster than unencapsulated acidic sheets.

. . .which we restated rigorously as follows: “We hypothesize that encapsulated acidic sheets will degrade faster than unencapsulated acidic sheets.” Note that in this hypothesis we were not yet bringing deacidification into the equation. Instead, we were isolating the effect of encapsulation on acidic papers, all else being equal.

1. We hypothesize that (\*)  
encapsulated acidic sheets will  
degrade faster than unencapsulated  
acidic sheets (†).

(\*) . . . for the grades we test . . .

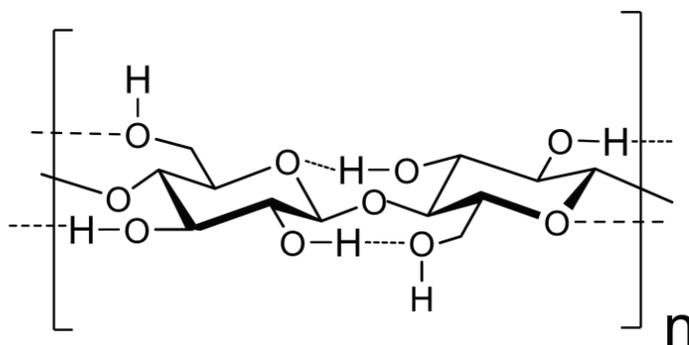
(†) . . . as measured by the  
techniques we use.

We had two boilerplate phrases that applied for all the hypotheses we tested in this research.

The first one was necessary because we were using historic materials. While we made an effort to obtain papers that represented grades found encapsulated in the library, museum, and archive today, other papers (due to chemical composition for example) may age differently.

The second boilerplate phrase really applies to all materials research and acknowledges that different analytical techniques tell you different things about the material you are studying. Some techniques test phenomena that answer the underlying question better. Some techniques are more precise than others, which enable you to see effects with greater clarity.

## Size Exclusion Chromatography (SEC)



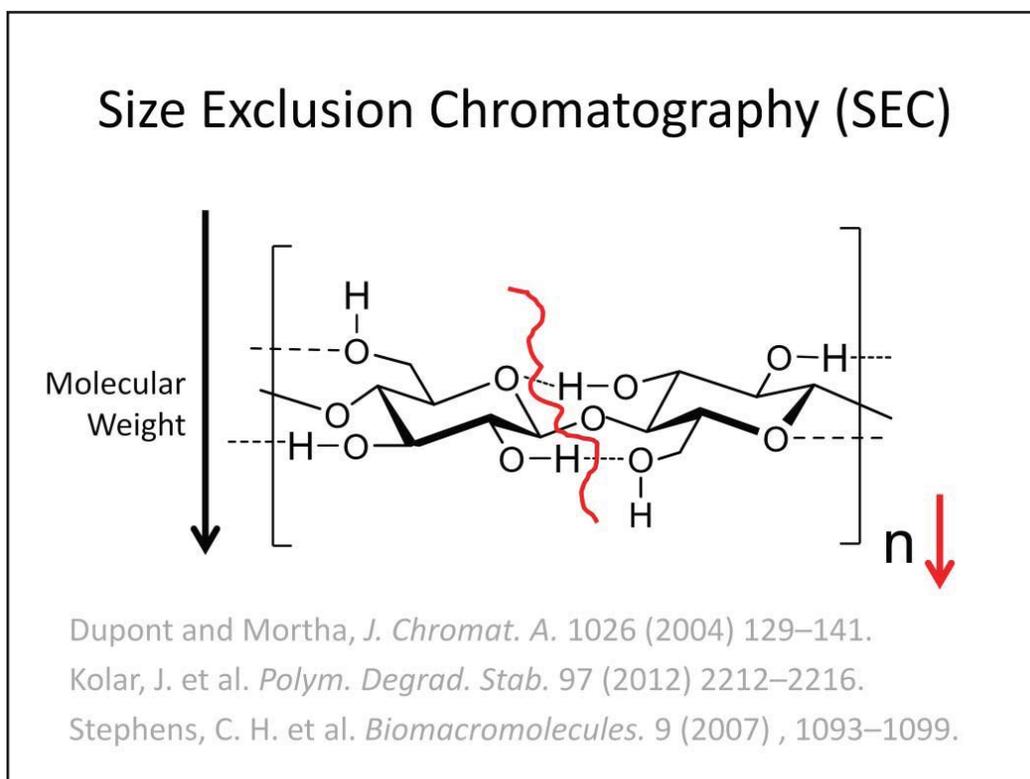
Dupont and Mortha, *J. Chromat. A.* 1026 (2004) 129–141.

Kolar, J. et al. *Polym. Degrad. Stab.* 97 (2012) 2212–2216.

Stephens, C. H. et al. *Biomacromolecules.* 9 (2007) , 1093–1099.

The analysis we will focus on in this presentation should be among the most sensitive techniques in our arsenal, size exclusion chromatography (SEC). Researchers in our field have increasingly adopted this technique within the last decade or so (references below) to perform molecular weight analyses (averages, distributions) on the cellulosic and hemicellulosic components of paper. While there are many components of heritage papers, cellulose usually forms the bulk of a heritage paper's content, and the complex structure of cellulose enables paper's strength.

We depict the most fundamental level of this structure (the molecular level) in this slide. Cellulose is a chain—a polysaccharide. The links of the chain are small sugar units, two of which are depicted above. From the molecular weight results given by SEC, you can calculate the number of those sugar units linked end to end. A typical bleached kraft paper has approximately 1300 sugar units, but the length of cellulose polymers can vary widely in heritage papers, with cotton and mulberry bast fibers providing longer chains.

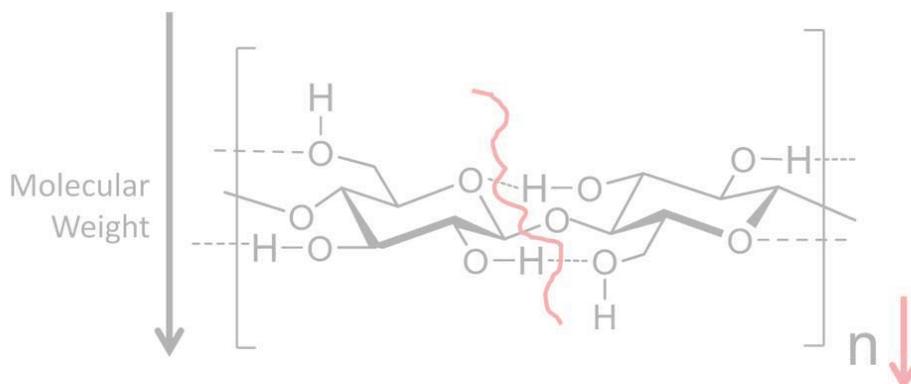


SEC is useful to monitor paper degradation because a loss of molecular weight during aging indicates the breakage of the chain and associated change in physical properties and loss of important strength criteria.

Specific to our study, there were three reasons why SEC is especially helpful to test our hypotheses:

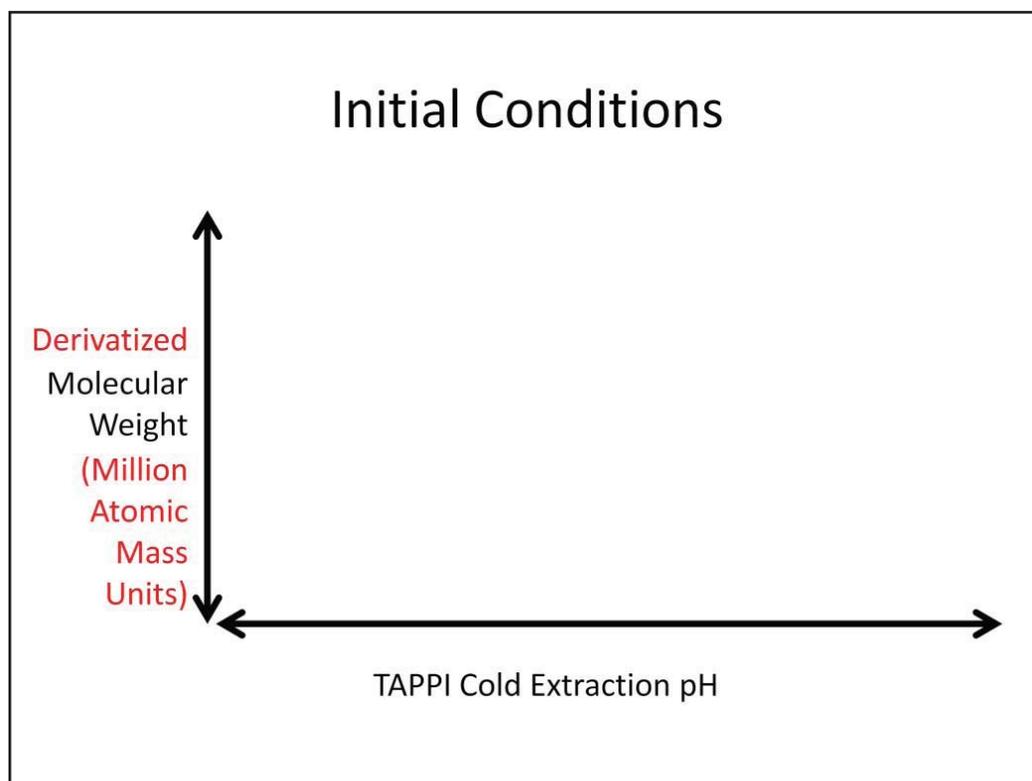
- First is the precision mentioned earlier, which enabled us to see the effects of aging with greater clarity.
- Second is that the loss of molecular weight is, in practice, an irreversible process. (The chain, once broken, does not reconnect.) If properly measured, changes of molecular weight can give a reliable assessment of degradation that is minimally subject to instrumental effects and environmental effects within the laboratory.
- The third reason why molecular weight was helpful to us is because it enabled us to make another important comparison: Deacidification should not break the cellulose chain, which is not sensitive to mild alkaline environments. (We confirm this for our study in a subsequent slide.) This fact enabled us to measure the single variable of aging following deacidification (versus not deacidified), without the results skewed by the effects of the deacidification process itself.

## Size Exclusion Chromatography (SEC)



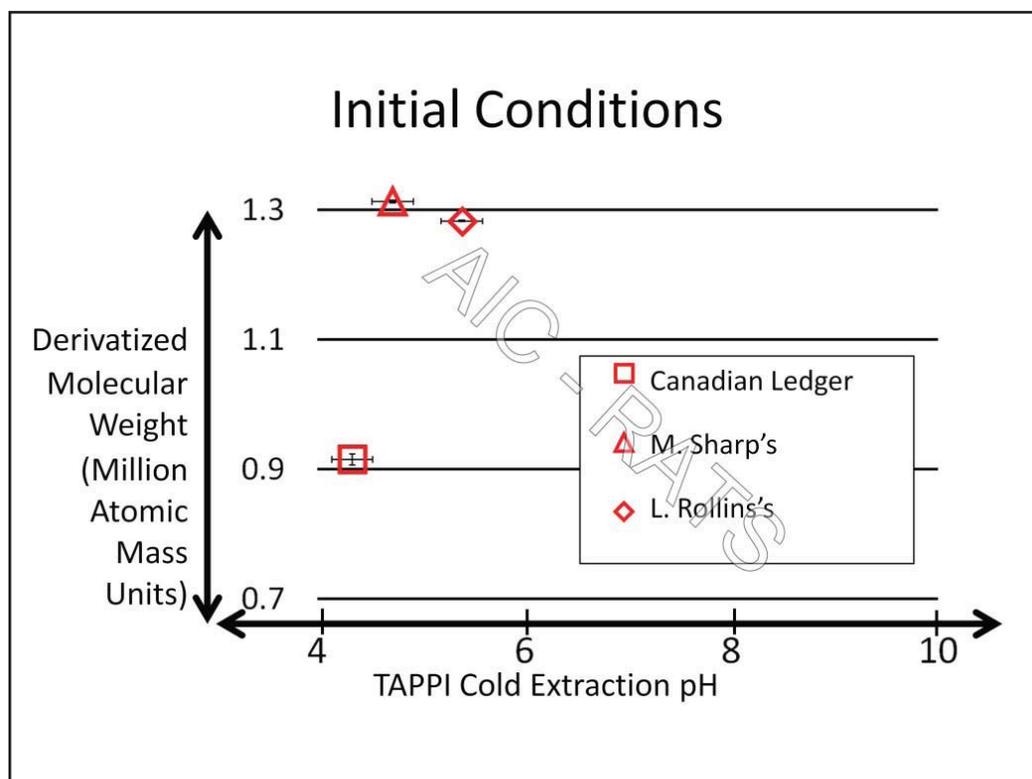
Stol, R., J. et al. *Anal. Chem.* 74 (2002) 2314–2320.

The procedure we used for size exclusion chromatography was word for word that outlined by Stol and coworkers (for pressure driven chromatography—they also discuss an electrophoretic technique). In this procedure, the polysaccharides undergo a chemical change (*a derivatization*) to carbanilate-substituted molecules that are soluble and separable (based on their molecular weight) in the mobile phase tetrahydrofuran.



So for the rest of this brief presentation, We are able to set the y-axis to derivatized molecular weight, using it both to present the initial conditions for our samples and subsequently our results. Because our hypotheses concerned the effects of aging under select conditions, we will report the derivatized molecular weight as obtained directly by SEC, rather than translating those values to some other criterion.

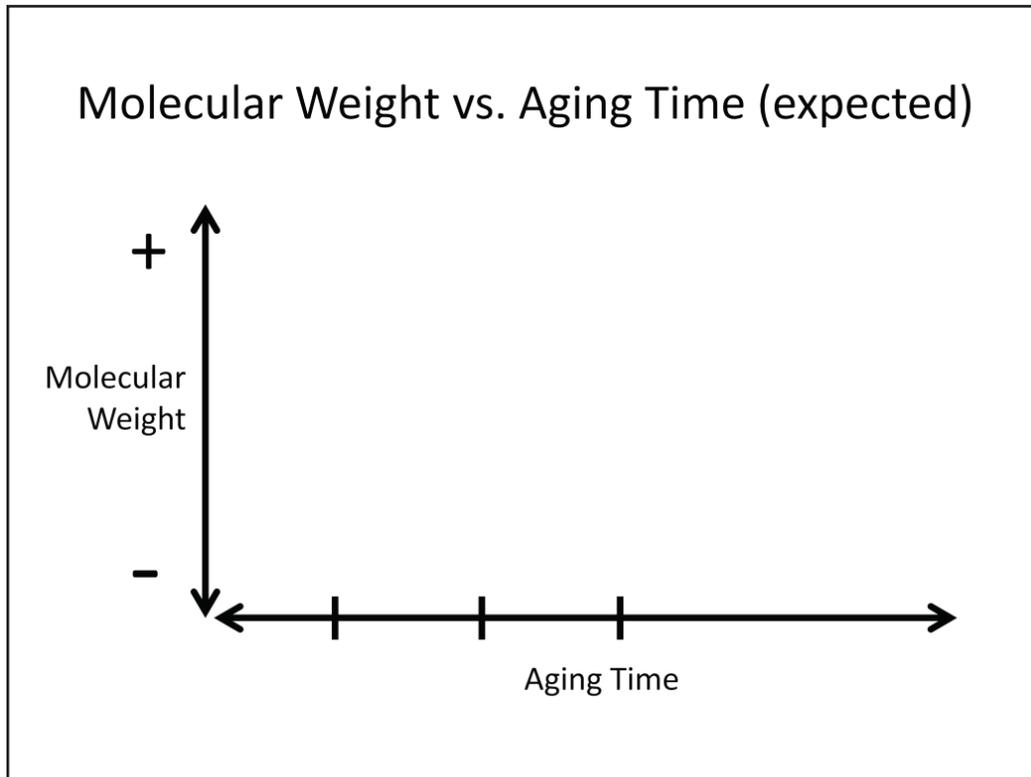
To show our initial conditions, we will first set the x-axis to the TAPPI cold extraction pH.



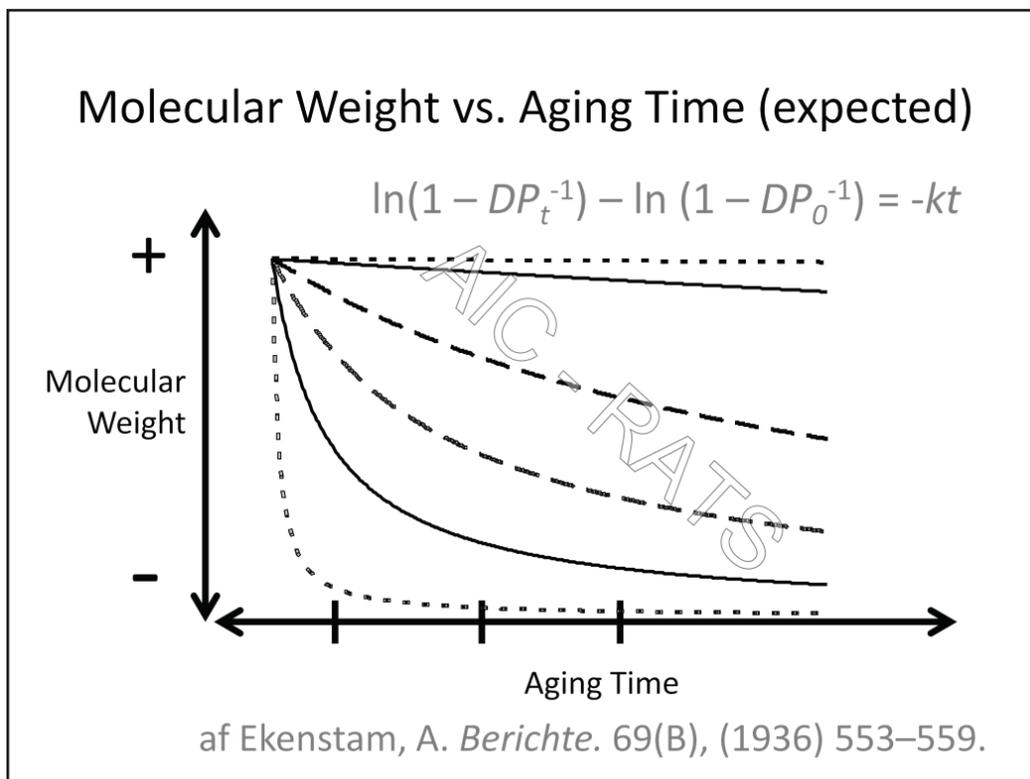
We plot the three grades we will focus on for the rest of this presentation in this graph. You do not have to remember which markers (diamonds, squares, etc.) correspond to which grades because we will denote them in subsequent slides.

Looking at this graph, a first observation is that the paper we call "Canadian Ledger" has a lower molecular weight than the other grades. Because these are historical specimens, we cannot definitively tell you why this is so. It may be due to conditions of prior aging, pulping, or fiber type—or a greater contribution from hemicelluloses, which have a lower molecular weight, in this grade compared to the others.

The primary observation to make on this slide for the purpose of our study is that all of these grades are acidic, measuring between pH 4 and 6. Therefore, these samples were usable to test our "Hypothesis 1," that encapsulated acidic sheets will degrade faster than unencapsulated acidic sheets.

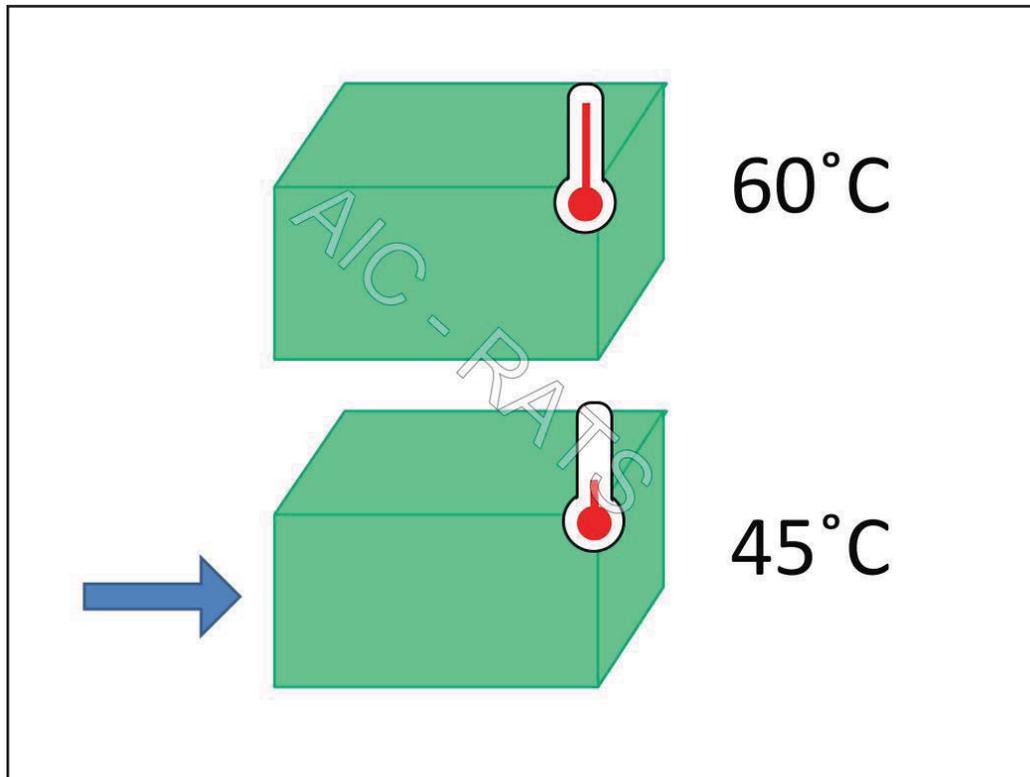


To present effects of accelerated aging on these samples, we will change the x axis to aging time.



First a note on the shapes of the plots we expect to see in these graphs, based on models of cellulose chain breakage. The af Ekenstam equation (shown above right) models the molecular weight of cellulose in terms of degree of polymerization ( $DP_t$ )—the number of repeating sugar units in a polysaccharide chain—as a function of time, given the initial degree of polymerization ( $DP_0$ ) and a specific rate constant that applies for the reaction ( $k$ ).

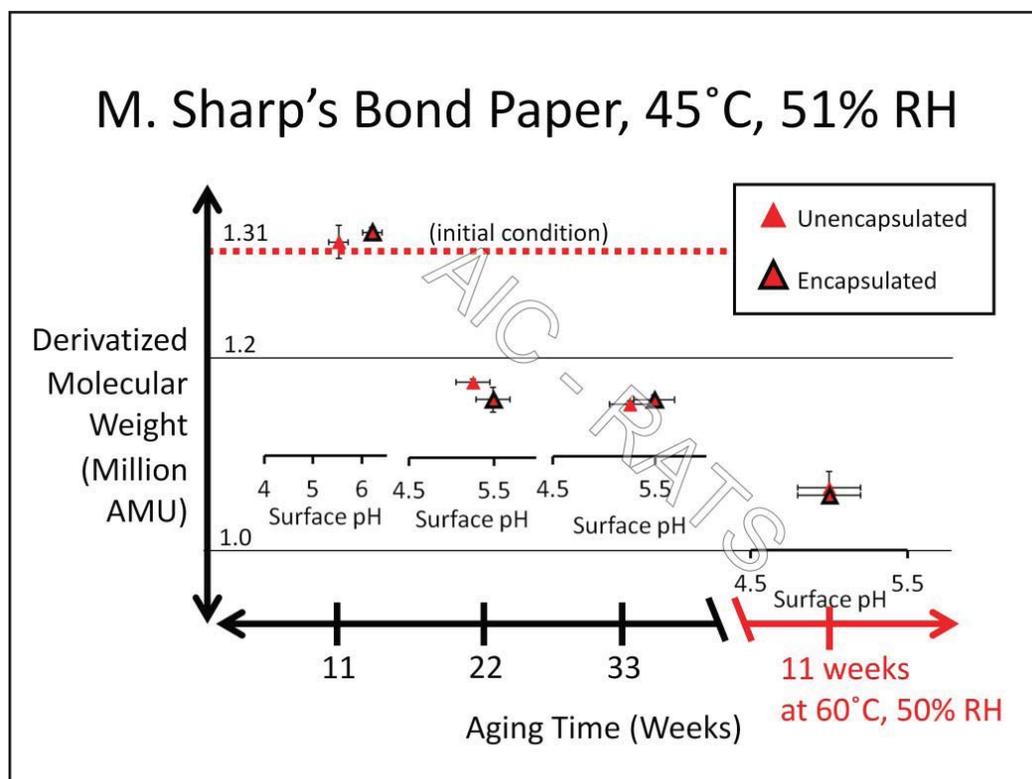
The plots on this graph are solutions for  $DP_t$  in the af Ekenstam equation, given a certain initial degree of polymerization and six different specific rate constants each on its own line. The curves describe the behavior expected when each chain scission (at a random location) produces two strands that are on average one half the length of the former.



Recall that one of the objectives of this project was to use longer-term accelerated aging at lower temperatures.

Hence, we were glad to observe that, as we worked up our data, significant effects were visible following aging at the lower temperature, 45°C. Therefore, the majority of the results we present here were aged at 45°C.

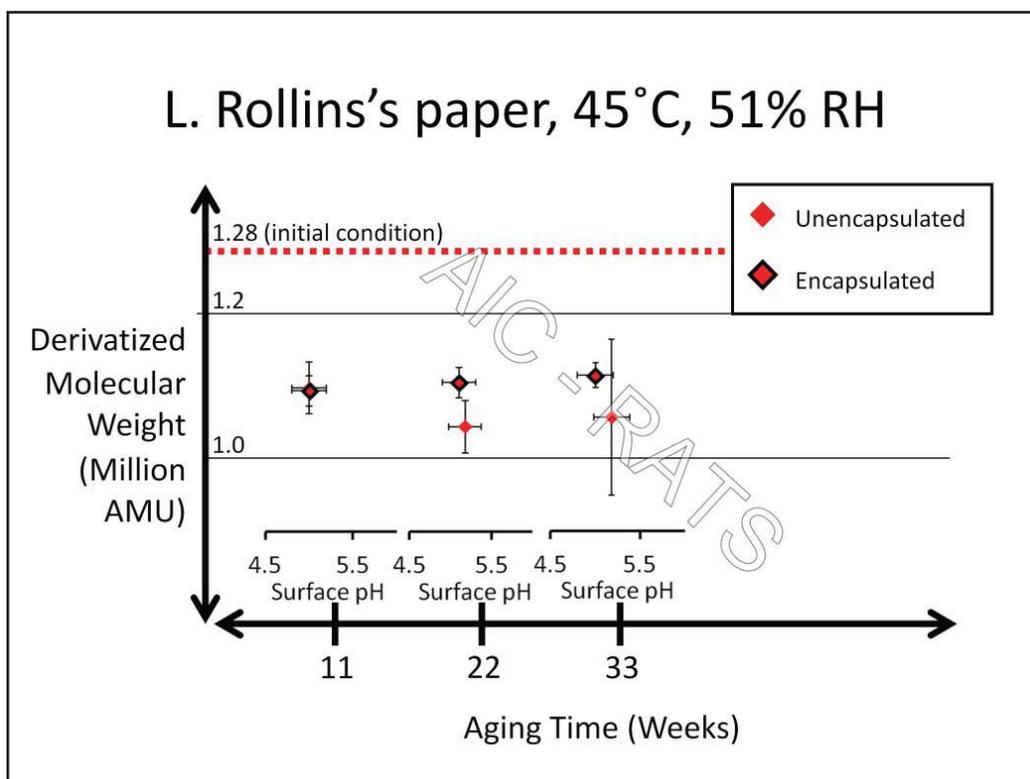




Moving to the results for the paper M. Sharp provided: Here we do not see a significant difference between the initial condition and the aged samples after 11 weeks at 45°C, 51% RH. This does not entirely conform to the af Ekenstam model, where we expect the greatest loss of molecular weight early in the aging process. We can only speculate on the cause of this behavior, but it may be due to the initial generation of degradation catalysts that will accelerate degradation later.

While after 33 weeks at 45°C, 51% RH the reaction appears to be leveling off, evidence that the paper would eventually degrade further at 45°C (and also at ambient temperatures) is provided by our results after 11 weeks at 60°C, 50% RH, where the molecular weight is yet lower.

Specifically addressing our hypothesis: The same observations we made for the Canadian Ledger paper hold. There is no significant difference in pH between the encapsulated acidic sheets and the unencapsulated acidic sheets. There is also no significant difference in terms of molecular weight. We make the same observation after 11 weeks at 60°C, 50% RH, suggesting that this aging trend continues.



Finally, we move to our final grade, the paper L. Rollins provided. Our results for this paper are “noisier,” meaning that we obtained a wider distribution in molecular weight. Partly because we’re using a historic grade, and partly because we did not perform a complete reverse engineering of these papers, we cannot isolate the reason for this behavior—whether there is a wider distribution of fiber type, differences in environmental exposure during its previous history, etc.

For this grade, the observations we made on the previous two grades hold, with one exception: Following 22 weeks at 45°C, 51% RH, the unencapsulated sheet is more than one standard deviation more degraded, but not more than a 95% confidence interval.

## Conclusion

*“Stewing in its own juices”*

### REFUTED

(\*) We do not see encapsulated acidic sheets degrading faster than unencapsulated acidic sheets<sup>(†)</sup>.

To conclude our discussion on the “stewing in its own juices” question: Our hypothesis, as we framed it, was refuted or disconfirmed. In the grades we tested, we did not see encapsulated acidic sheets degrading faster than unencapsulated acidic sheets in the analyses we performed.

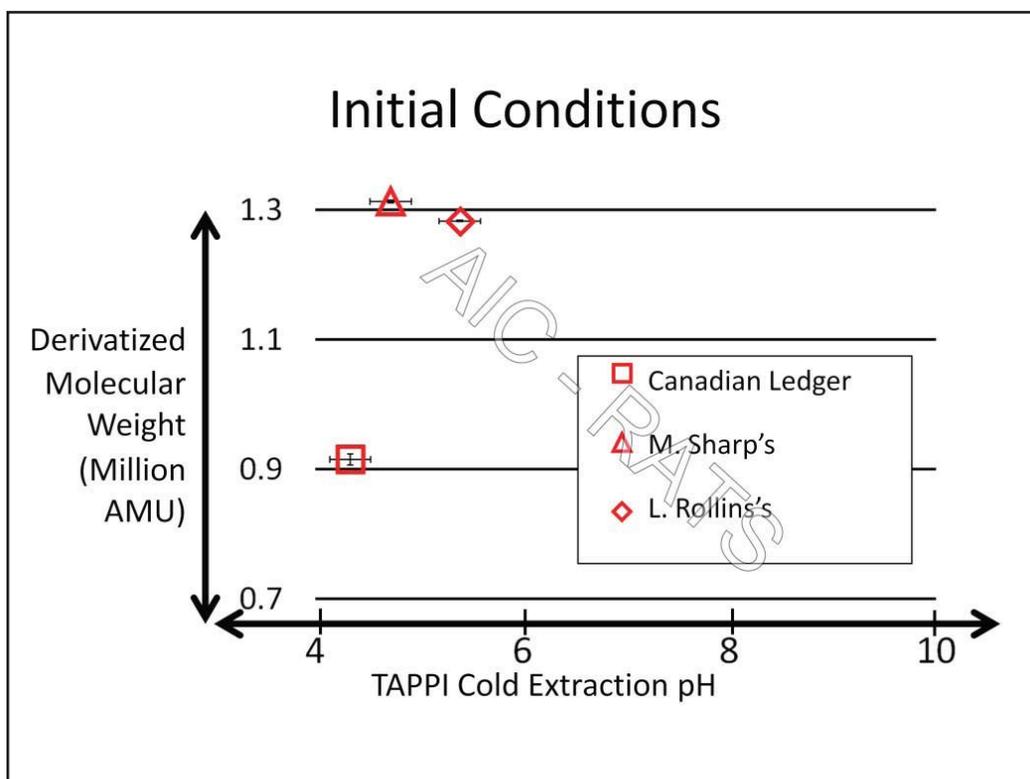
The application of this result is that, when it is a given that you cannot deacidify a paper—if there is some institutional or other prohibition, such a highly coated paper, etc.—these results argue that you are not causing greater harm by encapsulating.

## 2. The efficacy of deacidification in encapsulation

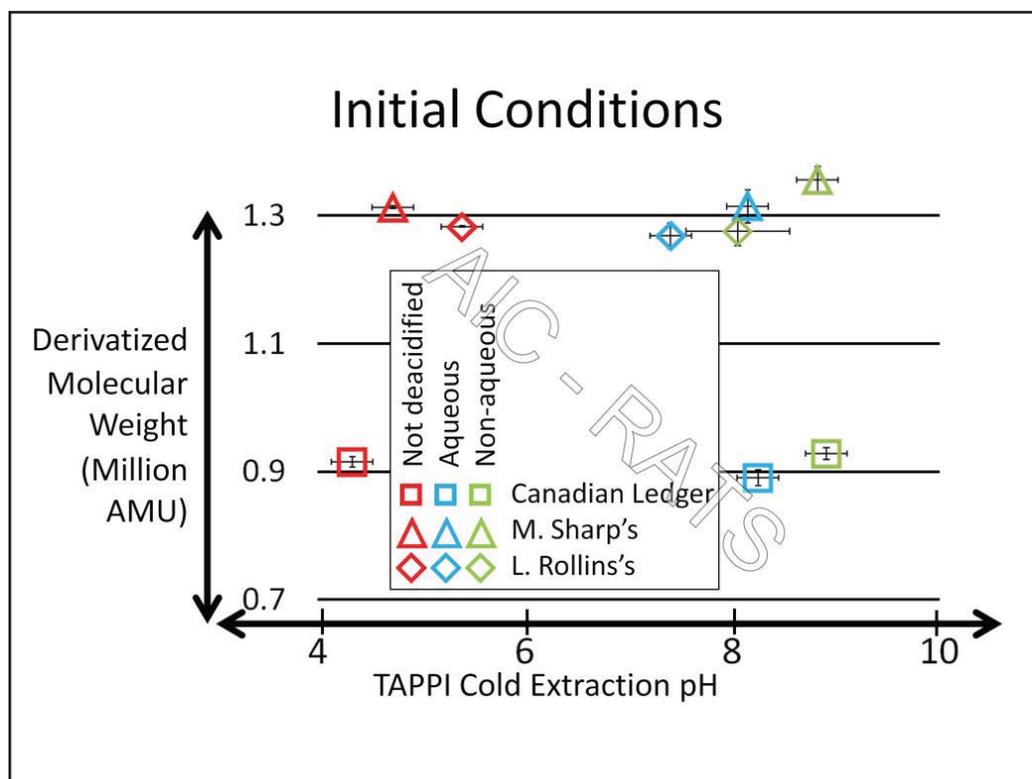
To proceed to our second and final hypothesis in this presentation: We will now look at results on the efficacy of deacidification to preserve encapsulated papers.

2. We hypothesize that<sup>(\*)</sup>  
deacidified encapsulated sheets  
degrade slower than acidic  
encapsulated sheets<sup>(†)</sup>.

(We will assume that you know our boilerplate phrases by now.) We stated this hypothesis to conform to the understanding in the field, that deacidification is helpful in the preservation of encapsulated sheets, “deacidified encapsulated sheets degrade slower than acidic encapsulated sheets.”



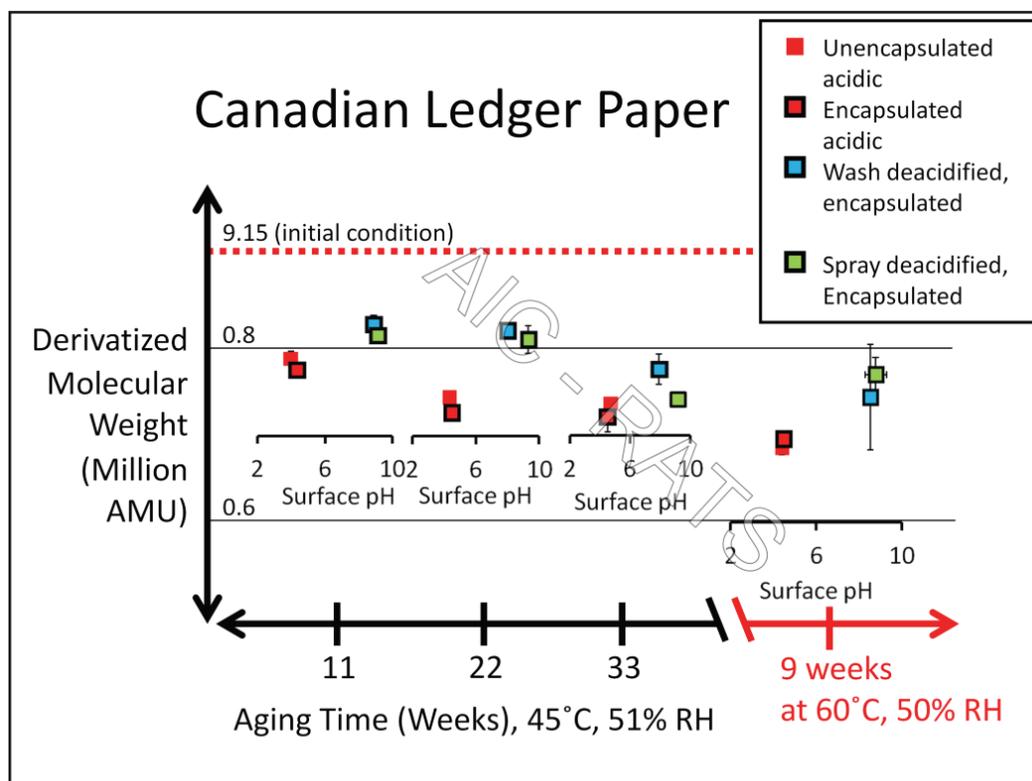
To move to our initial conditions: This slide of our three grades prior to deacidification, molecular weight versus TAPPI Cold Extraction pH, you have seen previously . . .



...and these are the molecular weights plotted vs. pH for the same three grades and directly following deacidification (aqueous—magnesium bicarbonate—blue markers, and non-aqueous—magnesium oxide—green markers).

From this slide you can see first that the deacidification was effective in increasing the TAPPI cold extraction pH. For any one grade the non-aqueous deacidified samples were more alkaline than the aqueous. This measurement is what we expected due to the differing acid dissociation constants of the respective alkaline agents.

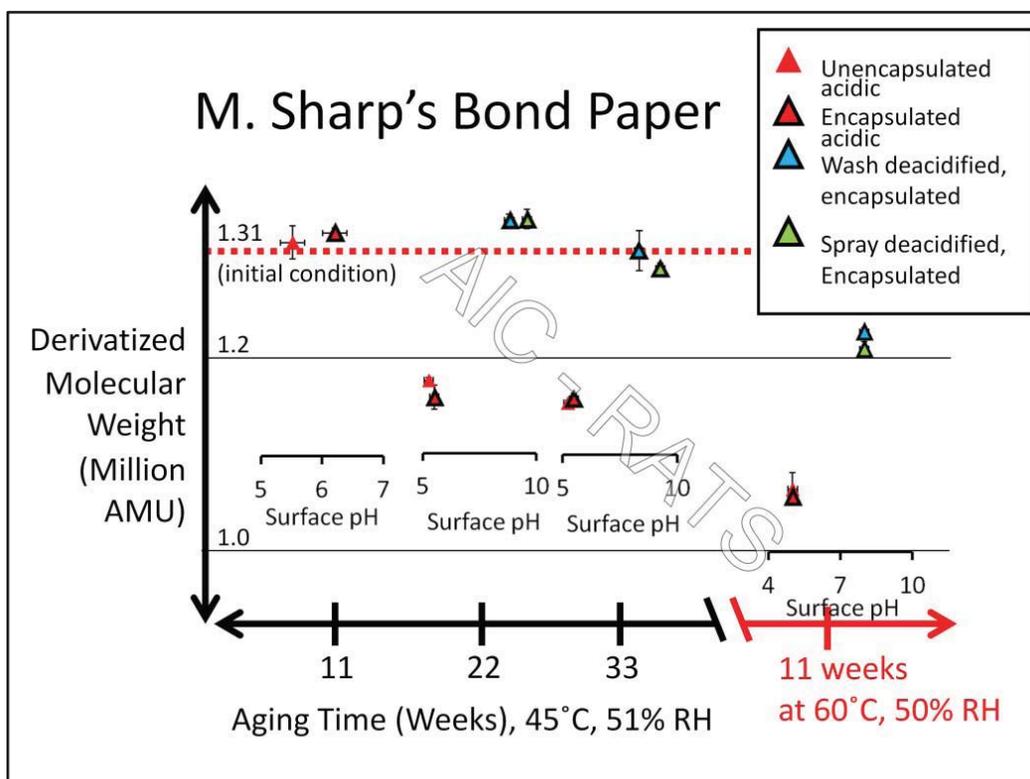
Second, and most importantly for our hypothesis, there was no significant difference between the undeacidified and deacidified samples in terms of molecular weight. Therefore we could be confident that any differences in molecular weight following aging were due to aging under the specified conditions, and not due to the deacidification process itself.



To present our results, we use a complex x axis as we did for the previous hypothesis, giving our data sets for 11, 22, and 33 weeks and surface pH for an x axis in a detail, which shows the efficacy of deacidification to keep the paper at a higher pH following aging.

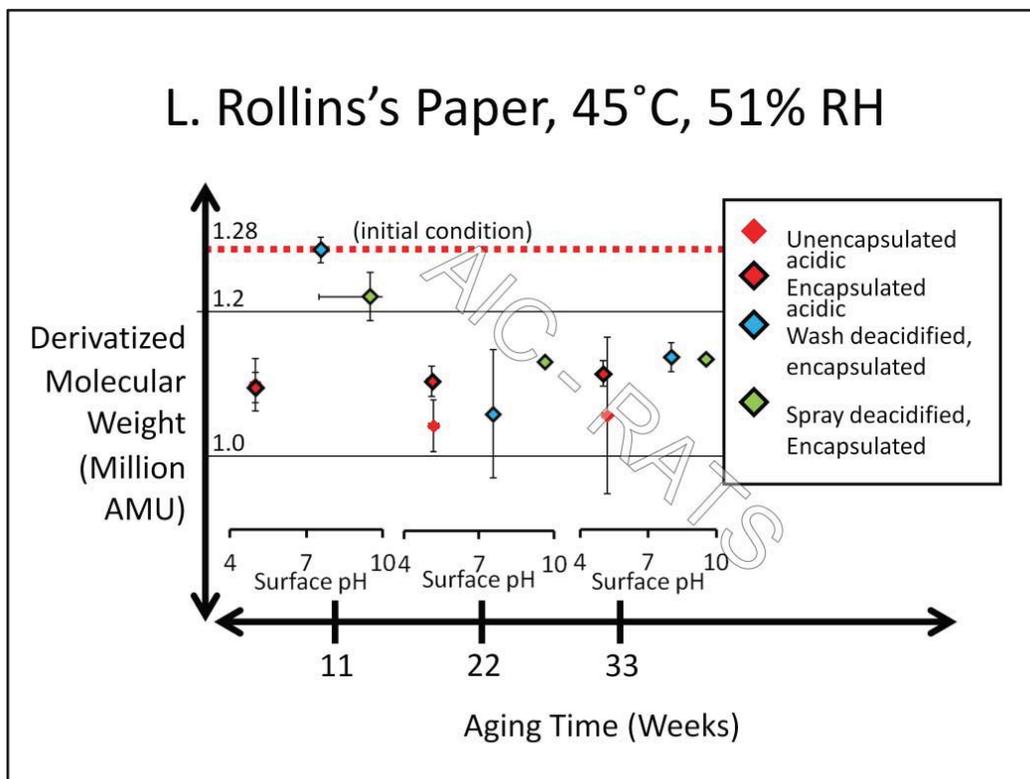
Results for the Canadian Ledger paper showed that both aqueous and non-aqueous deacidified papers do degrade under our conditions of aging (45°C, 51% RH) but not as much as the papers that have not been deacidified. After 11 weeks and 22 weeks, papers deacidified by both treatments were in significantly better condition (as measured by size exclusion chromatography) than those that were left acidic.

After 33 weeks we see an exception to this trend, where the non-aqueous deacidified paper degraded at a rate insignificantly different from the undeacidified paper. This, however, is not sufficient evidence to suspect the non-aqueous treatment of inefficacy: In fact, after 9 weeks at 60°C, 50% RH, it is the aqueous treatment that returned molecular weights insignificantly higher than the undeacidified papers.



The efficacy of deacidification to promote paper permanence was even more apparent in the bond paper M. Sharp provided. Here, the molecular weight of the deacidified papers remained approximately that of the initial condition even after 22 and 33 weeks at 45°C, 51% RH!

From the data at 45°C, 51% RH, it looked as though both deacidification treatments might protect the paper indefinitely according to our criterion. After 11 weeks at 60°C, 50% RH, however, some degradation of the deacidified sheets was apparent.



Finally, to the results for paper from L. Rollins: The uncertainty in the molecular weight measurements obtained previously continued here. While we saw a significant difference after 11 weeks for both treatments, we did not obtain significant differences after 22 weeks and 33 weeks.

## Conclusions (Protection by deacidification)

CONFIRMED, with notices<sup>(\*, †)</sup>:

- Protection not always significant
- Deacidification never hurts
- Performance of aqueous vs. non-  
aqueous equal

\* As measured in the grades we tested

† As determined by the analytical techniques we used

To state the conclusions for our study on the efficacy of deacidification to protect encapsulated papers:

In the grades we tested, and as measured by our analytical technique (SEC), we saw consistently—though not universally—better properties in the deacidified sheets following aging. We observed this for both the aqueous and non-aqueous treatments.

Where we did not see a significant difference between deacidified and undeacidified papers, we certainly did not observe degradation to be promoted by deacidification.

Therefore, the recommendation to deacidify a paper wherever applicable and possible prior to encapsulation is supported by this research.



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Thank you.  
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Finally, we thank Linda Rollins and Maureen Sharp for providing papers we tested in this research.



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