Description of document: Five interim reports from the University of Wisconsin Madison on grant PR5014112:9361, for "Investigation of Cellulose Nitrate Motion Picture Film Chemical Decomposition and Associated Fire Risk," 2012-2014

Request date: 03-December-2014

Released date: 15-December-2014

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National Endowment for the Humanities
Freedom of Information Act Officer
400 7th Street SW, 4th Floor
Washington DC 20506
[NEH Online FOIA Request Form]

NATIONAL ENDOWMENT FOR THE
Humanities

OFFICE OF THE CHAIRMAN

DEC 15 2014

VIA ELECTRONIC MAIL

Re: Freedom of Information Act Request 15-19

As the National Endowment for the Humanities (NEH) official responsible for inquiries under the Freedom of Information Act (FOIA), I am responding to your FOIA request, which NEH received on December 3, 2014. You requested "A copy of each interim report, interim presentation, the final report and the final presentation from the University of Wisconsin Madison associated with grant PR5014112: 9361, for investigation of cellulose nitrate motion picture film chemical decomposition and associated fire risk."

The information you requested, as maintained in our records, is attached. The grant project is still active and the final report and white paper are not due to NEH before September 30, 2015.

If you wish to appeal this determination, please write to NEH Chairman William D. Adams, at 400 7th Street, SW, 4th Floor, Washington, DC 20506 or via e-mail to WAdams@neh.gov. Your appeal must be in writing and received by NEH within thirty (30) days of the date of this letter (weekends and Federal holidays excluded). Your appeal rights are set out in the Code of Federal Regulations, at 45 C.F.R. § 1171.10. There is no fee for this information.

Sincerely,

Carole M. Watson

Carole M. Watson
Deputy Chairman

Attachments

Semi-Annual Performance Report

Report ID: 105404

Application Number: PR5014112

Project Director: Vance Kepley (vikepley@wisc.edu)

Institution: University of Wisconsin, Madison

Reporting Period: 1/1/2012-6/30/2012

Report Due: 7/31/2012

Date Submitted: 9/10/2012

Title Page

NEH interim report: January 2012-July 2012 (Project phase one)

Project title: Investigation of cellulose nitrate based film chemical decomposition and associated fire risk

Project ID number: PR-50141-12

Home institution: University of Wisconsin-Madison

Project partners: Wisconsin Center for Film and Theater Research/UW-Madison Department of Chemistry/Wisconsin Historical Society

Submitted by: Vance Kepley, Jr. (Project Director and Director of Wisconsin Center for Film and Theater Research, UW-Madison)

Narrative Report: PR-50141-12 (phase one)

The project is co-sponsored by the Wisconsin Center for Film and Theater Research (WCFTR) supported by the Wisconsin Historical Society, and by the Department of Chemistry at the University of Wisconsin-Madison. Professor Mahesh Mahanthappa of the Chemistry Department is co-PI on the project and oversees the laboratory dimension of the research. As director of the WCFTR and its film archive, Vance Kepley, coordinates the research into the historical record of nitrate safety/preservation issues. The project is also importantly supported by the Wisconsin Historical Society (WHS), which partners with WCFTR to manage the film archive. The expertise of WHS Preservation Coordinator Kathleen Mullen is crucial to the project, and she takes the lead in researching and evaluating archival practice related to cellulose nitrate films. In addition, working samples of cellulose nitrate film selected for chemical analysis are drawn from the WHS nitrate film inventory that Ms. Mullen oversees.

The campus working group formed in January 2012: Professor Mahesh Mahanthappa (Chemistry) and RA Glenn Thomas (Chemistry), Kathleen Mullen (Preservation Coordinator, Wisconsin Historical Society), Mary Huelsbeck (Assistant Director, WCFTR), Maxine Ducey (Head Film Archivist, WCFTR), PA Amanda McQueen (WCFTR), and Vance Kepley (Director, WCFTR). The working group met every 3 to 4 weeks as a committee of the whole. The general meetings involve reporting across subgroups about the ongoing research, as well as agreeing collectively on the next stage of activity. Subgroups, defined generally as the chemistry group (Mahanthappa, Thomas) and the archival group (Mullen, Ducey, Huelsbeck, McQueen), also regularly confer separately as the project moves forward, and email exchanges on particular queries take place on a regular basis.

An outside advisory committee was also established consisting of specialists Mike Pogorzelski of the Academy Film Archive, Edward Stratmann of the George Eastman House Archive, Heather Heckman of the University of South Carolina, and Douglas Nishimura of the Image Permanence Institute. The off-site advisory committee members receive minutes of all primary group meetings along with power point outlines summarizing stages of the on-going research. They are provided bibliography of all scholarly, historical, and scientific essays acquired in the bibliographical search (and they sometimes make suggestions on sources). They are solicited to provide feedback at regular points in the process, and particular specialized questions are directed to individual members of the outside committee. The members have been generous and helpful with their advice.

All members of the campus working group toured the archive at the beginning of the grant period and examined samples of nitrate cellulose film at the WHS storage area. This review helped guide decision making about sampling, as the nitrate inventory at WHS includes nitrate film reels in different stages of deterioration.

In the early meetings of the campus working group, decisions were made about selecting samples of nitrate film for testing in the laboratory, as well as identifying the near-term goals of the laboratory process. A sample size was duly determined. It is common to classify nitrate film into five categories based on levels of deterioration. Three sample sets were selected for early testing, one from 'stage 0" (before deterioration), one from "stage 2" (significant deterioration), and one from "stage 4" (extensive deterioration). The sample set promised to provide a useful set of outcomes for archivists handling films in various stages of deterioration. A photographic record of samples was made and the samples were classified according to age and condition. RA Glenn Thomas under the direction of Professor Mahanthappa performed extensive laboratory test on the samples, under various conditions. The stage of laboratory activity stressed thermogravimetric analysis and various related tests. TGA in conjunction with other measures can help determine flammability. The tests continued through the end of the phase one period.

The development of a comprehensive bibliography was also given a priority in the first phase of the project, and that was done largely by RA Amanda McQueen. The literature on cellulose nitrate film is extensive. It encompasses scientific papers, essays by archivists, literature by historians of film and photography, and practical manuals for practitioners using the film stock. By summer 2012, PA McQueen had acquired and posted some 179 articles and scientific papers in a Mendeley library that could be accessed by all members of the campus working group, and by the off-site advisory committee. The library has been a working resource for the chemistry group in particular; as various questions come up about nitrate's record of behavior in particular conditions, McQueen pursues leads into the appropriate literature. The bibliography remains in development, with annotation and indexing to be done as the next phase.

This interim report has described process rather than outcomes, as this is the first stage of the project. Reportable findings from the laboratory testing in particular will be clarified at a later stage. The process as a whole, in its two parts has generally been on pace with the schedule predicted in the original proposal. A third dimension of the project, in addition to the laboratory research and the historical research, is to be a survey of film archivists on their experiences with the management of nitrate film inventories. That is to be coordinated by Kepley and the archives group, with PA Amanda McQueen then running the survey. Preliminary planning on the survey has been done but not yet refined for application. For strategic reasons we have asked PA McQueen to concentrate her time in phase one on developing and upgrading the bibliography, since that resource includes timely information needed by other researchers in the project, especially the chemistry group. We expect to proceed with the survey during the upcoming academic year.

Semi-Annual Performance Report

Report ID: 105405

Application Number: PR5014112

Project Director: Vance Kepley (vikepley@wisc.edu)

Institution: University of Wisconsin, Madison

Reporting Period: 7/1/2012-12/31/2012

Report Due: 1/31/2013

Date Submitted: 1/31/2013

Title Page

NEH Interim Report: July 2012-December 2012

Project Title: Investigation of cellulose nitrate based film chemical decomposition and associated fire risk

Project ID number: PR-50141-12

Home Institution: University of Wisconsin-Madison

Project partners: Wisconsin Historical Society/ UW-Madison Department of Chemistry/ Wisconsin Center for Film and Theater Research

Submitted by: Vance Kepley (Wisconsin Center for Film and Theater Research)

Submission: January 30, 2013

Narrative Report (PR-50141-12)
Through December 2012

Personnel:

Oversight and planning responsibilities continued to be shared by a working committee representing the project's campus partners: Professor Mahesh Mahanthappa (co-PI, Department of Chemistry), Kathleen Mullen (Wisconsin Historical Society), Maxine Ducey (Wisconsin Center for Film and Theater Research), Mary Huelsbeck (WCFTR), and Vance Kepley (project director, WCFTR). Project assistants are Mr. Milton H. Rapollet-Podresa for chemistry research and Ms. Amanda McQueen for archival and historical research. Only one personnel change has taken place since the project began; in summer 2012 chemistry assistant Glenn Thomas left the project to be replaced by Mr. Rapollet-Podresa.

Laboratory Research:

In the first year of our project, the chemistry team (Mahanthappa and Rapollet-Podresa) designed and executed a series of experiments addressing the validity of correlations between the Image Permanence Institute (IPI) classification scheme for cellulose nitrate film condition, film molecular composition, and film thermal stability. Five primary analytical tools were used in our studies; (1) optical microscopy to document the physical condition of each film frame tested, (2) size-exclusion chromatography to assess correlations between film base molecular weight and IPI condition, (3) combustive elemental analysis and (4) proton nuclear magnetic resonance (^{1}H NMR) to determine elemental composition of the base layer, and (5) thermogravimetric analysis to assess film thermal stability.

Our studies employed three nitrate film samples, including an IPI Stage 0 1935 film (CN-0), and IPI Stage 2 1919 film (CN-2), and an IPI Stage 4 1919 film (CN-4). Frames of each film were cut from the original reel for analysis, and their position with respect to the core was carefully noted. These frames were initially analyzed by optical microscopy to assess the integrity of the film base and the gelatin layer. CN-0 sample exhibited the least amount of base scratching and with an intact gelatin layer, whereas the base layers in samples CN-2 and CN-4 were significantly abraded. The gelatin layer in CN-2 was intact, whereas CN-4 exhibited substantial gelatin damage and decay.

One commonly held notion is that the level of cellulose nitrate decay is related to the molecular weight of the polymer film base. Stimulated by this idea, we treated samples of each of the three films with bleach to remove the emulsion layer. The resulting cellulose nitrate base layers were subjected to molecular weight analyses by size-exclusion chromatography (SEC) in tetrahydrofuran at 22 °C, a well-established analytical technique in polymer science. We found that the molecular weight of the film base was not at all correlated with either film age or its level of decay. Therefore, we conclude that film molecular weight is not related to the IPI condition classification. Instead, the molecular weight of the base likely varied from batch to batch of film, as a consequence of variable materials sourcing, manufacturing, and processing conditions.

The decay of nitrate film is typically associated with nitrate ester hydrolysis ("de-nitration"), which generates nitric acid that is thought to foster autocatalytic degradation of the film base. The level of nitration in cellulose nitrate film base is typically two or three nitrate esters per monomer repeat unit in the polymer. Under the aforementioned hypothesis, de-nitration should manifest in lower nitrogen content in the more decomposed films. Elemental analyses and ^{1}H

NMR analyses provide a powerful means of evaluating the elemental composition of our film samples. We found that the nitrogen content of film is inversely related to the IPI Condition classification, confirming that de-nitration is associated with advanced film decay (assuming that all of the film samples had comparable initial nitration levels). ^1H NMR analyses further corroborate this conclusion that de-nitration occurs in the decay process. NMR analyses also indicate that the film samples typically contain as much as 25 wt% camphor, which was a plasticizer commonly used to enhance the supple character of cellulose nitrate film. Given the high vapor pressure of camphor (it sublimes at room temperature), it is somewhat surprising that the camphor remains trapped within the film even upon substantial decay. Given the extreme flammability of camphor, this finding implies that camphor may contribute significantly to the ultimate combustibility of nitrate film.

Thermogravimetric analysis (TGA) is a common method for studying the thermal stability of polymer samples. In this technique, the mass of a polymer sample is monitored as it is heated at some constant rate (*e.g.*, 5 °C/min) under a flow of nitrogen until it fully decomposes. The thermal stability of each film sample was assessed by analyzing both the decomposition profile and the ultimate decomposition temperature determined by TGA. Heating CN-4 resulted in bubbling of the gelatin layer at 182 °C, followed by sample deflagration at 196 °C (three reproducible trials). Bubbling of the gelatin layer of the CN-2 sample began at 159 °C, with complete deflagration of the sample at a much lower temperature of 182 °C. Note that removal of the gelatin layer from CN-2 did not change the deflagration temperature of this sample, implying that the presence of this layer does not influence the flammability of the cellulose nitrate base layer. Finally, CN-4 decomposes at 182 °C with no signs of gelatin bubbling. These results together suggest that the IPI stages of decay do correlate with the film base deflagration temperature and its ultimate thermal stability.

In summary, our studies to date indicate that the IPI condition classification does accurately correlate with certain physical properties of cellulose nitrate film. More explicitly, increasing IPI Condition numbers positively correlate with nitration level and the deflagration temperature observed by TGA. However, the IPI classification is not correlated with the molecular weight of the film base nor the amount of camphor present. Note that these studies provide correlations, yet the causes of these various effects remain unknown. Sample variations due to provenance, manufacturing conditions, and developing conditions likely contribute to the exact physical properties of any given film sample.

We are currently establishing protocols for performing accelerated aging tests on film samples under various temperature and relative humidity (RH) conditions, in order to understand the role of these environmental factors in determining the flammability profile of heritage nitrate films. As a first step in these studies, we collaborated with Professor Michael A. Hickner (Department of Materials Science & Engineering at the Pennsylvania State University) to study the water sorption behavior of cellulose nitrate film. Using differential vapor sorption (DVS) analyses, we quantitatively determined that CN-0, CN-2, and CN-4 uptake 1-4 wt% water between 20-80% RH at 30 °C. Furthermore, we found that CN-0 with the gelatin removed (using bleach) exhibits a much lower water uptake. Therefore, these analyses reveal that the gelatin layer attracts water, which is a necessary ingredient for film de-nitration and decomposition. Using DVS data obtained at both 30 °C and 60 °C, we plan to commence accelerated film aging trials at 60 °C that mimic low temperature archival storage practices. We will use the previously established "Arrhenius-type" kinetic analysis for accelerate aging of film reported by Nishimura and co-workers.

The potentially hazardous nature of "brown powder" arising from nearly complete cellulose nitrate film decay is the source of substantial anxiety in the film archivist community. Some sources report that the brown powder is a flammable and shock-sensitive solid that must be handled carefully, yet other reports suggest that the powdery residue is non-hazardous. As a means of assessing these various assertions about the dangers of brown powder, we obtained a brown powder sample from the Library of Congress. Chilworth Global, a certified chemical safety analysis company located in Princeton, NJ, analyzed this sample according to the BAM Fallhammer and the BAM Friction Sensitivity tests. In quantitative studies of the impact sensitivity of the brown powder, the material was determined to be "not particularly sensitive to ignition by mechanical impact." The sample was also deemed "not particularly sensitive to ignition by friction." Thus, we conclude that this brown powder sample is non-hazardous according to U. S. Department of Transportation standards. This result should be interpreted with caution, given that the provenance of various brown powder samples may affect their specific properties. One potential avenue of future investigation includes obtaining several other samples of brown powder for complete impact and friction sensitivity testing.

Bibliography and physical inspection projects:

Project assistant Amanda McQueen, directed by Mullen and Kepley, worked principally on two parallel research threads through the latter half of 2012, the development of an annotated bibliography on nitrate motion picture film and a procedure for the physical inspection and identification of extant nitrate film samples.

The annotated bibliography is designed to be a comprehensive, cross-disciplinary collection of sources on nitrate film stock. The sources include trade and popular press articles, historical accounts, literature reviews, websites and forum postings, conference proceedings, practitioner handbooks, safety standards and government publications. They derive from a variety of communities, including: archivists and conservators, chemists and polymer scientists, historians, film industry practitioners, safety or standards organizations, and government agencies. A PDF of each source is entered into the citation manager software EndNote, where it is provided with an abstract, annotation and relevant tags. The abstract is a straightforward account of the source's content, taken when possible from the source itself. The annotation describes how relevant each source is to the overall goal of the project and points out particularly noteworthy aspects of the source. Each source is then tagged with the following categories, as relevant: the type of cellulose nitrate, nitration level, plasticizers, film processing and handling, historical film fires, parameters of chemical studies, analytical techniques used, mechanisms for decomposition, variables affecting decomposition and flammability, brown powder stage, and public relations. The articles are also given a rating to indicate how detailed they are and how relevant they are to the project. Currently, we have almost 300 documents in our bibliography, about 60 of which have been annotated. Over the next few months, additional graduate students will begin working on the annotation process, and we will hopefully be able to complete the annotations during that time.

The physical inspection portion of the project is designed to determine whether there are correlations between what one can see and measure on the film stock and what the chemical test results show. If we determine that such correlations exist, then archivists and conservators may be able to examine the nitrate stock in their holdings using simple tools and determine its stability. Individual frames of our three sample films are examined and the information recorded on an inspection sheet. We measure the density of each frame with a densitometer, recording the minimum and maximum densities of the image track, and, for comparison, the density of the sprocket area. Using a micrometer, we measure the thickness of each frame in thousandths of an inch. The base is examined for brittleness, softness and yellowing; the image for stickiness and fading, and the frame as a whole for buckle, tears or folds and the presence of foreign matter like dirt, grease and oil, brown powder and adhesive residue. The damage is rated as light, moderate or heavy depending on how much of the frame is affected. We also count the number of broken sprockets, and measure in millimeters how much of the image has disappeared due to degradation. Finally, using a measured loupe, we are counting the number of millimeters of each frame that are scratched. One out of five frames will also be photographed using Reflectance Transformation Imaging, and all frames will be scanned.

Dissemination:

Various project members have done some preliminary dissemination. In September 2012, Kepley spoke as part of a panel on science and the arts at Wisconsin Institutes for Discovery (Madison, WI), describing the project in its early stages and its potential yield. In December 2012, several team members gave a panel presentation at the annual conference of the Association of Moving Images Archivists (AMIA), the main professional organization of American film archivists. The panel consisted of Ducey, Mullen, Kepley and grant author Heather Heckman (now at University of South Carolina), with Professor Mahanthappa participating via Skype for audience questions. The group provided a mid-course report on the project and anticipates returning to AMIA to share additional findings in 2013.

Schedule:

The one part of the project has been delayed against the grant application's originally proposed schedule is the survey of archivists and practitioners. The work of the chemistry team is assisted by the bibliography and visual identification projects, and priority went to those activities during latter half of 2012. The survey is due to be undertaken in spring 2013. The accelerated aging tests are also scheduled to be conducted during spring semester 2013.

Semi-Annual Performance Report

Report ID: 105406

Application Number: PR5014112

Project Director: Vance Kepley (vikepley@wisc.edu)

Institution: University of Wisconsin, Madison

Reporting Period: 1/1/2013-6/30/2013

Report Due: 7/31/2013

Date Submitted: 7/30/2013

Title Page

NEH Interim Report: January-June, 2013

Project title: Investigation of cellulose nitrate based film chemical composition and associated fire risk

Project ID number: PR-50141-12

Home Institution: University of Wisconsin-Madison

Project Partners: Wisconsin Historical Society/UW-Madison Department of Chemistry/Wisconsin Center for Film and Theater Research

Submitted by: Vance Kepley (Wisconsin Center for Film and Theater Research)

Submission: July 30, 2013

Narrative report (PR-50141-12)
January-June 2013

Personnel:

Oversight of the project continues to be shared within the Nitrate Study Committee, representing the project's various campus partners: Professor Mahesh Mahanthappa (co-PI, Department of Chemistry), Kathleen Mullen (Wisconsin Historical Society), Maxine Ducey (Wisconsin Center for Film and Theater Research), Mary Huelsbeck (WCFTR), and Vance Kepley (project director, WCFTR). Mr. Milton Rapollet-Podresa, graduate student in Chemistry, continues as the RA for laboratory research, and Amanda McQueen, graduate student in Communication Arts, continues as the PA for archival and historical research. Professor Mahanthappa and Mr. Rapollet-Podresa convene separately as the Chemistry Group, and Mullen, Ducey, Huelsbeck, McQueen, and Kepley convene as the Archives Group. Communication Arts graduate student Booth Wilson started working on an hourly basis during summer 2013 on supplemental funding provided by The Graduate School at UW-Madison.

Laboratory analysis:

During the last six months, the Chemistry Group established protocols for the proposed accelerating aging studies of heritage nitrate films under various temperature and relative humidity (%RH) conditions, in order to understand the impact of these environmental factors on the flammability profiles of these materials. The major objective of this phase of laboratory analysis is to understand whether or not nitrate film becomes more susceptible to thermal decomposition upon aging, as suggested by the certain historical accounts of nitrate film fires. Our studies focus on testing the effects of increased relative humidity and temperature on the condition of three nitrate film samples (1) an IPI Stage 0 1935 film (CN-0), (2) IPI Stage 2 1919 film (CN-2), and (3) an IPI Stage 4 1919 film (CN-4). Based on our previously reported nitrate film water sorption data, we opted to age these three films in controlled environment chambers at 60 °C under 25, 50, and 80 %RH to simulate storage under conditions ranging from a refrigerator to a humid film vault lacking careful humidity control. Stacks of five film contiguous frames were aged under these various humidity conditions for 0, 15, 30, 60, and 90 days in order to simulate the conditions of rolled film stored on a film reel. At each of these time points, samples are removed from the environmental chamber and analyzed by the IPI Acidity Test, visual inspection and documentation, size exclusion chromatography (SEC) to obtain the polymer film molecular weight, and thermogravimetric analysis (TGA) to obtain the thermal decomposition profile and deflagration temperature. According to the "Arrhenius-type" kinetic analysis for film decomposition previously reported by Nishmura and co-workers, the 90-day time point corresponds to aging a film kept at 36 °F (standard refrigerator temperature) for 13.8 years and the 365 day time point corresponds to aging the film for 55.7 years.

Preliminary analyses of the aged films are underway and have revealed some important yet not unexpected changes in the film condition. Aging CN-0 for up to 90 days under 25 %RH results in no obvious changes in the film condition upon visual inspection, and the IPI Acidity Test indicates that the film does not become acidic. Thus, low humidity conditions do not seem to trigger film decomposition. Aging the CN-0 film sample at 80 %RH results film decomposition from Stage 0 to Stage 2 over the course of 60 days. Additionally, we note that the film: (1) evolves a noxious and acrid odor associated with a brown gas that is likely NO_2, (2) becomes sticky and discolored, (3) qualitatively becomes more brittle, and (4) the emulsion loses its surface sheen. IPI Acidity tests indicate that the film pH drops to ~4.5, consistent with the decomposition by hydrolysis of the nitrate esters to generate nitric acid (HNO_3). In spite of these dramatic changes, size-exclusion chromatography analyses of CN-0 aged at 60 °C under 80 %RH indicate that the molecular weight of the film base does not change upon nitrate ester hydrolysis. CN-2 aged for 60 days under 80 %RH results in a similar change in condition from Stage 2 to Stage 3, evidenced by the formation of islands and bubbles in the gelatin layer on the nitrate film base. However, thermogravimetric analyses of all of the aged films shows that their thermal decomposition profiles are not appreciably different from the initial film samples (0 days of accelerated aging). Upon removing the emulsion from the CN-2 film aged for 60 days at 60 °C under 80 %RH by bleach treatment, we note that the decomposition profile of the film is dramatically different: the film is much more stable. The origin of this effect is a target of current investigations.

Currently, the aging trials are ongoing with anticipated data collection at the 180 and 365 day time points. In addition to the aforementioned analyses of the aged films, we have established a collaboration with Amanda Strom in the Materials Research Laboratory Core Facility at the University of California–Santa Barbara to perform tandem thermogravimetric analysis coupled with mass spectrometry to identify the nature of the volatile components evolved on heating nitrate film prior to deflagration. The results of these studies will be reported in due course.

Survey of practicing archivists:

The Archives Group of the Nitrate Study Committee met in December 2012 to develop a survey in the hopes of learning more about how institutions care for and how they are affected by the regulations governing nitrate film. After much discussion, a survey of twenty questions was developed. The questions focused primarily on three areas: how institutions store nitrate film, how government regulations affect the ability to collect, store and ship nitrate film, and people's knowledge and perception of nitrate film.

The survey was first sent just to the Nitrate Committee of the Association of Moving Image Archivists (AMIA) on March 9 and was sent to the AMIA listserv on May 31. The Committee is exploring ways the survey can be sent to the membership of the International Federation of Film Archives (FIAF), the Council of State Archivists (COSA), and the Society of American Archivists (SAA). As of July 12, 35 people or institutions had completed the survey. The Committee has tentative plans to present findings from the survey at the 2013 AMIA conference in Richmond, Virginia; the survey and its results will also be included on the section dedicated to the nitrate study on the WCFTR website which will be available by November 2013.

Annotated bibliography:

The annotated bibliography is designed to be a comprehensive, cross-discipline collection of sources on cellulose nitrate. The focus is on nitrate moving image stock, but included in the collection are also sources dealing with cellulose nitrate objects and still image stock. The sources include peer reviewed, trade and popular press articles, historical accounts, literature reviews, websites and forum postings, conference proceedings, practitioner handbooks, safety standards, and government publications, and they derive from a variety of communities, including: archivists and conservators, chemists and polymer scientists, historians, film industry practitioners, safety or standards organizations, and government agencies. A PDF of each source is entered into the citation manager software EndNote, where it is provided with an abstract, a straightforward account of the source's content; an annotation, a description of the source's relevance and any pertinent aspects; and relevant tags to aid in sorting and classification. The articles are also given a rating to indicate how detailed they are and how relevant they are to the project. Of the 300 documents in the bibliography, less than 1/3 still need to be annotated. Work on the annotated bibliography is continuing with the aid of a UW-Madison graduate student from the Communication Arts department, with the aim of completing the project over the summer or early into the fall. A PDF version of the annotated bibliography, with links to the articles themselves, will be included on the project website in an effort to disseminate our findings widely to the archival community. We hope that the ratings system and the classification tags will allow for easy navigation of the bibliography by visitors to the site, while the abstracts and the annotations will help visitors select sources that will be of the most use to their own work.

Physical inspection process:

The physical inspection portion of the project was designed to see if there are correlations between what we can see and measure on the film stock and what the chemical test results show. If we determine that such correlations exist, then archivists and conservators may be able to examine the nitrate stock in their holdings using simple tools and determine its stability. We examined individual frames of our three sample films, one frame being the sample size for the accelerated aging tests. We also examined samples of sheet film, one sample dated between 1900 and1910 and another dated from the 1920s. Sheet film samples about the size of a 35mm frame were cut from the center of a larger sheet for testing. We measured the density of each frame with a densitometer, and the thickness of each frame with a micrometer. The base was examined for brittleness, softness and yellowing; the image for stickiness and fading, and the frame as a whole for buckling, tears, or folds and for the presence of foreign matter. The damage was rated as light, moderate, or heavy, depending on how much of the frame was affected. We also counted the number of broken sprockets, and measured in millimeters how much of the image had disappeared due to degradation. Finally, using a measured lupe, we counted the number of millimeters of each frame that was scratched, estimating that each scratch covers about .05 mm. Much of our rating was determined by comparison, using the stage-0 film, which is in almost perfect condition, as a guideline for rating the damage evident on the stage-2 and stage-4 samples. One out of five frames was also photographed using Reflectance Transformation Imaging (RTI), and all frames were scanned in order to obtain a good visual of the physical damage. This portion of the project was completed in March 2013, and the samples were then sent over to the chemistry department for the accelerated aging trials. While the chemical tests have showed the importance of the emulsion layer in the degradation process, clear correlations between the physical inspection portion of the project and the accelerated aging trials are yet to be determined.

Progress:

The enterprise is on track with another semi-annual report scheduled for January 2013. In autumn we will construct a "nitrate project" web site as part of the redesign of the existing web site for Wisconsin Center for Film and Theater Research. It is expected to be ready by October 2013. The Archives Group has also submitted a proposal to the Association of Moving Image Archivists for a panel at the November 2013 meeting to report on research and findings. This would be a follow-up to a 2012 AMIA session in which we described the early phases of the project.

Semi-Annual Performance Report

Report ID: 105407

Application Number: PR5014112

Project Director: Vance Kepley (vikepley@wisc.edu)

Institution: University of Wisconsin, Madison

Reporting Period: 7/1/2013-12/31/2013

Report Due: 1/31/2014

Date Submitted: 1/31/2014

Title Page

NEH Interim Report: July-December 2013

Project Title: Investigation of cellulose nitrate based film chemical decomposition and associated fire risk

Project ID number: PR-50141-12

Home Institution: University of Wisconsin-Madison

Project partners: Wisconsin Historical Society/ UW-Madison Department of Chemistry/ Wisconsin Center for Film and Theater Research

Submitted by: Vance Kepley (Wisconsin Center for Film and Theater Research)

Submission: January 31, 2014

Narrative Report (PR-50141-12)
July-December 2013

Personnel:
Oversight and planning responsibilities continue to be shared by a working committee representing the project's campus partners: Professor Mahesh Mahanthappa (co-PI, Department of Chemistry), Kathleen Mullen (Wisconsin Historical Society), Maxine Ducey (Wisconsin Center for Film and Theater Research), Mary Huelsbeck (WCFTR), and Vance Kepley (project director, WCFTR). Project assistants were Mr. Milton H. Rapollet-Podresa for chemistry research, through much of the period, and Ms. Amanda McQueen for archival and historical research. There was one significant personnel change. Mr. Rapollet-Podresa ended his service as the Chemistry project assistant and was replaced by chemistry student Mr. Allen Wang. Mr. Booth Wilson, a film graduate student in the Communication Arts Department was hired on an hourly basis to produce a set of short video illustrations of chemistry research, described below.

Bibliography and Dissemination:
During the last part of 2013, PA Amanda McQueen substantially completed the upgrade of the project bibliography. The annotated bibliography is designed to be a comprehensive, cross-discipline collection of sources on cellulose nitrate. The focus is on nitrate moving image stock, but included in the collection are also sources dealing with cellulose nitrate objects and still image stock. The sources include peer reviewed, trade and popular press articles; historical accounts; literature reviews; websites and forum postings; conference proceedings; practitioner handbooks; safety standards; and government publications, and they derive from a variety of communities, including: archivists and conservators, chemists and polymer scientists, historians, film industry practitioners, safety or standards organizations, and government agencies. The bibliography is composed of 300 sources to date, though we hope to be able to add to it in the future. Each source has been provided with an abstract, a straightforward account of the source's content; an annotation, a description of the source's relevance and any pertinent aspects; and relevant tags to aid in sorting and classification. The articles are also given a rating to indicate how detailed they are and how relevant they are to the project. We are currently working on finding the most useful way to organize the information in the annotated bibliography, with the potential option of creating a searchable database for our website. Otherwise, we aim to make the bibliography available through the website in PDF form.

To help publicize our work on the grant project, are designing a website to be hosted through the website for the Wisconsin Center for Film and Theater Research. The website moves through the project chronologically, telling the narrative of the project's origins, and the steps that our historical and chemical teams have taken to begin answering our research questions. Included on the website is a detailed account of the project's background; explanations of the chemical analysis we performed on the samples and some preliminary results; the annotated bibliography; and the results of the survey that we sent to archival institutions, questioning them about their day-to-day practical handling of nitrate film. We have also included information about and thanks to the organizations that have funded and supported our project. A draft of the website was debuted at the AMIA conference in November 2013, and we are currently working on revisions to the content, with the hopes of having the website go live in the next few months.

An important component of the website is to be demonstrational videos. For the chemical analysis section of the website, short videos were created to help showcase and explain certain tests that our chemists performed on the nitrate samples. We believed that the archivists and historians who will be the primary visitors to our website may not be as familiar with the chemical tests we used, and we thought that visual demonstrations and explanations would be an interesting and informative way to explain them. We made four videos with our chemistry RA, Milton Repollet-Pedrosa, covering the following topics: the chambers for the accelerated aging trial, the process of thermogravimetric analysis, the process of gel permeation chromatography, and the process of nuclear magnetic resonance. A fifth video shows the history PA, Amanda McQueen, performing the visual inspection process of the samples in the laboratory at the Wisconsin Historical Society. All the videos contain a voice over explanation of the process being demonstrated and are designed to supplement prose explanations on the website. The videos were shot and edited by a Communication Arts graduate student with filmmaking experience, and were overseen by Amanda McQueen.

As part of the dissemination process, a report on the project was delivered at the American Association of Moving Image Archivists (AMIA) at the organization's December 2013 national meeting in Richmond, VA. The panel consisted of Mary Huelsbeck of WCFTR (chair), Kathleen Mullin of Wisconsin Historical Society, and Heather Heckman of the University of South Carolina, with Professor Mahesh Mahanthappa appearing via Skype. The panel provided the second report on the state of the nitrate project to an audience of professional archivists. This was a continuation of a report given a year earlier at the AMIA conference in Seattle, WA.

Chemical Analysis:

During the July 2013–January 2014 period, The Chemistry team continued the accelerated aging trials of heritage nitrate films under the previously established temperature and relative humidity (%RH) conditions to identify the role of these two environmental factors in governing the thermal stability and flammability of aging film stocks. Historical accounts of various nitrate film fires have suggested that these film stocks become less thermally stable and more susceptible to deflagration upon long–term storage. Multiple samples of each of three heritage nitrate film samples are being aged at 60 °C under 30, 50, and 80 %RH to simulate long–term storage under conditions ranging from a refrigerator to a film vault lacking environmental controls. The three film samples are: (1) an IPI Stage 0 1935 film (CN–0), (2) IPI Stage 2 1919 film (CN–2), and (3) an IPI Stage 4 1919 film (CN–4), wherein the Stage designation relates to the condition of the film according to the existing IPI classification scheme. In order to simulate the aging of film wound on a reel, each of our aging experiments employs a stack of five contiguous film frames that are loosely tied together through the film projector sprocket holes with a Teflon–coated copper wire. After 0, 15, 30, 60, 90, and 180 days of aging in our controlled environment chamber, we removed stacked samples and inspected them visually prior to conducting several quantitative chemical tests (*vide infra*). Nishimura and co–workers previously established that cellulose nitrate film decomposition follows Arrhenius–type kinetics whereby the rate of decomposition doubles with every 10 °C increase in temperature. Therefore, film samples aged for 180 days at 60 °C correspond to samples stored in a standard refrigerator (~36 °F) for 27.6 years.

In our aging trials, we have generally observed that: (1) all of the film samples evolve a noxious, brown gas with an acrid odor, (2) the samples become sticky and discolored, (3) they become brittle and difficult to handle, and (4) the emulsion loses its sheen and significantly fades and/or bubbles. The noxious brown gas appears to be nitrogen dioxide (NO_2, the same brown gas that leads to the "brown cloud" associated with urban air pollution), which originates from nitrate ester hydrolysis in the film base and subsequent decomposition of the resulting nitric acid (HNO_3) in air. The stickiness of the samples possibly results from the decomposition of the emulsion that we observe visually, which then promotes adhesion of the stacked film samples. The origin of the increased brittleness of the samples remains unknown, as it indicates the diminished efficacy of the camphor plasticizer incorporated into the film base during its manufacture. However, camphor is known to undergo decomposition to camphoric acid in the presence of concentrated nitric acid. Thus, we tentatively hypothesize that this decomposition pathway decreases the amount of camphor present and leads to embrittlement of the aged film base.

CN–0 Film Samples. We previously noted that we did not visually observe any appreciable changes in CN–0 samples aged at 30 %RH for up to 90 days, and that the IPI acidity tests did not indicate any change in the acidity of the samples. However, aging the same CN–0 sample at 80 %RH for 60 days resulted in its transformation from a Stage 0 to Stage 2 film, with a sticky emulsion layer. This physical change was accompanied by our observation of a lower pH (pH 4.5) in IPI Acidity Test analysis of this sample. This result is consistent with the aforementioned observation of a brown gas in the aging chamber, due to the generation of nitric acid (HNO_3) by nitrate ester hydrolysis.

We have recently completed our analyses of CN–0 samples aged for 0–180 days, using the IPI Acidity Test, size exclusion chromatography (SEC) to determine whether the cellulose nitrate polymer film base molecular weight is changing, and thermogravimetric analysis (TGA) to obtain information about its thermal decomposition profile and deflagration temperature. The IPI acidity tests for all of these samples demonstrate that the films becomes acidic, again consistent with the evolution of a brown gas in each of the controlled environment chambers. SEC analyses indicate minimal changes in the overall cellulose nitrate base polymers' molecular weights, in spite of the presence of a substantial amount of nitric acid. In general, the CN–0 samples aged at 60 °C under 30, 50, or 80 %RH for up to 0 days exhibit single stage decomposition (combustion) by TGA at temperatures ~ 180 °C with statistically insignificant deviations in the presence or absence of the emulsion layer (emulsion layers are removed by immersion of the film samples in bleach, followed by washing with de–ionized water). However, CN–0 samples with an emulsion layer aged for 180 days at all three relative humidity conditions bubble significantly near T ~ 170 °C prior to catastrophic thermal decomposition near ~180 °C. We surmise that this bubbling of the film arises from the volatilization of gases trapped in the film, in the gelatin layer, or at the interface between these two layers.

We have observed significant changes in the physical states of the final CN–0 samples (360 day time point) as of January 28, 2014 (see Figure 1). From the images shown below, ones see that the CN–0 aged under 30 %RH seems to have liquefied. This sample appearance is possibly consistent with the decomposition to Stage 3 nitrate film ("honey"). CN–0 aged under 50 %RH appears to have become brittle and

Figure 1. Photographs of CN–0 film samples after 10 months of accelerated aging at 60 °C at 30% (*left*), 50% (*center*), and 80% (right) relative humidity.

cracked, whereas CN–0 under 80 %RH appears to be a sticky stack of film frames on which the image layer has completely bleached. We will continue to monitor the physical appearance of these samples, prior to subjecting them to chemical analyses in late March 2014 after 360 days of accelerated aging.

CN–2 Samples. The CN–2 samples exhibit markedly different thermal decomposition profiles according to our TGA analyses. After 15 days of aging, the CN–2 specimens exhibit a staged weight loss with increasing temperature and no single catastrophic decomposition (decomposition onset ~ 180–190 °C; complete decomposition at $T \geq 250$ °C). The more gradual decomposition process observed for the CN–2 films is consistent with the notion that the degradation process occurs by hydrolysis of nitrate esters along the cellulose nitrate polymer backbone, which ultimately decreases the flammability of the resulting materials. (Note that these samples evolved from their initial state as Stage 2 films at the beginning of our trials to Stage 3 films after 60 days of aging at 80 %RH.) We surmise that the formation of islands and bubbles in the gelatin layer effectively allows for the release of any trapped gases, thus mitigating any bubbling prior to decomposition.

We expect our accelerated agings trials to end in late March, after which we will present our complete findings and chemical analyses.

Semi-Annual Performance Report

Report ID: 112804

Application Number: PR-50141-12

Project Director: Vance Kepley (vikepley@wisc.edu)

Institution: University of Wisconsin, Madison

Reporting Period: 1/1/2014-6/30/2014

Report Due: 7/31/2014

Date Submitted: 7/28/2014

Title Page

NEH Interim Report: January 1-June 30, 2014

Project Title: Investigation of cellulose nitrate motion picutre film chemical decomposition and associated fire risk

Project ID number: PR-50141-12

Home Institution: University of Wisconsin-Madison

Project partners: Wisconsin Historical Society/ UW-Madison Department of Chemistry/ Wisconsin Center for Film and Theater Research

Submitted by: Vance Kepley (Wisconsin Center for Film and Theater Research)

Submission: July 24, 2014

Interim Report (PR-50141-12)
January-June 2014

Personnel:

Oversight and planning responsibilities continue to be shared by a working committee representing the project's campus partners: Professor Mahesh Mahanthappa (co-PI, Department of Chemistry), Kathleen Mullen (Wisconsin Historical Society), and Mary Huelsbeck (Wisconsin Center for Film and Theater Research), and Vance Kepley (project director, WCFTR). WCFTR Film Archivist Maxine Ducey, who had served on the committee through 2013, retired in January 2014. The chemistry project assistant during this period was Mr. Allen Wang. Ms. Amanda McQueen, who had been the PA for archival and historical research, took another appointment during spring 2014 academic semester, and that PA position was vacant during most of the period in question.

With the archives history position vacant during spring 2014 the historical research was limited to refining the bibliography and doing some advance work on a website which will figure in dissemination. The PA position will be filled again in fall 2014 and the historical research will resume. One significant project to launch will be oral histories with veteran archivists, projectionists, and film laboratory workers about their experiences in handling cellulose nitrate movie film. We applied for and received a no-cost extension for the period July 2014-June 2015. The chemistry group, Professor Manthappa working with Mr. Wang, worked productively through the January-June 2014 period, completing accelerated aging trials. That research is described below.

Accelerated Aging Trials:

During the January 1–June 30, 2014 period, we completed our accelerated aging trials of heritage nitrate films under the experimental protocols described in earlier reports, whereby film samples were aged in controlled temperature and relative humidity environments to ascertain how these variables affect film base stability and flammability. Through these studies, we aimed to test the hypothesis that long-term storage of nitrate film leads to its decreased thermal stability and thus increases its deflagration risk during long-term storage. In order to simulate a range of possible of conditions under which film may age in household basements, refrigerators, and film vaults, we chose to age our film samples at 60 °C under 30, 50, and 80 %RH (relative humidity) conditions. Three film samples were chosen for this study: (1) an IPI Stage 0 1935 film (CN–0), (2) IPI Stage 2 1919 film (CN–2), and (3) an IPI Stage 4 1919 film (CN–4), wherein the "Stage" designation refers to the condition of the film according to the IPI classification scheme. In order to simulate the aging of film wound on a reel, we aged stacks of five contiguous film frames that were loosely tied together through the film projector sprocket holes using a Teflon–coated copper wire. After 0, 15, 30, 60, 90, 180, and 360 days of aging in our controlled environment chamber, we removed film frame stacks and inspected them visually prior to conducting several quantitative chemical tests (see below for details). Nishimura and co–workers previously established that cellulose nitrate film decomposition follows Arrhenius–type kinetics whereby the rate of decomposition doubles with every 10 °C increase in temperature. Therefore, film samples aged for 360 days at 60 °C correspond to samples stored in a standard refrigerator (~36 °F or 2 °C) for 55.7 years.

Our previous report for the July 2013–January 2014 reporting period described our findings through the 180 day sampling time point, along with hypotheses related to the evolution of noxious gas from the film samples, the sticky nature of the film samples after aging, and their embrittlement. In this report, we focus solely on our final analyses of samples associated with the 360 day sampling time point.

CN–0 Film Samples. We recently completed our analyses of CN–0 samples aged for 360 days, using the IPI Acidity Test and thermogravimetric analysis (TGA) to assess their thermal decomposition profiles and deflagration onset temperatures (T_{decomp}). As noted in our prior report, visual inspection of the aging CN–0 film samples after ~10 months (Jan. 28, 2014) at 60 °C revealed in the formation of a viscous liquid at 30% RH (possibly, the "honey" or "viscous froth" states of film decomposition), a brittle and rusty color solid at 50% RH, and a yellow-brown solid devoid of image at 80 %RH.

Comparative proton nuclear magnetic resonance (^{1}H NMR) analyses in dimethylsulfoxide (DMSO-d_6) of CN-0 samples aged for 360 days under 30, 50, and 80 %RH yielded dramatically different and surprising results. ^{1}H NMR of the 30% RH sample revealed that the typically broad peaks associated with a polymeric species were completely absent and replaced only with sharp resonances, which could be attributed to small molecules. The only ^{1}H NMR resonances observed are those for glucose and possibly nitroglucose, thus indicating that this film sample completely depolymerized. Analyses of the 50 %RH sample show that it exhibited the highest level of denitration, whereas the 80% RH sample exhibited the lowest level of denitration. Thus the denitration of the film stock decreases in the order:

$$30\ \%RH \sim 50\ \%\ RH > 80\ \%RH$$

Since hydrolytic denitration is expected to yield nitric acid, one would expect that the 50 %RH sample should be the most acidic. IPI Acidity Tests on these film samples demonstrate that the acidity of these samples decreases in the order:

$$50\ \%RH > 30\%\ RH > 80\%\ RH,$$

which correlates well with our expectations. TGA analyses also indicate that the samples exhibiting higher denitration levels decompose more gradually (30 and 50 %RH) with higher decomposition onset temperatures (T_{decomp}), whereas the minimally denitrated 80 %RH sample ignites with no statistically significant change in T_{decomp}.

CN–2 Samples. As part of our accelerated degradation trials, we also aged a CN-2 sample for 360 days at 60 °C under the most aggressive 80 %RH conditions. In the samples taken at 90 and 180 days, we noted that these films had appreciably denitrated by ^{1}H NMR and that the thermal decomposition occurred in stages, with a higher T_{decomp} and no single catastrophic deflagration. The 360 day samples from this batch also decompose only slowly, a result that is consistent with their increased denitration upon aging.

Preliminary Conclusions. Our accelerated aging trials demonstrate that aging pristine CN-0 film at 50% RH at 60 °C leads to the highest level of denitration to yield an extremely brittle, brownish solid that visually appears to be a precursor to "brown powder." As a consequence of its low nitration level (6% as compared to 18-20% for the pristine film), the aged material loses its flammability. Denitration in this sample to a less substituted cellulose also likely decreases the efficacy of camphor as a plasticizer, accounting for the brittle nature of the material. Thus, the film has decomposed into a non-hazardous solid. Aging the same CN-0 film under 30% RH at 60 °C surprisingly leads to its depolymerization to a glucose/water solution. Hence, aging under lower RH leads to a liquid decomposition product that is a non-hazardous nuisance. Finally, aging the CN-0 at 80% leads to the formation of a film that is devoid of its image, yet retains its flammability. The fact that lower RH conditions lead to more denitration with the consequent generation of non-hazardous materials run counter to our initial expectation high RH would cause greater denitration and minimize the hazards associated with the decomposed samples.

We are currently developing a chemical model that would explain these somewhat surprising results, in order to help to provide guidance to the archival community regarding mitigating hazards associated with long-term storage of heritage nitrate film.

Note that out findings may also provocatively suggest that the Kodak-recommended storage condition of 50% RH at 10 °C derives from the fact that this leads to the decomposition of the film base into a non-hazardous solid that is amenable to procedurally simple and routine chemical disposal procedures.