Chemical and Physical Testing of Cellulose Nitrate Samples (Excerpt)

3. Physicochemical Characterization of Cellulose Nitrate Film Samples

Our initial chemical characterization of the nitrate film samples described above sought to assess the validity of correlations between the five-stage classification scheme for cellulose nitrate condition, the molecular composition of the film, and its ultimate thermal stability. A substantial number of literature sources claim that the combustibility of nitrate films increases in the later stages of decomposition, albeit with a few exceptional references suggesting that flammability actually decreases in advanced states of decay. To assess the validity of these conflicting empirical correlations, we employed five different tools in the study of the three different heritage nitrate film samples described above: (1) the Image Permanence Institute (IPI) Acidity Test for nitrate film, (2) size-exclusion chromatography to correlate the molecular weight of the cellulose nitrate polymeric film base and the attributed stage of decay, (3) elemental analysis by combustion to determine quantitatively the chemical element composition of the film base, (4) proton nuclear magnetic resonance (^{1}H NMR) spectroscopy of dissolved nitrate film bases (gelatin, or emulsion, removed) to understand their chemical structures, with a specific emphasis on quantifying the nitration level of each sample, (5) thermogravimetric analysis (TGA) to assess the decomposition onset and deflagration temperatures of these samples, and (6) differential water sorption studies to measure water uptake of nitrate film samples. In the following sections, we describe the detailed results of our various analyses. Full descriptions of the experimental procedures, analytical instruments, and analysis parameters used are given in Appendix 3.

3.1 The IPI Acidity Test

Based on previous observations that nitrate film stock becomes increasingly more acidic as it decays by virtue of denitration and other chemical processes (Adelstein et al., *SMPTE J.*, **1995**, *104*, 281-291), the IPI established a standardized test for nitrate film known as the IPI Acidity Test. We adopted a variant of this test in which we soaked a 50 mg film sample in 5 mL of deionized water in a sealed container for 24 h at 22 °C to leach any acids into the aqueous solution, after which the pH of the solution was measured using pH paper. The pH, defined as pH = −log[H_3O^+], provide a direct measure of the acidity of the solution. We conducted IPI acidity tests on film frames taken from **CN-0**, **CN-2**, and **CN-4**. Since water takes up atmospheric carbon dioxide, which renders it acidic, and we did not degas the water prior to use in the IPI acidity test, all of the reported pH values are compared to the pH of a control sample of water. The results of our studies, listed in Table 2, are consistent with the general notion that the pristine film exhibits an undetectable acidity within the resolution of this experimental protocol, and that the acidity of the nitrate stock that exhibits advanced stages of decay increases (pH decreases).

Table 2. **IPI Acidity Test Results for Heritage Nitrate Film Samples.**

Sample	pH
CN-0	4.8
CN-2	3.5
CN-4	4.0
deionized water (control)	4.8

3.2 Size-Exclusion Chromatography (SEC) Analyses of Heritage Nitrate Molecular Weight:

One commonly held notion is that the level of cellulose nitrate decay is correlated with the molecular weight of the film base, since polymer backbone scission by acid-catalyzed cleavage is known to be one possible degradation pathway. One would expect such scission events to decrease the mechanical stability of the film, leading to the embrittlement typified by Stages 4 and 5 of nitrate deterioriation. Stimulated by this idea, we sought to quantify the molecular weights and molecular weight distributions of the film base using a well-known methodology in polymer science.

Size exclusion chromatography (SEC) is analytical method that enables quantitative determination of the mean molecular weight and breadth of distribution of molecular weights of a polymer sample. This method relies on a separation of the polymer chains based on their hydrodynamic volumes—that is, the size of the constituent polymer chains upon dissolution in a good solvent. SEC separation is achieved by passage of a dilute polymer solution through a separations column comprising porous gel beads having a variety of pore sizes under a constant flow of fresh solvent. The polymers are thus sieved according to their solvated size (see Figure 14): polymer chains that are too large to enter into the gel are excluded and exit the separations column first, while lower molecular weight polymers pass through the gel at a slower rate and elute later. By monitoring the concentration of

Solvent Flow Direction

Figure 14. Schematic depiction of the separation of a polymer sample by size-exclusion chromatography, which separates mixtures of polymers based on their molecular size, specifically, their hydrodynamic volumes (see text for details).

polymer in solution exiting the columns as a function of time, one can measure the molecular weight of the polymer and its molecular weight distribution against some calibration reference standard. Typical calibration standards for SEC analyses of chemically-substituted cellulosic polymers are either poly(styrene) standards in tetrahydrofuran (THF), poly(ethylene oxide) in 0.1 M LiBr in *N,N*-dimethylformamide, or poly(methyl methacrylate) in 0.1 M LiBr in *N,N*-dimethylformamide. Since these molecular weights are calibrated against a standard sample that is not cellulose nitrate itself, we draw only comparisons of the relative molecular weights of the samples that we analyzed, as we are primarily interested in trends in the sample set.
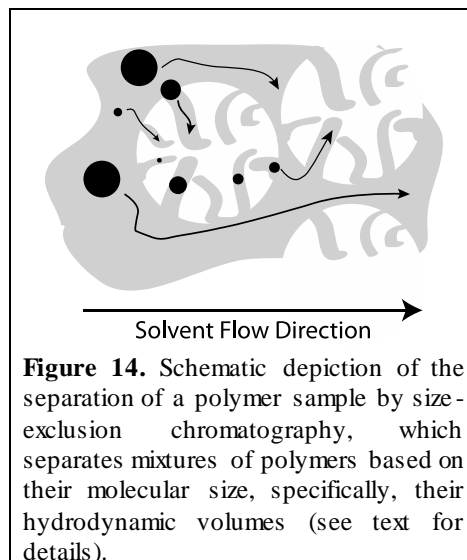
 In this study, cellulose nitrate samples were treated with bleach (~4–5 wt% sodium hypochlorite in water) to remove the emulsion layer and thus enable focused analyses of only the nitrate film base. The resulting nitrate base was then dissolved in THF at a concentration of ~1.5 mg/mL, and this solution was eluted through two commercial analytical SEC columns (see Experimental Section in Appendix 3 for details). Using differential refractive index detection, the volume of solvent required to elute each polymer sample completely from the set of two columns was measured, and these elution volumes were converted to molecular weights using a calibration curve based on 10 narrow dispersity, poly(styrene) standard samples.

The results of our initial SEC analyses of the three film samples against poly(styrene) standards in THF are listed in Table 3, wherein M_n is the number-average molecular weight of the sample. From these data, we see that the molecular weight of the film base is not at all correlated with the age of the film nor its level of decay. Therefore, we conclude that film molecular weight is not related to the five-stage condition classification. We speculate that the molecular weight of the nitrate base layer likely varied during the manufacture of each nitrate film batch, as a direct consequence of the variable sourcing of raw materials and the specific manufacturing and processing conditions. From a historical viewpoint, it is important to understand that cellulose nitrate film was already in widespread use prior to the broad acceptance of the notion that high molecular weight polymers existed by the scientific community. Thus, analytical methods for accurate quality control of the molecular weight of cellulose nitrate film based most likely did not exist at the time of manufacture of many nitrate film stocks. As a point of reference, analytical SEC was only invented and first disclosed in 1955–four years after the discontinuation of nitrate film manufacture.

Table 3. Results of SEC Analyses of Nitrate Film Samples	
Sample	Molecular Weight, M_n (kg/mol)[a]
CN-0	43.0
CN-2	8.0
CN-4	19.0

[a] Number-average molecular weight (M_n) determined by SEC with refractive index (RI) detection in tetrahydrofuran at 22 °C calibrated using 10 narrow dispersity poly(styrene) standards.

We note that previous studies of nitrate film degradation by Edge et al. (*Eur. Polym. J.*, **1990**, *26*, 623-630) and Hill and Weber (*J. Res. Nat. Bur. Stand.*, **1936**, *17*, 871-881) employed viscometry to assess the relative molecular weights of nitrate film samples exhibiting different degrees of degradation. Measurement of the intrinsic viscosity (IV) using an Ubbelodhe viscometer was a common technique for molecular weight measurement prior to the widespread availability of modern analytical SEC instrumentation. IV provides a gross measure of the overall molecular weight of the polymer, whereas SEC utilizes a separations column to sieve the polymer into its components, thereby allowing determination of the number average molecular weight and breadth of the molecular weight distribution; the latter quantity is not available from traditional viscometry studies.

Both analytical SEC and viscometry suffer from the important caveat that the quantitative results depend upon the solvent in which the analysis is conducted. More explicitly, if the solvent is not a good solvent for the polymer, the analysis may give an erroneous result. Since cellulose nitrate film samples with varying levels of nitration may not be soluble to the same extent in tetrahydrofuran as a solvent, we report all subsequent SEC analyses in 0.1 M LiBr in *N,N*-dimethylformamide against poly(methyl methacrylate) standards. We again reiterate that we use SEC analyses to draw only comparisons of the relative molecular weights of the various samples to understand trends in our heritage nitrate film artifacts. We again reiterate that we use SEC analyses only to draw comparisons to the relative molecular weights of the various samples to understand trends in our heritage nitrate film artifacts.

3.3. Quantitative Elemental Analysis of Film Samples

Cellulose nitrate is derived from the nitration of cellulose, which is a polymer of glucose containing exclusively β-glucoside linkages. The degradation of cellulose nitrate occurs by two hydrolysis (literally, "cutting by water") mechanisms: (1) cleavage of the nitrate esters that decorate the

cellulosic backbone in a process known as "denitration," and (2) cleavage of the β-glucoside linkages that comprise the cellulose backbone to yield glucose and low molecular weight, variably nitrated glucose oligomers (see Figure 15). Note that denitration is the reverse reaction of the nitration reaction performed on cellulose to manufacture nitrate film base layers. Denitration is most likely an autocatalytic process, since it liberates corrosive and noxious nitric acid (HNO₃) that can further catalyze both denitration and β-glucoside cleavage of the polymer chains. Both processes reduce, by different mechanisms, the suppleness and overall mechanical integrity of the film in a manner consistent
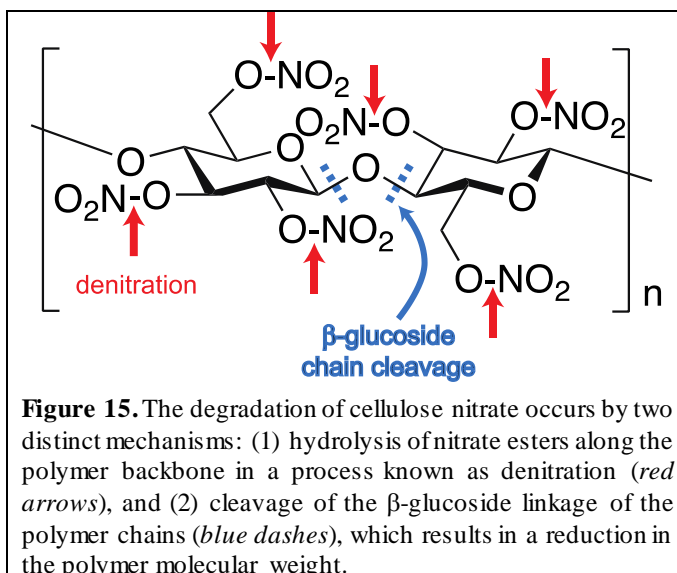

Figure 15. The degradation of cellulose nitrate occurs by two distinct mechanisms: (1) hydrolysis of nitrate esters along the polymer backbone in a process known as denitration (*red arrows*), and (2) cleavage of the β-glucoside linkage of the polymer chains (*blue dashes*), which results in a reduction in the polymer molecular weight.

with advanced stages of materials degradation. Denitration yields a less nitrated cellulose, which can form hydrogen bonds that increase its mechanical rigidity. Chain scission reactions reduce the molecular weight of the resulting polymer, which generally degrades its mechanical performance.

We hypothesized that the five stages of nitrate film deterioration would correlate strongly with the level of film denitration, because the HNO₃ liberated by this process would degrade the emulsion layer of the film by a combination of chemical degradation of the gelatin and oxidation of the silver particles comprising the image in the emulsion layer. One means of testing this hypothesis is to determine the elemental composition of bleached film samples (gelatin removed). We specifically expected to observe lower nitrogen contents in the more severely degraded film samples.

Controlled combustion of carefully weighed, bleached film samples in the presence of excess oxygen and subsequent quantitative analyses of the liberated gases furnishes one means for assessing the elemental composition of the film samples. Samples were sent to Columbia Analytical Labs (Tuscon, AZ) for routine combustion analysis to determine the carbon, hydrogen, nitrogen, and sulfur (CHNS) content of a sample frame from each film reel. Oxygen content was determined by mass balance, based on the initial sample mass. We included sulfur in our analysis, since cellulose nitrate manufacturing typically employed sulfuric acid (H₂SO₄) as a catalyst for the nitration process. However, H₂SO₄ acts as more than a catalyst, as it may become covalently attached to the polymer backbone during the nitration process. While the number of sulfate esters formed in film manufacture is small, the presence of sulfate esters could impact the long-term film stability, since their hydrolysis generates H₂SO₄ that may also catalyze film denitration. The results of our combustion analyses are shown in Table 4.

Supple samples of cellulose nitrate film comprise a combination of cellulose trinitrate (shown in Figure 15) and dinitrate (having two less –NO₂ groups than in Figure 15) repeat units. Lower degrees of nitration of the cellulose backbone were typically less desirable for film applications, due to their relatively brittle nature. For the trinitrate, one expects the nitrogen content of the film to be 13.7 wt%. The dintrate isomer instead contains 12.1 wt% nitrogen. We would have thus

Table 4. Elemental Composition from Combustion Analysis and Proton Nuclear Magnetic Resonance Spectroscopy

	Weight Fraction of Elements Present from Combustion Analysis (C,H,N,S)					Weight Fraction of Elements Present from ^{1}H NMR Analysis[a]				
Sample	% wt Carbon	% wt Hydrogen	% wt Nitrogen	% wt Sulfur	%wt Oxygen[b]	% wt Carbon	% wt Hydrogen	% wt Nitrogen	% wt Sulfur[c]	% wt Oxygen[b]
CN-0	30.18	3.21	10.97	0.20	55.44	29.55	3.25	11.84	0.20	55.15
CN-2	32.29	3.82	10.38	0.39	53.10	32.34	3.67	11.16	0.39	52.45
CN-4	32.24	3.67	10.03	0.33	53.73	31.96	3.63	11.09	0.33	52.99

[a] ^{1}H NMR analysis was conducted in DMSO-d_6 at 22 °C and spectral assignments derived from Hounslow *et al.*, *Aust. J. Chem.*, **1992**, *45*, 627. [b] Oxygen was assumed to comprise the balance of the sample mass in the combustion analysis experiments per convention. [c] Sulfur content used in calculation of the elemental composition of the film derived from combustion analysis.

expected the nitrogen content for the pristine **CN-0** to be bracketed by these two values. However, the nitrogen content was lower than expected for the excellent condition of **CN-0**. We return to this issue in Section 3.4.

Consistent with our initial hypothesis, the weight fraction of nitrogen in the film samples decreases with increasing stages of decay. While the change in nitrogen content may seem small, this difference is measurable, and its impact on the brittleness of the film sample is readily apparent: **CN-4** is much more brittle than the supple **CN-0**.

3.4. Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy Studies:

We also performed solution proton nuclear magnetic resonance (^{1}H NMR) spectroscopy analyses on gelatin-free film samples (bleach treated to remove the emulsion) dissolved in perdeuterated dimethyl sulfoxide (DMSO-d_6) or perdeuterated acetone (acetone-d_6) at 22 °C. ^{1}H NMR is a commonly employed chemical analysis tool for determining the structure and atomic connectivity of organic molecules that contain both carbon and hydrogen. Hounslow and co-workers (*Aust. J. Chem.*, **1992**, *45*, 627-634) previously reported detailed ^{1}H NMR spectral assignments for cellulose nitrate in DMSO-d_6 and acetone-d_6, which allow for identification of the various nitration patterns along the backbone (*e.g.*, trinitration at positions 2, 3 and 6 of the constituent glucose rings *versus* dinitration at positions at 3 and 6, *etc*.). By using our knowledge of the structure discerned from ^{1}H NMR spectra of **CN-0**, **CN-2**, and **CN-4,** along with quantitative integration of the peaks associated with specific protons along the backbone in the range δ 3.6–5.10 ppm in DMSO-d_6, we calculated the relative amounts of cellulose trinitrate and dintrate present in each sample of film base (Table 5). The nitration level varies in a subtle yet detectable manner, with ~ 2.39-2.46 nitrate functionalities per monomer unit. While the differences in the flexibility of the film appear somewhat inconsistent with these relatively small differences in the nitration of the polymer, the polymer molecular weight may significantly affect the observed mechanical properties. However, it is also

Table 5. Degree of Nitration of Heritage Nitrate Film Samples Determined by ^{1}H NMR Spectroscopy in DMSO-d_6 at 22 °C

| Sample	[dinitrate]:[trinitrate][a]	Degree of Nitration [b]
CN-0	1.23:1	2.46
CN-2	1.38:1	2.42
CN-4	1.56:1	2.39

[a] Determined by quantitative ^{1}H NMR. [b] Calculated degree of nitration per monomer unit (with a maximum value of three nitrate moieties per monomer).

possible that the relative brittleness of **CN-2** and **CN-4** arises from different phenomena.

In the course of the above ^{1}H NMR analyses of all of the nitrate film samples, we noticed a large number of sharp peaks in the chemical shift range δ 0.5-3.0 ppm that were consistent with the presence of a significant quantity of a small molecule. Detailed analyses of the spectral data enabled assignment of these peaks to camphor. Quantitative ^{1}H NMR studies indicate that the amount of camphor is as much as 20 wt% in the samples, which accounts for the lower than expected nitrogen content observed by elemental analysis (see Table 4, Section 3.3). Camphor, a terpenoid natural product, was typically added to nitrate film as a plasticizer to increase the suppleness of the film by lowering its glass transition temperature. By accounting for the presence of camphor in the film, we were able to use the ^{1}H NMR analyses to calculate the relative molar amounts of carbon, hydrogen, nitrogen, and oxygen present in each sample. Using the absolute sulfur content derived from combustion analyses of the samples, we were able to quantify the carbon, hydrogen, nitrogen, sulfur, and oxygen content in an absolute manner. The results of these NMR studies (Table 3) are in good agreement with those expected based on combustion analyses. These findings are also consistent with denitration as one of the major degradation pathways for nitrate film stock.
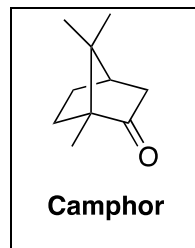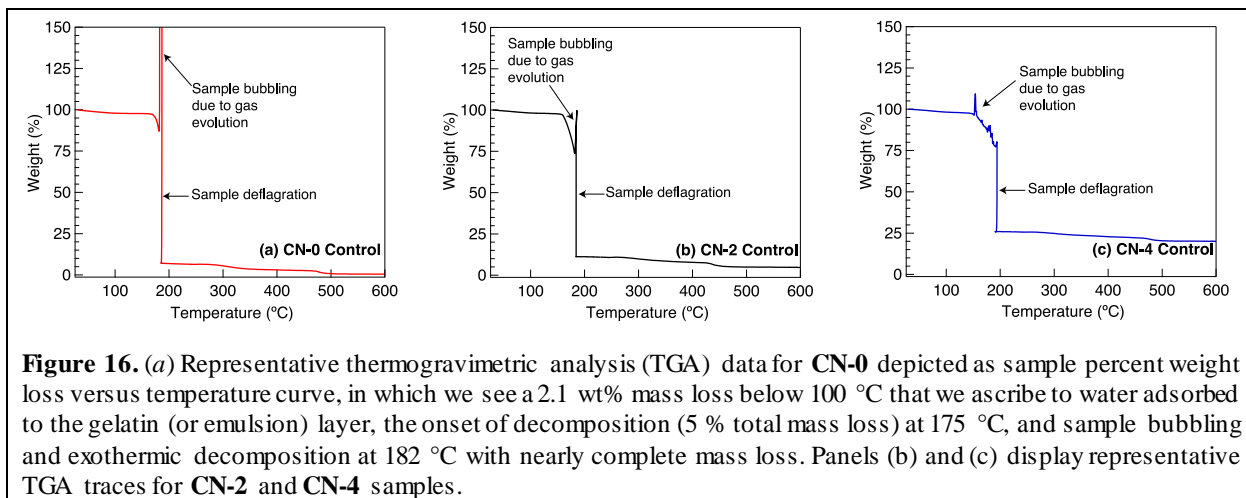
We note that nitric acid is known to react with camphor by an oxidative ring-opening reaction that yields camphoric acid. Consequently, we suspect that some of the observed peaks in ^{1}H NMR spectra of the nitrate film base layers may arise from camphoric acid. Due to our inability to resolve the peaks associated with camphor and camphoric acid, we have ascribed all of the observed NMR signals to camphor. The degradation of camphor to camphoric acid reduces the amount of effective plasticizer in the more degraded film samples, which may conspire with the molecular weight to embrittle **CN-4**. (Camphoric acid is apparently not a plasticizer for cellulose nitrate.) To the best of our knowledge, this degradative reaction of the plasticizer and its impact on nitrate film stability has not been previously documented in nitrate literature.
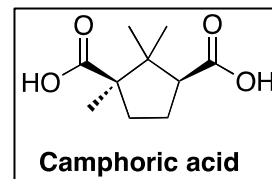
The presence of camphor in these films is significant for fire protection purposes, since camphor is a highly volatile and combustible solid (vapor pressure of 4 mm Hg at 70 °C or 168 °F). While we do not know the initial camphor content in the film at the time of manufacture, the fact that we could observe $\geq$ 20 wt% camphor in the film samples suggests its possible role in nitrate base layer flammability. Given its high vapor pressure, it is somewhat surprising that one cannot detect the distinctive odor of camphor when handling nitrate film. Upon abrading the surface of a single **CN-0** film frame with sand paper (320 P grade with an average particle diameter of 642 μm), we noted the smell of camphor emanating from the film. Since abrasion apparently affects the ability of camphor to escape from the film, we attempted to quantify the level of surface abrasion of the film samples with their physical properties as part of our visual inspection project (see Section 2). However, attempts to correlate surface abrasion with the overall condition of the film failed to yield any substantive insights, and further studies along this line of investigation ceased.

3.5. Observation of the Thermal Decomposition of Heritage Nitrate Film by Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a well-known 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 a constant ramp rate (e.g., 10 °C/min) under a flow of oxygen (20 mL/min flow rate) until it fully decomposes, as evidenced by nearly complete mass loss. We assessed the thermal stability of each film sample by analyzing its decomposition profile: the onset of decomposition (T_{decomp}, defined as the temperature at which 5% mass loss in observed) and the deflagration temperature (T_{deflag}) at which the sample combusted. TGA samples were taken from the center of each film frame, which included both the nitrate film base as well as any remaining gelatin (emulsion) layer. Sample TGA traces for **CN-0**, **CN-2**, and **CN-4** are shown in Figure 16. Sample deflagration gave rise to a unique TGA profile, in which bubbling of the emulsion would cause an apparent initial increase in mass, followed by exothermic sample combustion with significant mass loss. Spontaneous sample combustion typically left behind a residue that decomposed at temperatures $T \geq 300$ °C. A summary of the data from these initial TGA analyses of "as is" film samples (prior to accelerated aging) is given in Table 6.

Figure 16. (*a*) Representative thermogravimetric analysis (TGA) data for **CN-0** depicted as sample percent weight loss versus temperature curve, in which we see a 2.1 wt% mass loss below 100 °C that we ascribe to water adsorbed to the gelatin (or emulsion) layer, the onset of decomposition (5 % total mass loss) at 175 °C, and sample bubbling and exothermic decomposition at 182 °C with nearly complete mass loss. Panels (b) and (c) display representative TGA traces for **CN-2** and **CN-4** samples.

From the data in Table 6, we see that the decomposition onset temperature (T_{decomp}) decreases with increasing stages of decay, as **CN-4** exhibits a T_{decomp} that is ~ 15 °C lower than that of **CN-0**. It is important to recall that this decomposition onset temperature is simply the temperature at which the sample has lost 5% of its original mass—the reasons for the mass loss are not known. The deflagration temperatures of all of the samples are reasonably similar. With the **CN-0** samples, we noted that the surface of the gelatin (image or emulsion) layer developed significant bubbles, consistent with gas evolution from the nitrate base layer (*e.g.*, camphor and nitrogen oxides derived from nitric acid). In order to understand whether the presence of the gelatin (image or emulsion) layer affects the combustibility of the film, we removed the gelatin from the nitrate film stock by brief immersion in 5 wt% NaOCl in water (commercial bleach solution), followed by rinsing with deionized water and air drying. Subsequent TGA analyses of the sample without gelatin exhibited indistinguishable profiles, with complete combustion occurring at ~180 °C. Thus, the gelatin layer apparently plays a minor role in the ultimate thermal stability of the nitrate film samples.

Admittedly, our TGA does not directly mimic the decomposition of nitrate film in a canister within a film vault. A film vault is typically held at constant temperature with modest air circulation, and any gases released by the film remain confined within its storage can and in contact with the film itself. Our thermogravimetric analysis protocol is a dynamic test in which the temperature is raised from 22 °C to some elevated temperature at a constant ramp rate (10 °C/min) under a constant flow of oxygen (20 mL/min),

Table 6. Summary of Initial Thermogravimetric Analyses of Heritage Nitrate Samples[a]

Sample	T_{decomp} (°C)[b]	T_{deflag} (°C)[c]	Notes
CN-0	175 ± 1.6	184 ± 6.6	sample surface bubbles significantly prior to complete combustion
CN-2	156.7 ± 4.5	182.9 ± 4.6	complete combustion
CN-4	152.9 ± 2.8	184.9 ± 5.9	complete combustion
CN-4 no gelatin	155.6 ± 1.9	181.9 ± 1.0	complete combustion

[a] Testing conditions: TGA was run under a 20 mL/min purge of pure oxygen with a ramp rate of 10 °C/min up to 220 °C followed by a jump to 600 °C. Unless otherwise noted, the film samples were tested without removal of the gelatin layer. [b] Decomposition temperature (°C) is defined as the temperature at which 5 % weight loss is observed. [c] Deflagration temperature is defined as the temperature at which the sample completely and exothermically burns (see text for details).

while sample weight loss or decomposition is monitored. To specifically understand nitrate combustibility under the conditions in an archive, one would ideally conduct time-dependent TGA at a fixed temperature of interest (*e.g.*, 30 or 40 °C). To the best of our knowledge, there are no direct nor general correlations between the decomposition and deflagration temperatures measured by dynamic TGA and those arising from the constant temperature time-dependent analyses. We note that the time-dependent studies are extremely time- and resource-intensive, rendering them unwieldy in the context of the large sample set that we sought to survey in our accelerated aging studies. Thus, we utilized the dynamic TGA studies to glean useful information regarding the presence of any volatile compounds in the samples, while also measuring their ***relative*** flammabilities.
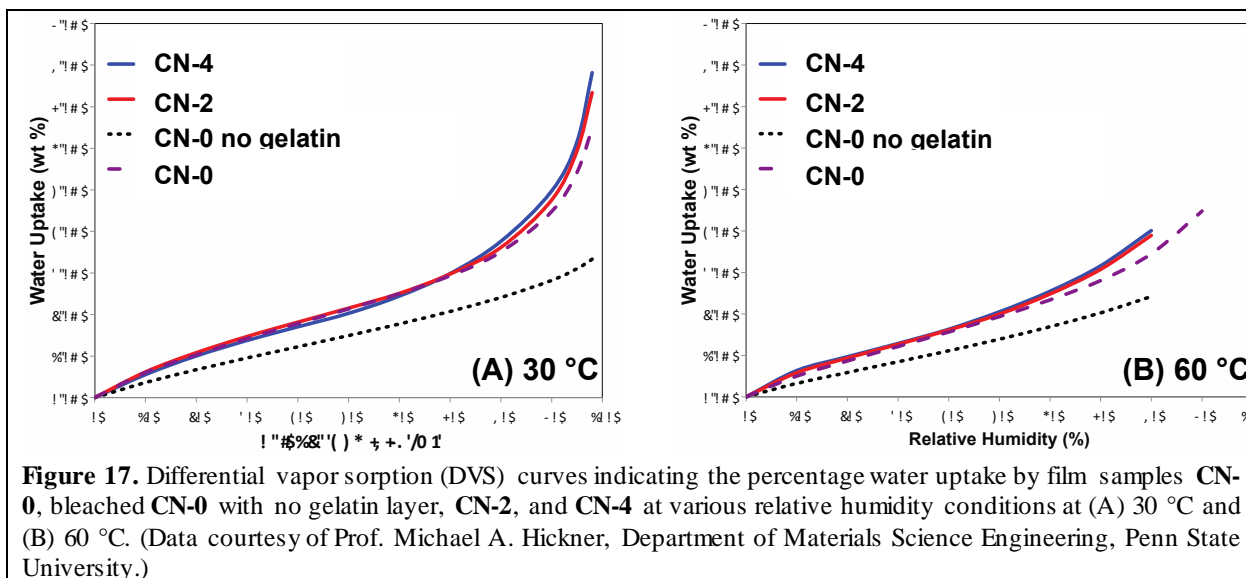
3.6 Differential Vapor Sorption to Quantify Water Uptake by Cellulose Nitrate Film

Since water is a key ingredient in the denitration and hydrolysis reactions that irreparably degrade cellulose nitrate film, we sought to study the water uptake characteristics of these film samples at both 30 °C and 60 °C under a variety of relative humidity (%RH) conditions. In collaboration with Professor M. A. Hickner (Department of Materials Science Engineering at the Pennsylvania State University), we performed differential vapor sorption analyses of **CN-0**, **CN-2**, and **CN-4** film samples. In these experiments, film samples were placed on a sensitive balance and equilibrated in a controlled environment with varying relative humidities. Relative humidity (%RH) is defined as:

$$\%RH = \frac{partial\ presssure\ of\ water\ vapor}{equilibrium\ saturated\ vapor\ pressure\ of\ water}$$

By measuring the equilibrium sample mass under each relative humidity condition at a given temperature, we obtained the water uptake curves shown in Figure 17. From these data, we see that the "as is" film samples exhibit water uptake curves that are nearly identical, with 1.3 wt% water uptake at 30 %RH, 2.1 wt% water uptake at 50 %RH, and 4.0 wt% water uptake at 80 %RH

at 60 °C. Thus, the water uptake is nearly independent of the condition of the gelatin layer. Upon bleaching **CN-0** to remove the gelatin layer, we observed a noticeable decrease in the water uptake characteristics of the isolated cellulose nitrate base. Unfortunately, this suggests that the gelatin layer holding the image that we wish to preserve acts as sponge that draws water to the film that accelerates its degradation.

Figure 17. Differential vapor sorption (DVS) curves indicating the percentage water uptake by film samples **CN-0**, bleached **CN-0** with no gelatin layer, **CN-2**, and **CN-4** at various relative humidity conditions at (A) 30 °C and (B) 60 °C. (Data courtesy of Prof. Michael A. Hickner, Department of Materials Science Engineering, Penn State University.)

3.7 Summary of Initial Physicochemical Studies of Nitrate Film Stability

Our studies up this point indicate that the five-stage classification model accurately correlates with only a few physical and chemical properties of cellulose nitrate films. Increasing stages of decay correlate with lower nitration levels and lower decomposition onset temperatures observed by TGA. However, the five-stage model is not correlated with the molecular weight of the film base, the amount of camphor present, its water sorption characteristics, nor its deflagration temperature. We note that the water uptake of the film samples primarily depends on whether the gelatin layer is present, but not on its condition. These studies provide only correlations, the origins of which are somewhat unclear. Sample variations due to provenance, manufacturing conditions, and developing conditions likely contribute to the exact physical properties.

3.8 Assessing of the Reliability of Visual Inspection of Nitrate Degradation

Given the data generated by the chemical testing performed on our samples, we were unable to make any quantitative connections between what an archivist can observe visually and the flammability profile of a sample of nitrate film. Thus, we do not believe that our visual inspection process or the use of RTI would be useful to archivists and conservators in ascertaining the potential fire risk associated with their nitrate holdings.

4. Accelerated Aging Studies

Accelerated aging of nitrate film under fixed relative humidity conditions at elevated temperatures have been previously reported by Edge et al. (*Eur. Polym. J.*, **1990**, *26*, 623-630), Hill and Weber (*J. Res. Nat. Bur. Stand.*, **1936**, *17*, 871-881), and Adelstein *et al.*(*SMPTE J.*, **1992**, *101*, 336-346;

SMPTE J., **1995**, *104*, 439-447). These earlier studies focused on the physical and chemical consequences of aging small sample sets (*e.g.*, no more than four distinct samples of variable provenance) at temperatures ranging 50–100 °C under dry air, modest relative humidities, and 95% relative humidity (denoted 95 %RH) for variable lengths of time (typically, less than 50 days). By studying how the properties of the film samples change as a function of aging temperature at various time points, Edge *et al.* and Adelstein *et al.* suggest that the degradation of heritage nitrate film obeys zero order or pseudo-first order Arrhenius kinetics. Under this common reaction rate description, one expects and one observes that the rate of decomposition approximately doubles with every increase in the reaction temperature by ~10 °C. While nitrate film degradation does seem to obey Arrhenius-type reaction kinetics up to 80 °C according to work by Edge *et al.*, changes in the mechanism of decomposition through competing pathways alter the observed kinetics above 80 °C.

Based on these previous studies, we sought to gain deeper insights into the degradation of heritage nitrate films **CN-0**, **CN-2**, and **CN-4** under various relative humidity conditions by accelerated aging under 60 °C for up to 365 days. By studying the physical and chemical properties of the film samples removed from these conditions at various aging time points using visual inspection, the IPI acidity test, SEC, ^{1}H NMR, and TGA, we sought to understand how storage environments impact the flammability profiles of these materials. The major objective of this study was to understand whether or not nitrate film becomes more thermally unstable or flammable over time, as suggested by historical accounts of nitrate film fires.

We established detailed testing protocols whereby the pristine film **CN-0** was aged under 25, 50, and 80 %RH at 60 °C in separate controlled environment chambers, while **CN-2** and **CN-4** were aged only under the most aggressive 80 %RH condition at 60 °C in environmental chambers. These accelerated aging conditions were selected in order to mimic storage environments ranging from

a refrigerator to a humid film vault lacking careful humidity control. Prior to accelerated aging, five contiguous film frames from each sample reel were cut, stacked, and fastened together using a Teflon-coated copper wire threaded through the sprocket holes located at the edges of the film. We intended for these film stacks to mimic the conditions of rolled film stored on reels within a film canister, within the limited space constraints of our accelerated aging apparatus. Each film stack was placed in a test tube of sufficient diameter (~2.6 cm) to avoid folding or rolling the film, and six film-loaded test tubes were placed in wide-mouth glass jars containing a seventh test tube filled with a specific saturated water/salt mixture to maintain the desired relative humidity condition within the container (see Figure 18). These sample containers were thermostatted at 60 ± 2 °C using an oven equipped with a PID temperature controller. A saturated $MgCl_2(aq)$ solution was used to maintain 30 %RH, saturated $NaBr(aq)$ for 50 %RH, and saturated $KCl(aq)$ for 80 %RH at 60 °C as measured using commercially available NIST-calibrated hygrometers at periodic intervals. We note that small variations in relative humidity were observed (±7% from the target value).
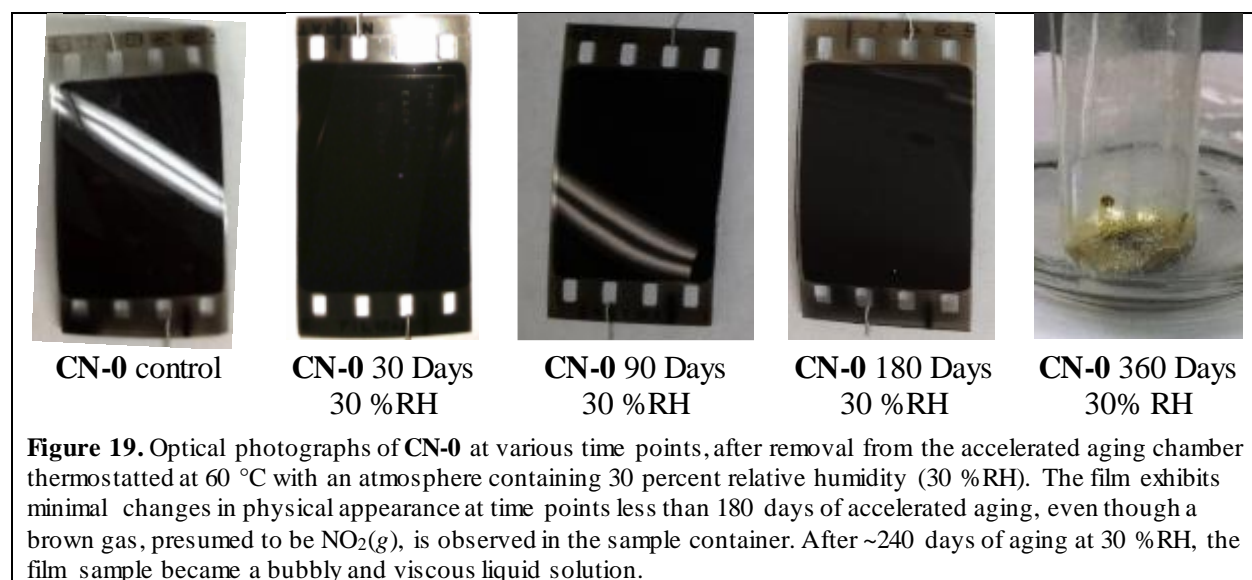

Figure 18. A wide-mouth glass jar with six film-loaded test-tubes and one test tube containing a water/salt solution to maintain the desired relative humidity, which was directly measured using a NIST-calibrated hygrometer.

By removing sample stacks after 15, 30, 60, 90, 180, and 360 days of accelerating aging, we assessed how the physical and chemical state of the film changed as a function of time. Assuming that the degradation of our nitrate samples conforms to the previously reported Arrhenius kinetics, the 90-day time point in our 60 °C accelerated aging tests corresponds to ~13.8 years of aging in a 36 °F (2.2 °C) refrigerator. Under the same assumptions, 365 days of accelerated aging at 60 °C corresponds to 55.7 years of storage in a 36 °F refrigerator or 220 years in a 0 °F (-18 °C) freezer.

In the following sections, we describe the results of our analyses of film samples subjected to these accelerated aging conditions under various relative humidities. After providing detailed findings for each sample aging condition in separate sections, we comparatively analyze the aggregate data to draw some conclusions from these experiments.

*Accelerated Aging of **CN-0** at 30 %RH:*

| **CN-0** control | **CN-0** 30 Days 30 %RH | **CN-0** 90 Days 30 %RH | **CN-0** 180 Days 30 %RH | **CN-0** 360 Days 30% RH |

Figure 19. Optical photographs of **CN-0** at various time points, after removal from the accelerated aging chamber thermostatted at 60 °C with an atmosphere containing 30 percent relative humidity (30 %RH). The film exhibits minimal changes in physical appearance at time points less than 180 days of accelerated aging, even though a brown gas, presumed to be $NO_2(g)$, is observed in the sample container. After ~240 days of aging at 30 %RH, the film sample became a bubbly and viscous liquid solution.

Aging **CN-0** at 60 °C under a 30 %RH atmosphere caused significant changes in the physical appearance of the film samples as documented in the photographs shown in Figure 19. We note that the physical appearance of the film was relatively unchanged after up to 90 days, and only a small amount of a brown gas is observed to build up in the sealed aging chamber over time. This brown gas is tentatively identified as $NO_2(g)$, arising from the denitration of the film. Film denitration generates nitric acid (HNO_3), which is in equilibrium with water and $N_2O_5(g)$ that may thermally decompose into $NO_2(g)$ and other nitrogen oxide byproducts. After 180 days of accelerated aging, the samples lose their sheen. Remarkably, the film degrades into a puddle of viscous, pale yellow liquid after ~240 days of aging. This decomposed product may be related to the "viscous froth" that appears on the surface of degraded nitrate film that falls under the Stage 4 classification.

Detailed analyses of the chemical constitution of the film reveal that this 30 %RH aging condition does not appear to cause the denitration of the film (Table 7). The IPI Acidity tests on samples removed at all of the time points indicate that the film pH ~ 5.5. Note that pH 5.5 is comparable to

Table 7. Results of Chemical and Physical Analysis of CN-0 Samples aged at 60 °C under 30 %RH

Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test[a]	5-5.5	4.5-5.0	5.5	5.5	5.5	6.0	4.0
^{1}H NMR [(NO$_2$)$_2$)]:[(NO$_2$)$_3$] [b]	1.23	1.227	1.21	1.28	1.25	1.303	n.d.[d]
Decomposition Onset Temp (°C) [c]	170.4±0.6	169.3±0.5	169.6±0.3	170.5±2.9	180.5±0.3	180.7±1.4	n.d.[d]
Deflagration Temp (°C) [c]	183.0±7.9	178.0±0.5	177.6±0.3	180.0±1.0	189.7±2.5	191.7±2.1	n.d.[d]

[a] Determined by soaking 50 mg of film in 5 mL water at 22 °C for 24 h and subsequent pH measurement. [b] From quantitative ^{1}H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-d_6, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). [c] Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. [d] n.d. = not determined.

that of a control sample of water. (Note: the pH of water exposed to air is pH 5.5 due to the dissolution of $CO_2(g)$ from the atmosphere.) ^{1}H NMR spectroscopy further demonstrates that the ratio of cellulose [dinitrate]:[trinitrate] remains nearly constant at ~1.2-1.3. These minor variations are within the error of the measurement and are thus considered statistically insignificant. These two chemical analyses suggest that the film remains largely intact until catastrophic degradation occurs at longer times.
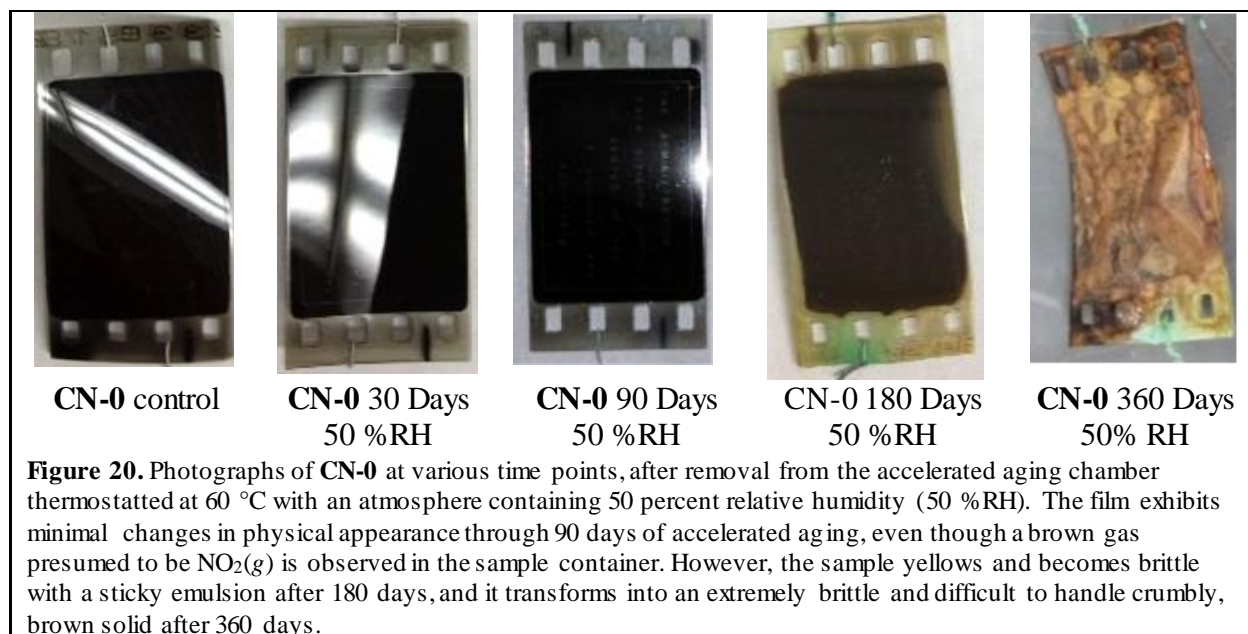
TGA analyses of **CN-0** aged at 30 %RH demonstrate that the film samples exhibit similar thermal profiles to the initial **CN-0** samples, with a slight decrease in combustibility after 90 days. Table 7 listed the decomposition onset temperature (T_{decomp}), at which the sample exhibits 5 % weight loss, and the deflagration temperature (T_{deflag}) for film bearing an emulsion layer. Both T_{decomp} and T_{deflag} remain near 170 and 180 °C, respectively, up to the 90 day time point. After 180 days of aging, these two temperatures increase by nearly 10 °C. However, we note that the shapes of the

TGA profiles indicate that the samples initially bubble due to gas evolution and they subsequently deflagrate at a single temperature with nearly complete weight loss. In order to understand the effect of the gelatin (or emulsion) layer on flammability, we conducted TGA analyses on samples for which the gelatin layer had been removed by immersion in bleach and exhaustive washing with deionized H_2O. Removal of the gelatin layer did not change the observed values of T_{decomp} and T_{deflag} in a statistically significant manner.

TGA analysis could not be completed for the final 360 day sample that decomposed into a puddle of viscous liquid, but we conducted additional analyses aimed at identifying the molecular species present in the solution. ^{1}H NMR spectra of the liquid reveal a forest of sharp peaks, indicating complete degradation of the polymer into small molecule fragments. However, attempts to assign these peaks failed due to the density of peaks observed, likely arising from a complex array of nitrate film decomposition products. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) analyses of a sample in 10 mM CH_3COONH_4 in CH_3CN in positive ion detection mode showed that the mass-to-charge ratio (m/z) arising from the key molecular fragments

observed in this analysis were m/z = 256, 270, 284, 360, 390, and 446 g/mol. The m/z = 270 fragment may correspond to a dinitroglucose arising from depolymerization of the cellulose nitrate film stock into its constituent monomers.

*Accelerated Aging of **CN-0** at 50 %RH:*

| **CN-0** control | **CN-0** 30 Days 50 %RH | **CN-0** 90 Days 50 %RH | CN-0 180 Days 50 %RH | **CN-0** 360 Days 50% RH |

Figure 20. Photographs of **CN-0** at various time points, after removal from the accelerated aging chamber thermostatted at 60 °C with an atmosphere containing 50 percent relative humidity (50 %RH). The film exhibits minimal changes in physical appearance through 90 days of accelerated aging, even though a brown gas presumed to be $NO_2(g)$ is observed in the sample container. However, the sample yellows and becomes brittle with a sticky emulsion after 180 days, and it transforms into an extremely brittle and difficult to handle crumbly, brown solid after 360 days.

Photographs of **CN-0** aged under a 50 ± 5 %RH atmosphere at 60 °C display a different course of physical degradation, as shown in the photographs in Figure 20. In the first 90 days of the film aging, the samples physically appear unchanged and a significant amount of a brown gas is observed to accumulate in the sealed aging chamber. As previously mentioned, we surmise that this noxious brown gas is $NO_2(g)$ arising from the thermal decomposition of nitric acid liberated from the film by hydrolysis. After 180 days, the film loses its sheen and the emulsion becomes uneven and sticky. At the final 360 day time point in this accelerated aging trial, we find that the film samples are extremely brittle, rusty brown solids. These final samples exhibit many of the physical attributes of deteriorated film stock that may ultimately decay into brown powder.

The results of both the IPI acidity test and ^{1}H NMR spectroscopic analyses of the film are consistent with the decay of these heritage nitrate samples by denitration (Table 8). The results of the IPI acidity test indicate that the film becomes significantly acidic after 180 days of accelerated aging with a measured pH = 3.5; it becomes even more acidic at 360 days (pH = 2.5). ^{1}H NMR spectroscopy shows that the ratio of cellulose [dinitrate]:[trinitrate] increases from a baseline value of 1.23 to 7.18 after 360 days of accelerated aging. Thus, the film appreciably denitrates as compared to the samples aged at 30 %RH. SEC analyses further indicate that the nitrate film base molecular weight is relatively invariant after 180 days of accelerated aging, and it precipitously drops as it denitrates.

The observed denitration of the film manifests in substantial changes in the thermogravimetric analyses of the samples aged at 50 %RH for varying amounts of time (Table 8). The decomposition

Table 8. Results of Chemical and Physical Analysis of CN-0 Samples aged at 60 °C under 50 %RH

Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test[a]	5.0-5.5	4.5-5.0	5.5	5.5-6.0	5.5	3.5	2.5
^{1}H NMR [(NO$_2$)$_2$)]:[(NO$_2$)$_3$] [b]	1.23	1.237	1.257	1.287	1.27	1.817	7.177
M_n (kg/mol)	13.1	10.5	9.1	9.2	11.2	15.1	3.5
$Đ = M_w/M_n$	3.04	3.30	3.48	3.27	2.56	2.23	1.85
Decomposition Onset Temp (°C) [c]	170.4±0.6	170.3±0.5	168±1.0	170.6±1.2	180.4±0.9	181.1±0.4	156.2±8.0
Deflagration Temp (°C) [c]	179.4±0.5	178.5±0.3	179.2±0.5	187.5±1.0	189.7±4.8	193.1±2.4	gradual decomp.[d]

[a] Determined by soaking 50 mg of film in 5 mL water at 38 °C for 24 h and subsequent pH measurement. [b] From quantitative ^{1}H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-d_6, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). [c] Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. [d] No deflagration observed: gradual decomposition above 200 °C observed for both the native film and the bleached sample (gelatin removed).

onset temperature (T_{decomp}) initially increases from 170 °C to 181 °C between 0–180 days, and then it drops to 156 °C at 360 days. While this trend may seem counterintuitive, one must recognize that T_{decomp} measures only the temperature at which 5% weight loss is observed. The origin of the weight loss could vary. We speculate that as the film denitrates, it becomes more hydrophilic, and thus the 5 % weight loss temperature decreases as the film takes up water that is expelled at a lower temperature. (As noted in the differential vapor sorption studies above, highly nitrated cellulose **CN-0** hardly takes up 3 wt% water at 50 %RH.) On the other hand, we observe that the deflagration temperature (T_{deflag}) increases monotonically with time. The TGA profiles for the film aged for 180 days or less exhibit initial

Figure 21. Overlay of TGA traces for **CN-0** samples aged at 50 % RH after 180 and 360 days. The 180 day sample exhibits some weight loss, gas evolution and bubbling, and a sharp deflagration point, whereas the 360 day sample degrades gradually due to its high level of denitration.

bubbling due to gas evolution, followed by catastrophic deflagration. However, the sample aged for 360 days exhibits a slower, staged degradation with signs of deflagration (see Figure 21). Thus, we observe that the film aged for 360 days at 50 %RH is ***not*** combustible.
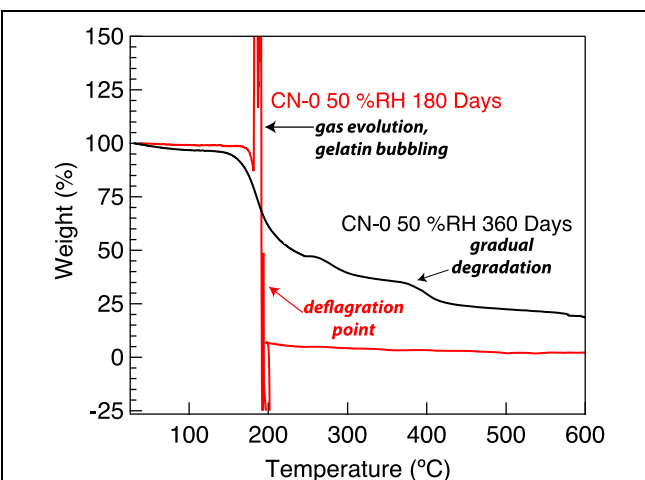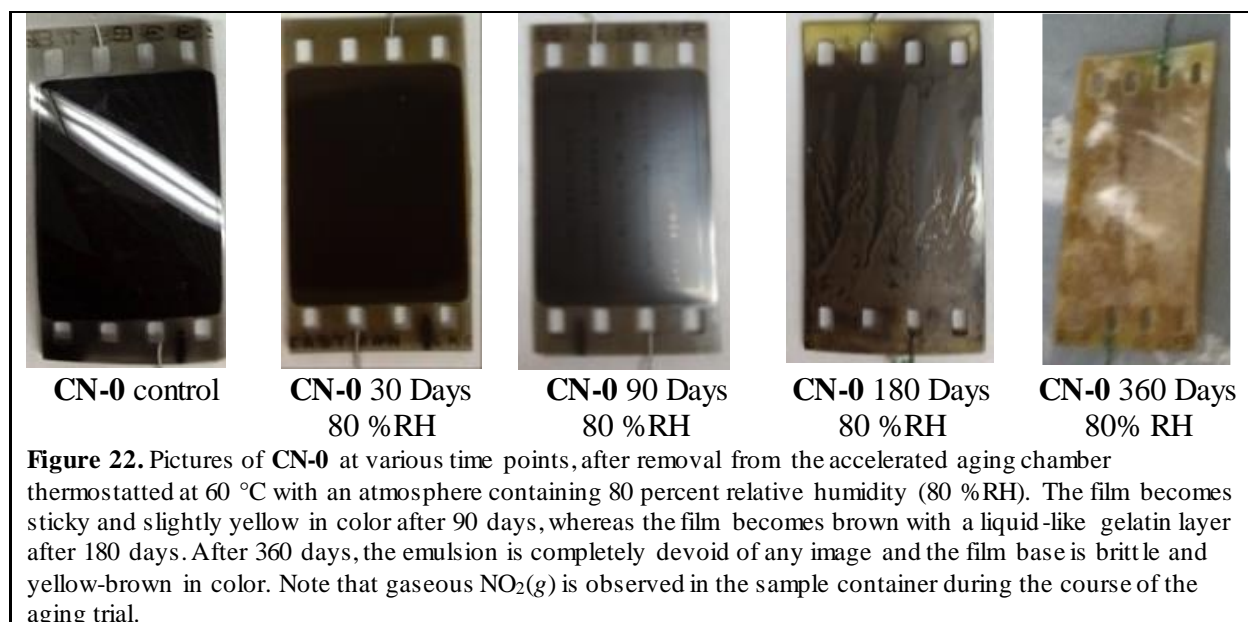
Accelerated Aging of CN-0 at 80 %RH:

Aging **CN-0** at 60 °C under an 80 %RH atmosphere results in the fastest degradation of the emulsion and yellowing of the nitrate film base layer as assessed by simple physical inspection (see Figure 22). After only 90 days under these conditions, the film emulsion is sticky and the base

Figure 22. Pictures of **CN-0** at various time points, after removal from the accelerated aging chamber thermostatted at 60 °C with an atmosphere containing 80 percent relative humidity (80 %RH). The film becomes sticky and slightly yellow in color after 90 days, whereas the film becomes brown with a liquid-like gelatin layer after 180 days. After 360 days, the emulsion is completely devoid of any image and the film base is brittle and yellow-brown in color. Note that gaseous $NO_2(g)$ is observed in the sample container during the course of the aging trial.

layer is yellow. These changes in the physical appearance of the film are accompanied by the formation of brown $NO_2(g)$ in the aging chamber, which arises from HNO_3 decomposition. The gaseous product seems to react further with the gelatin layer. Thus, the film degrades from a Stage 0 pristine film to a Stage 2 material after only 90 days in our aging chamber. Degradation proceeds further to yield a liquid-like gelatin layer and a brown film base after 180 days of aging. Complete image degradation and embrittlement of the yellow-brown nitrate base layer occurs after 360 days.

IPI acidity testing suggests that the pH of the film drops to ~4.5 after 60 days of aging, and that the acidity generally hovers in the range pH = 4-5 throughout the aging trial (see Table 9). ^{1}H NMR analyses indicate that the film does denitrate to some extent, with the apparent ratio of cellulose [dinitrate]:[trinitrate] increasing from 1.23 to 1.4. Thus, the chemical composition of the film does not appear to appreciably change during aging at 80 %RH. The latter assertion is corroborated by the fact that the molecular weights of the film determined from SEC analyses were relatively invariant at all time points. These chemical findings are strikingly discordant with the results of the visual inspection of these aged samples at each time point, providing further evidence that the five-stage classification scheme for nitrate film degradation does not always accurately reflect the true chemical state of the film or its potential hazards.

The relatively small changes in the chemical composition of the film described above are also consistent with the thermogravimetry results from these samples aged at 80 %RH (Table 9). The T_{decomp} and T_{deflag} values are relatively invariant with time, suggesting that the film flammability is least affected by the 80 %RH aging condition. Furthermore, TGA profiles for these samples indicate that the film forms bubbles due to gas evolution prior to nearly complete combustion.

Table 9. Results of Chemical and Physical Analysis of CN-0 Samples aged at 60 °C under 80 %RH

Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test[a]	5.0-5.5	5.0	5.5	4.5	5.0-5.5	4.0	5.0
^{1}H NMR $[(NO_2)_2)]:[(NO_2)_3]$ [b]	1.23	1.207	1.240	1.290	1.290	1.403	1.34
M_n (kg/mol)	13.2	9.7	14.4	13.1	14.2	12.5	14.4
$Đ = M_w/M_n$	3.04	3.57	2.65	2.39	2.41	2.39	1.96
Decomposition Onset Temp (°C) [c]	170.4±0.6	170.0±0.3	170.8±0.7	171.4±1.8	180.6±0.9	173.2±7.6	172.0±0.5
Deflagration Temp (°C) [c]	183.8±7.9	179.4±1.4	179.6±1.0	179.6±1.2	191.3±1.2	187.5±4.7	179.0±1.6

[a] Determined by soaking 50 mg of film in 5 mL water at 22 °C for 24 h and subsequent pH measurement. [b] From quantitative ^{1}H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-d_6, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). [c] Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C.
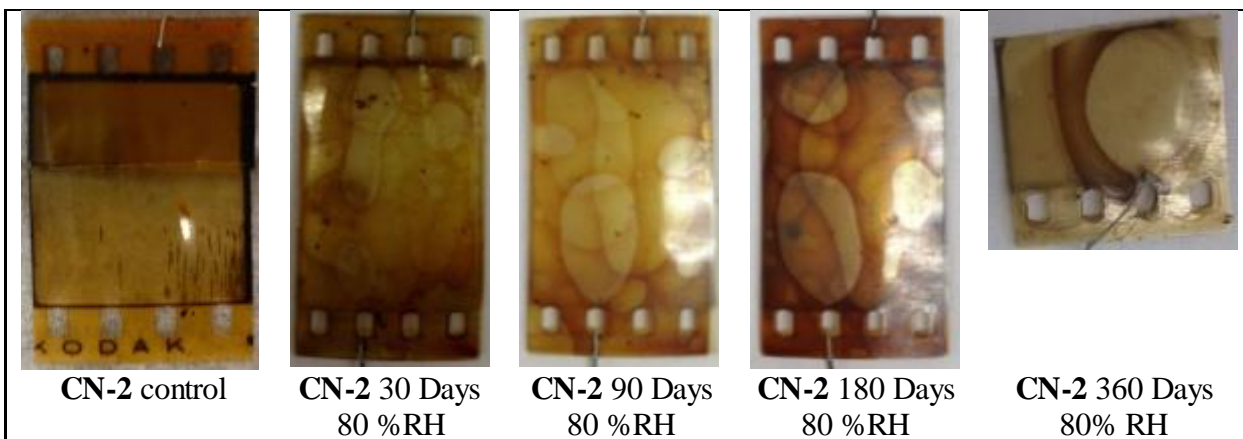
Accelerated Aging of CN-2:

| **CN-2** control | **CN-2** 30 Days 80 %RH | **CN-2** 90 Days 80 %RH | **CN-2** 180 Days 80 %RH | **CN-2** 360 Days 80% RH |

Figure 23. Photographs of **CN-2** at various time points, after removal from the accelerated aging chamber thermostatted at 60 °C with an atmosphere containing 80 percent relative humidity (80 %RH). The film evolves from its Stage 2 condition to a brittle, yellow material after 90 days with a sticky and bubbly emulsion later more characteristic of the Stage 3 classification.

In order to understand better how a partially degraded film sample decomposes, we also aged samples of **CN-2** under 80 %RH conditions for up to 360 days. This aging condition was selected by virtue of our initial intuition that higher relative humidity conditions would lead to greater levels of denitration and dramatic changes in the flammability profile of the film (*vide infra*). In Figure 23, one qualitatively observes the degradation of **CN-2** from Stage 2 to Stage 3, evidenced by the formation of islands and bubbles in the gelatin layer on top of the film base. This drastic change in the physical appearance of the film is accompanied by its acidification to pH 3.5 after 60 days, as determined by the IPI Acidity Test (Table 10). We note that the acidity of the film recovers to

Table 10. Results of Chemical and Physical Analysis of CN-2 Samples aged at 60 °C under 80 %RH

Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test[a]	3.5-4.0	4.0	4.0	3.5	3.5-4.0	4.5	4.0-4.5
^{1}H NMR[b] $[(NO_2)_2)]:[(NO_2)_3]$	1.38	1.427	1.508	1.593	1.563	1.660	1.773
Decomposition Onset Temp (°C) [c]	161.1±0.8	157.1±0.9	156.4±0.6	160.0±0.3	160.8±0.3	161.3±1.7	166.7±0.5
Deflagration Temp (°C) [c]	179.9±0.3	gradual decomp	175.5±4.3	179.7±1.6	gradual decomp	182.1±1.2	186.7±0.4[d]

[a] Determined by soaking 50 mg of film in 5 mL water at 38 °C for 24 h and subsequent pH measurement. [b] From quantitative ^{1}H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-d_6, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). [c] Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. [d] The unbleached film deflagrates, whereas the bleached film (gelatin removed) exhibits only gradual decomposition at temperatures $T \geq 200$ °C.

some extent to pH 4.5 at longer times, possibly due to the equilibrium formation of gaseous nitrogen oxides due to thermolysis of HNO_3. Since our sampling methodology involved opening the sealed container to extract samples at prescribed time points, the nitrogen oxides were allowed to escape from the container. By effectively removing the nitrogen oxides from the aging canister atmosphere, we may have artificially decreased the detected acidity of the film.

TGA studies of the aged **CN-2** film samples demonstrated wide variability in their deflagration behavior (Table 10). The decomposition onset temperature (T_{decomp}) was nearly invariant at ~ 160 °C at all time points in our study. However, the deflagration temperature (T_{deflag}) was nearly constant at ~180 °C, with the exceptions of the samples aged for either 15 and 90 days. The latter two samples do not deflagrate; instead, they exhibit gradual thermal decomposition profiles akin to that shown in Figure 12 for CN-0 aged under 50 %RH after 360 days. We are unsure of the source of this variability in combustibility within this sample set. We initially suspected that the presence or absence of the gelatin layer and any metal salts arising from image decomposition could play a role in the flammability profile, yet the bleached film samples (gelatin removed) exhibited the invariant TGA profiles with the exception of the sample aged for 360 days.

Accelerated Aging of CN-4:

As a corollary study to our **CN-2** aging trials, we also aged one sample of **CN-4** for 360 days at 80 %RH. We limited this analysis to a single data point after 360 days of accelerated aging, due to: (1) space limitations in our temperature-controlled chamber, and (2) the fact that **CN-4** samples lack any intrinsic value due to the complete degradation of the image. Consequently, this analysis aimed only to understand the final stages of nitrate film decay. As with the aged **CN-2** samples, aging **CN-4** for 60 days at 80 %RH results in the film becoming more brittle and discolored (see Figure 24). Comparative ^{1}H NMR analyses of **CN-4** prior to and after aging show that it does denitrate to some extent (see Table 11). However, the level of denitration is low, and thus the flammability profile of the samples assessed by TGA are nearly identical with deflagration

occurring at ~187 °C. Thus, the film retains its flammability under the high relative humidity aging condition long after the image is degraded beyond use.
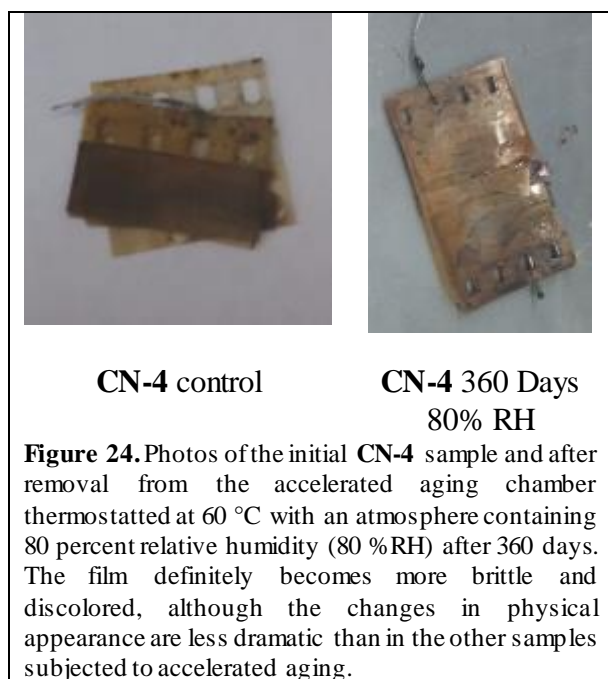

CN-4 control   **CN-4** 360 Days
80% RH

Figure 24. Photos of the initial **CN-4** sample and after removal from the accelerated aging chamber thermostatted at 60 °C with an atmosphere containing 80 percent relative humidity (80 %RH) after 360 days. The film definitely becomes more brittle and discolored, although the changes in physical appearance are less dramatic than in the other samples subjected to accelerated aging.

Table 11. Results of Chemical and Physical Analysis of CN-4 Samples aged at 60 °C under 80 %RH

Time (days)	0	360
pH from IPI Acidity Test[a]	3.0–3.5	4.5
^{1}H NMR $[(NO_2)_2)]{:}[(NO_2)_3]$ [b]	1.563	1.823
TGA		
Decomposition Onset Temp (°C) [c]	152.1±2.8	155.6±6.2
Deflagration Temp (°C) [c]	184.0±2.8	186.7±3.5

[a] Determined by soaking 50 mg of film in 5 mL water at 38 °C for 24 h and subsequent pH measurement. [b] From quantitative ^{1}H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-d_6, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). [c] Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. [d] Deflagration does not occur: the sample decomposes gradually with the first major weight loss occurring at a temperature T ≥ 200 °C.

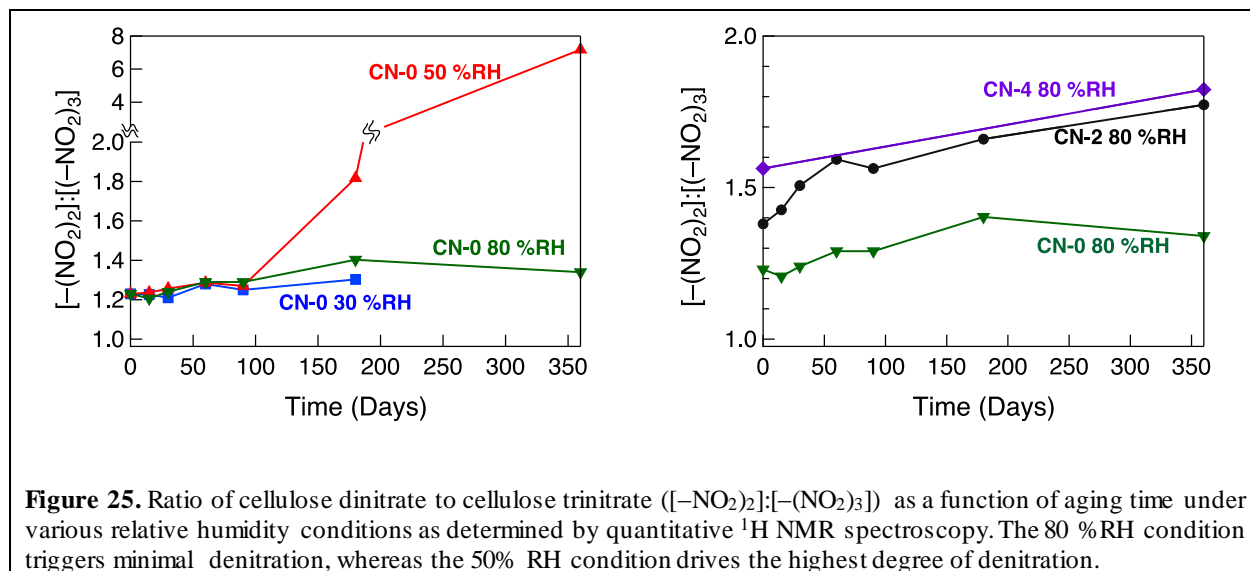*Cumulative Analysis of the Accelerated Aging Data:*

Comparison of the data collected on all of the film samples subjected to accelerated aging trials under various relative humidity conditions at 60 °C provides some new insights into the deterioration behavior of cellulose nitrate film. At the lower relative humidity conditions (30 and 50 %RH), we observed that the emulsion layer remains intact up to ~90 days; the emulsion subsequently loses its sheen and takes on an uneven appearance. The 30 %RH sample unexpectedly depolymerized after ~240 days of aging into what we tentatively assign as an aqueous solution of partially nitrated glucose oligomers. However, the sample aged at 50 %RH becomes a rusty brown solid that is extremely crumbly. We speculate that further aging of this sample might lead to the formation of "brown powder." These results starkly contrast to those obtained for **CN-0** aged under an 80 %RH atmosphere, wherein the samples become sticky after 90 days, the emulsion becomes a sticky liquid after 180 days, and complete image degradation ensues by 360 days.

The aggregated ^{1}H NMR data for the **CN-0** samples aged under different RH conditions and the **CN-0**, **CN-2**, and **CN-4** samples aged at 80 %RH are presented in Figure 25. From these data, one clearly sees that: (1) the denitration of **CN-0** upon aging decreases in the following order

30 % RH ~ 50 %RH > > 80 %RH,

(2) the 80 %RH condition leads to only low levels of denitration, even after 360 days of accelerated aging at 60 °C, and (3) IPI acidity tests of the film show that the pH decreases in the order

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

Figure 25. Ratio of cellulose dinitrate to cellulose trinitrate ($[-NO_2)_2]:[-(NO_2)_3]$) as a function of aging time under various relative humidity conditions as determined by quantitative ^1H NMR spectroscopy. The 80 %RH condition triggers minimal denitration, whereas the 50% RH condition drives the highest degree of denitration.

These results are somewhat surprising, as we initially expected that the denitration process would occur most quickly for the samples aged at the highest relative humidity condition. This expectation was based on the notion that water is required for the hydrolysis of the nitrate esters, which is the reverse process of the manufacturing process for nitrate film from cellulose: higher water concentrations should drive denitration. However, the data suggest that the 50 %RH condition drives denitration to the greatest extent and that the 30 %RH condition results in hydrolysis of both the nitrate esters and the backbone β-glucoside linkages to yield a syrupy solution. SEC data further demonstrate that the molecular weight of the film base is relatively unchanged at the highest relative humidity condition, yet the molecular weight drops upon aging at lower relative humidities (see Figure 26).

The chemical composition of the aged nitrate film samples is strongly correlated with the corresponding thermogravimetric analysis profiles, with higher levels of nitration implying lower deflagration temperatures. These data are plotted in Figure 27. The decomposition onset
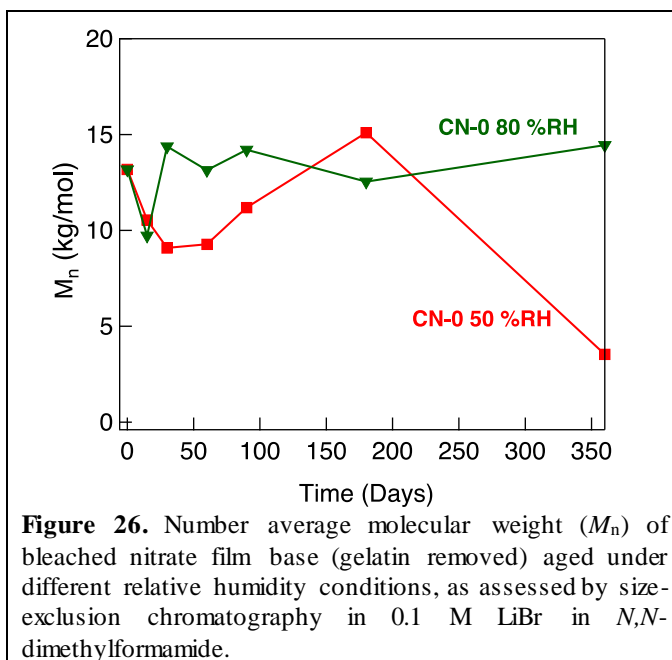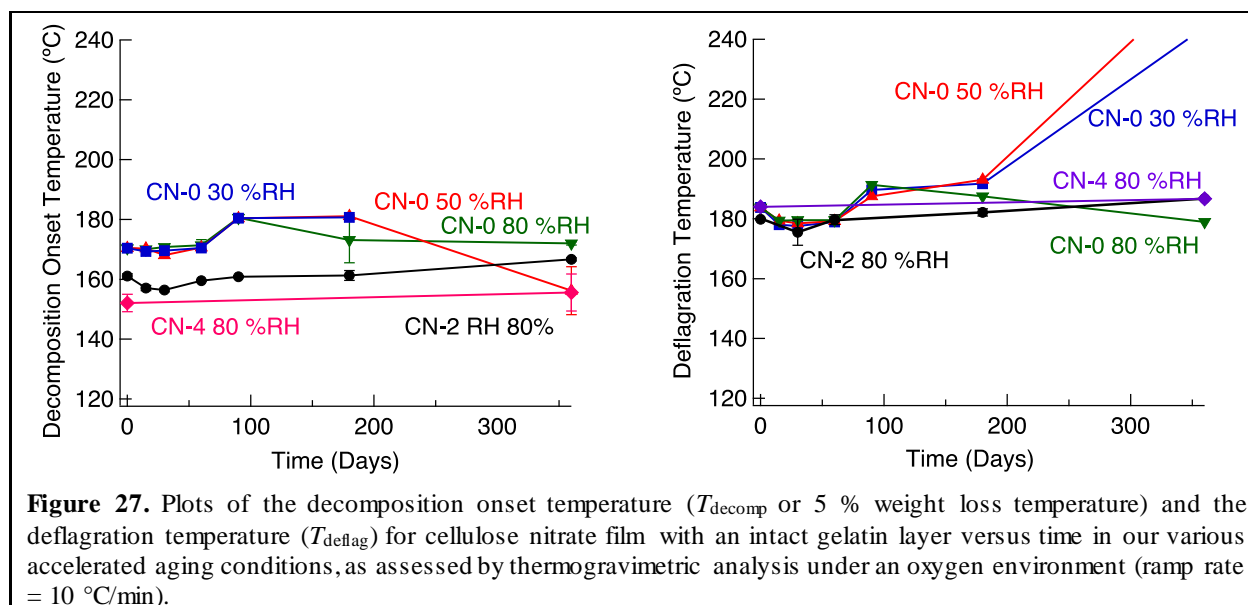

Figure 26. Number average molecular weight (M_n) of bleached nitrate film base (gelatin removed) aged under different relative humidity conditions, as assessed by size-exclusion chromatography in 0.1 M LiBr in N,N-dimethylformamide.

Figure 27. Plots of the decomposition onset temperature (T_{decomp} or 5 % weight loss temperature) and the deflagration temperature (T_{deflag}) for cellulose nitrate film with an intact gelatin layer versus time in our various accelerated aging conditions, as assessed by thermogravimetric analysis under an oxygen environment (ramp rate = 10 °C/min).

temperature (T_{decomp}) is relatively invariant for the **CN-0** aged under different relative humidity atmospheres. While this observation may seem surprising, it is important to remember that the decomposition onset temperature reflects the temperature at which the film sample has lost 5 % of its initial mass during heating at 10 °C/min from 22 °C. Slight decreases in T_{decomp} may arise from denitration of the film that increases its water uptake, so that the mass loss at temperatures $T \leq T_{decomp}$ originates from water evaporation. Except for the **CN-0** aged under 30 %RH or 50 %RH that significantly denitrate, all of the other film samples have deflagration temperatures (T_{deflag}) in the range ~170–180 °C that are consistent with their low levels of denitration. The 50 %RH **CN-0** sample aged for 360 days does not deflagrate and instead decomposes gradually as shown in the TGA profile Figure 18.

While the observed trend of high levels of film denitration at lower relative humidity aging conditions seems counterintuitive, a simple chemical model accounts for our observations. To understand acid-catalyzed degradation of nitrate film, one must consider the underlying thermodynamics of nitrate ester hydrolysis and the kinetics (or rate) of hydrolysis. From a thermodynamic viewpoint, water is a necessary ingredient for the hydrolysis reaction, and the presence of increasing amounts of water (*e.g.*, higher relative humidities) increases the thermodynamic driving force for the hydrolysis reaction. However, thermodynamics only assesses reaction feasibility—*not* the rate at which it occurs. The rate of the hydrolysis reaction depends on the concentrations of the reactants—specifically, the concentration of nitrate esters, nitric acid, and water. Since the reaction is heterogeneous (one in which the reactants are present in more than one phase, including gases, liquids, and solids), one must formally write the reaction rate as a product

of the activities of each species. The activities of each species reflect the "effective active amount" of each reactant in the mixture, which may deviate either positively or negatively from the actual reagent concentration. Thus, the hydrolysis of nitrate film depends sensitively on the activities of both water and the nitric acid (HNO_3) catalyst. Sasahira *et al.* studied the activities of water (a_{water}) and nitric acid (a_{HNO3}) in nitric acid solutions (*J. Nucl. Sci. Technol.–T.*, **1994**, *31*, 321-328). Based on the data reported therein, we calculated the product of the activities $a_{water}*a_{HNO3}$ for a variety

of [water]:[nitric acid] ratios. We find that this product of activities reaches a maximum at a mole fraction $x_{HNO3} = 0.42$ and $x_{water} = 0.58$. In other words, the *rate of the hydrolysis reaction is expected to peak at some intermediate relative humidity.*

This detailed chemical picture may also be understood in more qualitative terms. At low relative humidity, the HNO_3 present in the film is poorly hydrated and thus its effective active concentration is relatively low. We speculate that the small amount of water present competes with the cellulose backbone oxygens to preferentially solvate the acidic protons. Thus, the backbone β-glucoside linkages cleave to depolymerize the film base into nitroglucose oligomers. At intermediate relative humidities, the effective active concentration of acid increases due to the better solvation of the HNO_3 by the larger amount of water. This improved solvation of the HNO_3 leads to acid dissociation to form H_3O^+ which catalyzes nitrate ester hydrolysis. At very high relative humidities, the dissolved H_3O^+ ions become so stable that they are unavailable to participate in the hydrolysis of either the β-glucoside backbone linkages or the nitrate esters. Hence, hydrolysis is fastest at intermediate water concentrations and intermediate relative humidities.

We found that the 50 % RH humidity accelerated aging condition initially enables maintenance of the film image carried by the emulsion layer, followed by decomposition of the nitrate stock into a non-hazardous solid.

5. Assessing the Hazards of "Brown Powder" Arising from Nitrate Film Decomposition

The potentially hazardous nature of the "brown powder" arising from the nearly complete decay of cellulose nitrate film (Stage 5 of the decomposition model) is the source of substantial anxiety in the film archivist community. Literature and anecdotes about the powder stage of nitrate are particularly contradictory; some—such as the International Standard *ISO 10356*—maintain that the powder is comparable to the flammability of paper, while others—such as Kodak's legal *Material Safety Data Sheet*—claim that it is "shock sensitive," like gunpowder or nitroglycerine. Additional research has also suggested that the powder might be formed by a reaction between the cellulose nitrate base and metal storage cans, further complicating our understanding of the powder's relationship to nitrate film's decomposition. We therefore sought to quantitatively evaluate the shock and friction sensitivity of brown powder by direct mechanical analysis, as a complete understanding of its controversial properties significantly affects how curators of nitrate collections handle and dispose of film stocks that have degraded beyond any useful condition.

By soliciting various sources (who wish to remain anonymous), we obtained four samples of brown powder from two geographically diverse major film archives, hereafter referred to as "Archive 1" and "Archive 2." The provenance and other characteristics of these brown powder samples are provided in Table 12.

Table 12. Characteristics of Acquired Brown Powder Samples			
Sample Name	Archive	Sample Mass (g)	Film Stock
A1–1	1	5	unknown
A1–2	2	30	1929, no manufactuer markings
A1–3	2	30	1937, probably KODAK stock
A2–1	2	5	unknown

These samples were specifically chosen due their variable provenance and to the fact that the shock and friction sensitivity tests required a minimum of five (5) grams of brown powder.

We sought to test the shock sensitivity of these four brown powder samples using a well–established standard, which could potentially inform the community of nitrate archivists of how best to handle and transport brown powder samples. The 2009 *United Nations Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria* (5th edition, 2009; https://www.unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev5/English/ST–SG–AC10–11–Rev5–EN.pdf, accessed on Dec. 1, 2015) describes a battery of tests for determining the sensitivity of potentially dangerous materials to a variety of conditions to which they may be subjected during shipment. Section 13.4.2 therein provides a detailed description of the BAM Fallhammer test as one means of quantifying the shock sensitivity of a solid substance. Summarily, this test involves impacting a solid sample (~ 40 mm^3) with weights of precisely known mass that are dropped from a precisely measured height. The test is typically conducted at least five times to ensure reproducibility. Since the potential energy of the mass in its initial condition is completely converted into kinetic energy imparted to the sample upon impact, one can determine the minimum amount of energy (measured in Joules (J)) required for the impact to cause a flash, flame, or explosion. U.N. recommendations state that materials with a limiting impact energy of ≥ 2 J are too shock sensitive to transport.

Chilworth Technology Inc. is a commercial safety and compliance analysis company that routinely conducts BAM Fallhammer tests using an apparatus developed by the Bundesanstalt für Materialforschung und Materialprüfung (BAM or German Federal Institute for Materials Research and Testing, located in Berlin, Germany). We sent samples of each of the brown powder samples to Chilworth for testing. For all four samples, the BAM Fallhammer test demonstrated that the required energy for flame, flash, or explosion was > 60 J, with no change in the sample appearance when compared before and after testing. Their analyses demonstrated that the samples were "not particularly sensitive to ignition by mechanical impact."

The BAM Friction Test is another metric by which the *U.N. Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria* document advised testing the friction sensitivity of a material. Described in Section 13.5.1 therein, the BAM Friction Test involves dragging a porcelain peg of a precisely known mass over a sample of the test material on a porcelain plate at a constant rate. Since the mass of the porcelain peg is known, the friction force (measured in Newtons (N)) exerted upon the material may be calculated. The threshold mass and thus the threshold value of the friction required for flame, flash, or explosion is measured. This test is conducted at least six times to ensure reproducibility of the results. For reference, the UN Manual listed the limiting friction load for dry nitrocellulose (13.4 wt% nitrogen) as 240 N, and the relatively stable explosive TNT has a threshold friction value of 360 N. According to tests conducted by Chilworth Technology Inc., the limiting friction load associated with all four of the brown powder samples was > 360 N. According to Chilworth's analytical team, these results indicate that these samples are "not sensitive to ignition by friction."

Therefore, our studies suggest that the samples of brown powder solicited from geographically distinct sources and variable provenances were non–hazardous solids. This result is consistent with qualitative shock sensitivity tests conducted by a member of the chemistry research team, using a

standard tool hammer to impact samples of a fifth brown powder sample of unknown provenance. Attempts to analyze the composition of the latter brown powder sample by ^{1}H NMR spectroscopy were hampered by its poor solubility in hot deuterated water (D$_2$O) and DMSO–d_6. The fraction of the solid soluble in DMSO–d_6 exhibits a spectrum comparable to that of a significantly denitrated cellulose nitrate film stock. Against the caveat that we have tested a limited number of brown powder samples with only partially known provenance, we conclude that brown powder is non–hazardous on the basis of our dataset.