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# Burn After Viewing, or, Fire in the Vaults: Nitrate Decomposition and Combustibility

Heather Heckman

#### Abstract

Although the fire risks associated with nitrate film stock are widely known, understanding of the relationship between nitrate decomposition and combustibility remains weak. This paper surveys the contradictory descriptions of decomposition and combustibility of motion picture film in current archival and safety literature, evaluates their sources, and compares them to descriptions by image stability researchers and chemists. Throughout, the author argues that the dialogue among the archival, safety, and scientific communities is inadequate and that no community has satisfactorily established the evolution of flammability as nitrate decomposes. The author concludes by outlining a plan for nitrate research and advocacy over the short, medium, and long terms.

rchivists commonly assume (accurately, no doubt) that most people know one thing about nitrate film: it burns. Flammable, inflammable, and combustible, if ignited, nitrate—or cellulose nitrate, or nitrocellulose<sup>1</sup>—film stock cannot be extinguished. It burns in the absence of oxygen, conveniently producing its own supply even when completely submerged under water. Once it starts burning, it releases explosive gases, which the burning films ignite. Most people in the archival community know two more things about nitrate film: it inevitably decomposes in an autocatalytic reaction that erases any and all images it once carried, and, as it decomposes, it ignites still more easily. Nitrate films—they will burn. Sometimes, they will even explode.

<sup>©</sup> Heather Heckman.

I wish to thank Rachel Parker, Mark Minett, Peter Gottlieb and the members of his spring 2009 advanced seminar in archiving, and Mary Jo Pugh and the reviewers at the *American Archivist* for all their sound insights and criticisms.

<sup>&</sup>lt;sup>1</sup> Nitrocellulose, though commonly used as a synonym for cellulose nitrate (as indeed it is in this paper), is not a preferred term in the scientific community.

But among moving image archivists and cinephiles, there is also widespread respect and nostalgia for nitrate motion picture film. For more than fifty years, nitrocellulose was the film stock of choice among filmmakers the world over. Though it may seem far-fetched to today's readers, nitrocellulose was highly prized not just for its lustrous images, but also for its durability. Until the 1950s, it clearly outperformed safety stocks in terms of tensile strength and resistance to shrinkage and warp. It took decades of improvement to safety stock before the film industry agreed that the loss in durability was worth the gain in fire safety—and even then, nitrate maintained a slight edge over safety stock in durability tests.<sup>2</sup>

Surveying this split in opinion, Leo Enticknap recently observed, "Nitrate is still waiting for history's verdict, and it'll be a long time coming."<sup>3</sup> Yet, when it comes to issues of fire safety, we have already waited far too long for such a verdict. "The cost of nitrate," to borrow terminology from the International Federation of Film Archive's (FIAF's) *This Film Is Dangerous*, is elevated: in noncommercial archival contexts alone, nitrate fires have taken at least five lives and destroyed literally millions of feet of our cinematic heritage. Moving images lost to nitrate fires include "all the films that had been produced by both camps during the [Spanish] Civil War"; at least fifty unique actuality films documenting Czech life in the interwar period; nearly all of the pre-1951 holdings of one of Egypt's major film studios; more than 12.5 million feet of unique Universal outtakes; "irreplaceable material" held in Canada's National Film Board Archives; all but three of early master Victor Sjöström's silent Swedish works; and an unknown number of unique titles held by the Cinematheque Française.<sup>4</sup>

Still, the strict regulations on nitrate storage, projection, transportation, and even destruction have drawn complaints from many film archivists, who find that nitrate has a much more pedestrian cost: it is increasingly difficult to maintain in fire-code compliant conditions—and it's rather tricky to dispose of too. Large repositories have to contend with the construction expenses of *NFPA* 40–compliant cabinets and vaults,<sup>5</sup> but the problem is probably more acute for

<sup>&</sup>lt;sup>2</sup> Lab tests demonstrated that safety stock could withstand 520 projections, while nitrate could withstand 644. Both numbers, however, were more than adequate for Hollywood's distribution practices in the mid-twentieth century. Leo Enticknap, "The Film Industry's Conversion from Nitrate to Safety Film in the Late 1940s: A Discussion of the Reasons and Consequences," in *This Film Is Dangerous: A Celebration of Nitrate Film*, ed. Roger Smither and Catherine Surowiec (Brussels: FIAF, 2002), 209. In 1936, the statistics showed a much wider margin: safety film could only be projected approximately fifty times, while the average nitrate print was projected at least 200 times in distribution. See Henry Anderson, "Fire Safety in the Motion Picture Industry," *Quarterly of the National Fire Protection Association* 30, no. 1 (July 1936): 27.

<sup>&</sup>lt;sup>3</sup> Leo Enticknap, "Nitrate's Still Waiting," The Velvet Light Trap 64 (Fall 2009): 87.

<sup>&</sup>lt;sup>4</sup> Roger Smither and Catherine A. Surowiec, eds., "A Calendar of Film Fires," in *This Film Is Dangerous*, 444–53.

<sup>&</sup>lt;sup>5</sup> See National Fire Protection Association, *NFPA 40: Standard for the Storage and Handling of Motion Picture Film* (Quincy, Mass.: NFPA, 2007), 6–9.

small repositories with nitrate holdings. Consider the difficulty of shipment: Legally, unless a staff member has completed HAZMAT (hazardous materials) training (and this is rarely the case at small institutions), an outside contractor must package the film for shipment. Few HAZMAT contractors, however, will agree to handle as small a volume of hazardous materials as a single motion picture film. As an example, at my own institution, it took more than three months to arrange for the shipment of a nitrate short only a few minutes in length. The task is no easier for films that must be moved to approved disposal sites than it is for films that are being sent to labs for preservation copying. Shipment can be so difficult that the National Park Service's Conserve O Gram actually recommends that Park Service employees exploit a loophole that allows unregulated transport by government workers in government vehicles. The document strongly advises, however, that the driver not "park the car and leave it in the sun for long periods," or "run the heater excessively."<sup>6</sup> What's more, these regulations now affect a much broader portion of the archival community, since in 2000, *NFPA 40* was expanded to cover flat film as well as roll film.<sup>7</sup> Thus, for the first time, the same fire protection standard covers both moving image photographs and still photographs (although it should be noted that distinctions between the two are made in the document and that the regulation of motion picture film remains stricter).

The underlying problem is that we still know comparatively little about the relationship between nitrate decomposition and nitrate combustibility. Folk wisdom and outright rumor continue to dominate the discourse around nitrate film stock, a situation that must be remedied before nitrate's place in archival institutions (and even history) can be fully assessed. This paper seeks to evaluate the nitrate threat as it has been reported both in archival literature and in the sources that have informed that literature. The "touchstone" archival publications for my research are therefore drawn largely, though not exclusively, from the pages of *This Film Is Dangerous*. To evaluate the assumptions and conclusions of those publications, I also revisited the articles they cite, the majority of which come the *Journal of the Society of Motion Picture Engineers (JSMPE)*<sup>8</sup> and the *Quarterly of the National Fire Protection Association (QNFPA)*. To a lesser extent, the search also led me to scientific journals focused on chemistry and plastics. Thus, this paper reviews and evaluates the literature of at least three broad communities: moving image archivists and other members of the motion picture industry; fire

<sup>&</sup>lt;sup>6</sup> National Park Service, "Handling and Shipping Cellulose Nitrate Film," *Conserve O Gram* 2, no. 20 (June 2003): 1.

<sup>&</sup>lt;sup>7</sup> See NFPA, *NFPA 40*, 1. Previously, flat film was covered by *NFPA 42*, *Standard for the Storage of Pyroxylin Plastic.* 

<sup>&</sup>lt;sup>8</sup> The Journal of the Society of Motion Picture Engineers (commonly abbreviated JSMPE) became the Journal of the Society of Motion Picture and Television Engineers (JSMPTE) in 1949 and the SMPTE Journal in 1955.

protection agencies and other safety organizations; and, finally, image stability researchers and other chemists.

In the pages that follow, I attempt to do five things: First, I seek to explain what nitrate motion picture film stock *is*, with a brief overview of its circumstances of invention and production. Second, I survey the contradictory descriptions of decomposition and combustibility in current archival and safety sources, focusing particularly on the language used in manuals and standards. Third, I revisit the sources of those descriptions in a historical review of articles published in *JSMPE* and *QNFPA*. Fourth, I examine recent research by image stability researchers and chemists to draw a picture of the scientific community's understanding of nitrate decomposition. Finally, I conclude by suggesting future avenues for nitrate research and advocacy. Throughout, I argue that the dialogue among the archival, safety, and scientific communities is inadequate and that no community has satisfactorily established the evolution of flammability as nitrate decomposes.

#### Celluloid Memories: Development and Production of Nitrate Film Stock

Nitrate film stock is a derivative of "guncotton," a substance whose discovery is usually attributed to German-Swiss chemist Christian Friedrich Schönbein in the 1840s. Created by the treatment of cotton cellulose with nitric acid (or more frequently, a mix of sulfuric and nitric acids), guncotton, as its name suggests, was a highly flammable powder originally intended for military use. Six times more powerful than standard gunpowder and almost entirely smokeless, guncotton was also *very* unstable. Because of its tendency to spontaneously combust (a tendency further exacerbated by the nonstandardized conditions of its manufacture), guncotton's weapons applications were largely abandoned in the mid-nineteenth century.

However, the treatment of cotton cellulose with an acid mixture proved to have other, more promising uses. Further experimentation led to the discovery that the dissolution of nitrated cellulose in an ethyl alcohol mixture yielded a clear, viscous liquid. If dried, the liquid formed a transparent, solid sheet—it formed, in other words, the world's first plastic. Variations in the ratio of acid to cellulose, and subsequently in the ratio of nitrated cellulose to alcohol mixture (called the plasticizer),<sup>9</sup> created plastics of varying strength. Known as cellulose

<sup>&</sup>lt;sup>9</sup> In the case of flexible film stock, the plasticizer was almost always some combination of "alcohol, ether, acetone, amyl acetate, and camphor." See John Reed, "Nitrate? Bah! Humbug!," in *This Film Is Dangerous*, 220.

nitrate, nitrocellulose, or celluloid,<sup>10</sup> entrepreneurs looking for a material that could imitate luxury materials at a fraction of the cost quickly adopted the plastic.

Used to approximate " 'ivory, tortoise-shell, horn, hard wood, india rubber [*sic*], gutta percha' "<sup>11</sup> and other high-priced media, celluloid went into mass production and found its way into homes in a plethora of forms, ranging from coatings for collars and cuffs to false teeth, from dolls to dinnerware, and from billiard balls to the ubiquitous comb.<sup>12</sup> Though now the most famous form of the first plastic, photographic and motion picture film in fact accounted for only a fraction of the celluloid market. All celluloid products have at least two things in common: they are flammable and they are unstable. Exposed to fire, all celluloid burns; over time, all celluloid chemically decomposes in ambient conditions.<sup>13</sup>

This is not to say that all celluloid was created equal. Early moving picture film, for example, was more highly "nitrated" than other celluloid objects. Whereas most household plastics were made with 11 percent nitrogen content, motion picture film stock was made with a higher nitrogen content, more closely approaching the 12 to 14 percent threshold characteristic of guncotton.<sup>14</sup> As a result, the British Celluloid Committee of the early 1910s observed, " 'The trade in cinematograph films requires special consideration'...Because...'The celluloid used in the manufacture of films is more highly nitrated than ordinary celluloid', ignites more readily, and 'burns more fiercely'."<sup>15</sup> Later, film stock

<sup>&</sup>lt;sup>10</sup> "Celluloid" was the name given the material in 1870 by the Hyatt brothers, who ran an early cellulose nitrate manufacturing company, the Albany Dental Plate Company. See Deac Rossell, "Exploding Teeth, Unbreakable Sheets, and Continuous Casting: Nitrocellulose, from Guncotton to Early Cinema," in *This Film Is Dangerous*, 39. Technically, nitrate is the *only* film stock that can rightfully be called celluloid, though safety stock is also derived from a cellulose base. Polyester stock contains no cellulose whatsoever.

<sup>&</sup>lt;sup>11</sup> Alexander Parkes, quoted in Rossell, "Exploding Teeth," 38. Gutta percha is a naturally derived rubber.

<sup>&</sup>lt;sup>12</sup> In Great Britain, at least, combs were considered "the largest cause of fire" of all celluloid home goods (a category that included movies for home projection). Clyde Jeavons, "Playing with Fire," in *This Film Is Dangerous*, 237. Even today, celluloid is still in production for the manufacture of at least two house-hold items, guitar picks and ping-pong balls, both of which are highly flammable. A small amount of cellulose nitrate material can also be found in some acetate stocks. See A. Tulsi Ram and James L. McCrea, "Stability of Processed Cellulose Ester Photographic Films," *SMPTE Journal* 97 (June 1988): 474–83; Karel A. H. Brems, "The Archival Quality of Film Bases," *SMPTE Journal* 97 (December 1988): 991–93.

<sup>&</sup>lt;sup>13</sup> It should be noted that *all* materials degrade over time—it is the speed of degradation that makes plastic a special case. Though they do not biodegrade as readily as other materials, plastics chemically degrade at a much faster rate. Object decomposition is actually a major problem for all classes of plastic and particularly plagues museum conservators. See, for example, Sylvia Katz, "The Degradation and Disappearance of Cellulose Nitrate Objects," in *This Film Is Dangerous*, 198–201.

<sup>&</sup>lt;sup>14</sup> Katz, "The Degradation and Disappearance of Cellulose Nitrate Objects," 198.

<sup>&</sup>lt;sup>15</sup> Quoted in Jeavons, "Playing with Fire," 238–39.

manufacturers reduced the nitrogen content of their product to the standard 11 percent level.<sup>16</sup>

The remarkable lack of standardization across cellulose nitrate production is more troubling. In the words of film technology historian Deac Rossell, "the production of a clear and flawless sheet of celluloid by any method was something akin to black magic." Rossell reports that in the late nineteenth century, one celluloid chemist admitted, " 'We still do not know today to what process the formation of celluloid is to be attributed.' "17 The production of nitrocellulose film stock was so inconsistent, at least over its first decade of demand, that "many filmmakers used multiple suppliers of raw stock, perhaps out of necessity or perhaps tracking the 'good' batches that reached the market."<sup>18</sup> Market imperatives that encouraged differentiation between companies compounded the variations in the output of individual companies. Partly for competitive reasons and partly to avoid patent infringement, different manufacturers used different solvent "recipes," resulting in structurally unique plastic outputs. For example, a translucent base characterized Eastman's early film stock, intended for Edison's Kinetoscope peepshow devices. Eastman's competitor, European Blair, developed the first transparent base, designed for film projection proper.<sup>19</sup>

Over time, and as film stock manufacturing companies like Eastman Kodak in the United States and Agfa in Germany solidified their monopolistic market shares, nitrate film stock production tended to become more consistent. Nevertheless, variations between batches probably persisted and were likely only exacerbated by differences in storage conditions over the past decades.<sup>20</sup> Research conducted at the Image Permanence Institute concluded, "there is a

<sup>&</sup>lt;sup>16</sup> Katz, "The Degradation and Disappearance of Cellulose Nitrate Objects," 198. The First World War resulted in another major change in the production of cellulose nitrate. The organic nitrate salts necessary for cellulose nitrate production were almost exclusively mined by British interests in Chile. In an effort to slow German arms development, the British cut the nitrate salt line. German chemists responded with the development of the ammonia oxidation process, a means of producing nitrocellulose synthetically. See Michael Chanan, "Nitrate Railways," in *This Film Is Dangerous*, 26. Considerably cheaper, nitric acid produced through the synthetic German process quickly replaced nitric acid made from nitrate salts in celluloid manufacturing worldwide.

<sup>&</sup>lt;sup>17</sup> Rossell, "Exploding Teeth," 43.

<sup>18</sup> Rossell, "Exploding Teeth," 46.

<sup>&</sup>lt;sup>19</sup> Rossell, "Exploding Teeth," 45.

<sup>&</sup>lt;sup>20</sup> Anecdotal evidence of such variations can be found in two recollections of Library of Congress nitrate vault manager George Willeman: In 1997, Willeman found a hole burned through the center of a single frame of a 1913 production, "in total defiance of its extreme combustibility." For a scanned image of the frame, see "The Asbestos Screen and the Not-So-Flammable Nitrate," in *This Film Is Dangerous*, 33. More remarkable still, in the late 1990s, Willeman inspected a set of negatives for early Mary Pickford Biograph shorts. Upon opening the can, he was greeted with a "crusty brown mass of deterioration." Willeman almost gave up the inspection as futile, but instead looked closer and realized a set of titles added by a collector in the 1920s, rather than the original negative, had degraded. Willeman recalls, "Even where the Biograph film was right up against the 1922 Kodak stock, there was no sign of deterioration! I was, to say the least, truly amazed." See George R. Willeman, "The 'Tenacity' of Nitrate Film," in *This Film Is Dangerous*, 587.

wide variation in the stability of nitrate base films."<sup>21</sup> In a telling—if somewhat extreme—example, a 1932 Kodak print had a predicted lifespan of fifty years, while a print on stock manufactured that same year by Dupont had a predicted lifespan of 600 years.<sup>22</sup> The irregularity of nitrate film is, to put it mildly, a mixed blessing for film archivists. The fact that surviving prints have made it this long suggests that they will remain in good condition for the moving image long term. Unfortunately, this does not guarantee chemical similarity of extant prints, a limitation that should inform the reading of the remainder of this paper.

#### A Five-Step Process: Manuals and Standards

At last count in 2001, more than 180 million feet of nitrate motion picture film sat in archival vaults worldwide.<sup>23</sup> We can reasonably presume that the majority of this footage will remain in archival vaults for the long term. Migration is costly<sup>24</sup> and always involves data loss. Furthermore, the image stability findings of the Image Permanence Institute strongly suggest that the life expectancy for most of the nitrate prints that have survived this long outstrips the life expectancy of any new acetate prints created.<sup>25</sup> For these reasons, the "Nitrate Won't Wait" campaign that fueled the early film preservation movement has come under attack by film archivists and scholars.<sup>26</sup> The "Nitrate Won't Wait" idea held that all nitrate films were both unstable and dangerous, and that their contents therefore had to be copied to acetate to survive. In many cases, the nitrate originals were then destroyed. Archivist Sam Kula (who remembers "with shame

<sup>&</sup>lt;sup>21</sup> P. Z. Adelstein et al., "Stability of Cellulose Ester Base Photographic Film: Part IV—Behavior of Nitrate Base Film," *SMPTE Journal* 104 (1995): 369.

<sup>&</sup>lt;sup>22</sup> Adelstein et al., "Stability of Cellulose Ester Base Photographic Film: Part IV," 363. In this way, cellulose nitrate film base is distinct from cellulose acetate and polyester film bases, which have relatively consistent lifespans (though acetate's projected lifespan at 20 degrees Celsius and 50 percent relative humidity is only forty years, whereas polyester's is a thousand). See P. Z. Adelstein, J. M. Reilly, and F. G. Emmings, "Stability of Photographic Film: Part VI—Long-term Aging Studies," *SMPTE Journal* 111 (April 2002): 142–43.

<sup>&</sup>lt;sup>23</sup> According to the United Kingdom's Nitrate Project, "186,786,000 feet of pre-1953 nitrate film," to be precise. See Sam Kula, "Mea Culpa; How I Abused the Nitrate in My Life," in *This Film Is Dangerous*, 169.

<sup>&</sup>lt;sup>24</sup> It can cost tens of thousands of dollars to copy a nitrate short to safety or polyester stock. Feature preservation costs are even higher. A study conducted at the Danish Film Institute concluded that cold storage of nitrate originals is cheaper than digital preservation copying. See Jesper Stub Johnson and Thomas C. Christensen, "Optimizing Preservation and Presentation of Cellulose Nitrate Film Collections," in *IS&T's 2004 Archiving Conference*, ed. F. Frey and R. Buckley (San Antonio, Tex.: The Society for Imaging and Technology, 2004), 120. It should be noted, however, that the authors did not do a cost comparison for film-to-film preservation copying projects.

<sup>25</sup> See fn 24.

<sup>&</sup>lt;sup>26</sup> For an extended, and very convincing, version of this argument, see Karen Gracy, *Film Preservation: Competing Definitions of Value, Use and Practice* (Chicago: Society of American Archivists, 2007).

turning up at FIAF one year with buttons saying 'NITRATE CAN'T WAIT'")<sup>27</sup> now attributes nitrate's low public approval rating to the campaign. "So why," he asks, "does nitrate have the reputation as the film stock from hell?"

Well, one reason is that it served our purposes as archivists to play up its weaknesses while ignoring its strengths. You cannot raise funds from governments and foundations by reminding them that nitrate was the workhorse of the industry for sixty years; that immense quantities of nitrate film were safely in circulation in every corner of the globe and under the most adverse circumstances imaginable; and that the number of people injured in fires in which nitrate was involved, and was very seldom the cause, was, statistically, totally insignificant by comparison.<sup>28</sup>

Though most North American motion picture archives with substantial nitrate holdings have abandoned copy-and-destroy policies, such policies persist in some archival repositories and in the language of documents like *ISO 10356, Cinematography*—*Storage and Handling of Nitrate Motion Picture Films*, which seems to assume that migration remains the ultimate goal for all nitrate film: "Rolls of nitrate-base film that have not yet deteriorated shall be placed in individual metal cans (aluminum or stainless steel) with fitted but unsealed closures until they can be duplicated to safety film"<sup>29</sup> (my emphasis).

The American National Fire Protection Association has also tended to err on the conservative side. *NFPA 40* relegates the admission that "It is presently recognized that substantial amounts of nitrate film will be retained for its historical value," to an annex "included for informational purposes only."<sup>30</sup> Meanwhile, the document's "Origin and Development" preface still cites only one explicit justification for nitrate storage, which dates to 1979: "due to the large quantities of cellulose nitrate motion picture film in various archives, the Committee decided to revise *NFPA 40* and to maintain it as an active NFPA standard until these archive collections are reprinted onto safety film or destroyed."<sup>31</sup> Whereas actual practice at institutions like the Library of Congress, the George Eastman House, the Academy Film Archive, and the UCLA Film and Television Archive favors long-term preservation of nitrate originals, official policy recommendations continue to promote the destruction of those same originals.

This discrepancy stems in part, I believe, from the lack of consensus about nitrate decomposition and combustibility. It is well known that the flashpoint of

<sup>31</sup> NFPA, NFPA 40, 1.

<sup>27</sup> Kula, "Mea Culpa," 169.

<sup>&</sup>lt;sup>28</sup> Kula, "Mea Culpa," 168.

<sup>&</sup>lt;sup>29</sup> International Organization for Standardization, ISO 10356: Cinematography, Storage and Handling of Motion Picture Films (Geneva: ISO, 1996), section 8.

<sup>&</sup>lt;sup>30</sup> NFPA, NFPA 40, 16. Oddly, this quotation is included in a section on projection.

cellulose nitrate film drops as it begins to decay. Exposure to temperatures of less than 120 degrees Fahrenheit can ignite a roll of nitrate film, which, within seconds, becomes impossible to extinguish.<sup>32</sup> Since nitrate production has ceased worldwide, archival nitrate holdings are entirely composed of aging stock. Thus, from a safety perspective, it is absolutely crucial that moving image archivists understand the link between decomposition and combustibility. A survey of archival and safety literature, however, reveals disturbing disparities.

Current standards and manuals hold that nitrate decay is inevitable, but accelerated by exposure to heat or moisture. Motion picture films should be stored in metal or other U.S. Department of Transportation–approved cans in cool, dry environments. Archivists should regularly inspect films for signs of decay, which is typically described as a five-step process. The National Film Preservation Foundation's *Film Preservation Guide* provides a very simple version:

- 1. Image fading. Brownish discoloration of emulsion. Faint noxious odor.
- 2. Sticky emulsion. Faint noxious odor.
- 3. Emulsion softens and blisters with gas bubbles. More pungent odor.
- 4. Film congeals into a solid mass. Strong noxious odor.
- 5. Film disintegrates into brownish powder.<sup>33</sup>

This basic structure is relatively consistent across sources, though some variation exists. The first stage is sometimes described as yellow or amber.<sup>34</sup> The description of the third stage may be limited to "annular," or ring-shaped, portions of the emulsion.<sup>35</sup> Some accounts include a "viscous froth" in the fourth stage.<sup>36</sup> Finally, the fifth stage might be described as "rust-colored" or acrid.<sup>37</sup>

<sup>&</sup>lt;sup>32</sup> The temperature at which nitrate burns at ignition is relatively low, but the rate at which it burns is fast, allowing it to reach dangerous temperatures within seconds. Effectively, once ignited, its temperature cannot be lowered below combustion level. It is also impossible to smother cellulose nitrate fires, since the material produces its own oxygen as it burns.

<sup>&</sup>lt;sup>33</sup> The Film Preservation Guide: The Basics for Archives, Libraries, and Museums (San Francisco: National Film Preservation Foundation, 2004), 16. This description is attributed to FIAF's film preservation manual: Eileen Bowser and John Kuiper, A Handbook for Film Archives (New York: Garland, 1991): 18–19.

<sup>&</sup>lt;sup>34</sup> See, for instance, Jean-Louis Bigourdan, "From the Nitrate Experience to New Film Preservation Strategies," in *This Film Is Dangerous*, 55; Eastman Kodak, *Photographic Films (Cellulose Nitrate Film Base) Material Safety Data Sheet* (Rochester, N.Y.: Kodak, 2003), 1; ISO, *ISO 10356*, Annex B; NFPA, *NFPA 40*, 15.

<sup>&</sup>lt;sup>35</sup> See, for instance, ISO, ISO 10356, Annex B. In a rather poetic variation, a FIAF document refers to these rings as "blisters of 'nitrate honey.' " See International Federation of Film Archives, Handling, Storage and Transport of Cellulose Nitrate Film (Brussels: FIAF, 1991), 9.

<sup>&</sup>lt;sup>36</sup> See, for instance, Kodak, Photographic Films (Cellulose Nitrate Film Base) MSDS, 1; ISO, ISO 10356, Annex B.

<sup>&</sup>lt;sup>37</sup> See, for instance, Kodak, Photographic Films (Cellulose Nitrate Film Base) MSDS, 1.

Though it lists the five stages in an appendix,<sup>38</sup> the main text of *ISO 10356* departs rather strikingly from the norm:

The very first indication of deterioration is an alteration of the image. Monochrome silver images develop spots (which can be extensive) of reduced density that also acquire an iridescent sheen. Thereafter, with further deterioration, the typical odour develops, followed by physical changes including inter-layer adhesion plus weakening of the emulsion and base.<sup>39</sup>

Meanwhile, no sources link any of the stages to any sort of concrete timeline, giving novice nitrate archivists little information about the relative urgency of a given film's decay status.

Most sources contend that combustibility increases with decomposition and strongly advocate immediate disposal of film in the last two stages of decomposition, when, it is widely agreed, the film can no longer be duplicated. Films in stages 4 and 5, the consensus holds, should be submerged in water and transported to an authorized disposal facility for incineration.<sup>40</sup> However, *NFPA 40* is considerably more conservative, stating, "Any films that, upon examination, show yellow discoloration, fading of the image, undue brittleness, stickiness of the emulsion, or any other signs of deterioration" (in other words, any films in *any* stage of decomposition) "should be copied onto safety film as soon as practical" and then, presumably, destroyed.<sup>41</sup>

A startling disparity emerges when *ISO 10356* is compared to Kodak's legal *Material Safety Data Sheet (MSDS)*. The former holds that flammability increases through the third stage of decomposition, but drops off in the fourth and fifth stages: "By the time the film reaches category e) [stage 5] it has lost virtually all of its nitrate groups, and its flammability has then been reduced to approximately that of the cellulose itself, i.e. comparable to the flammability of paper."<sup>42</sup> In contrast, Kodak's 2003 *MSDS* describes film in the powder stage as

<sup>&</sup>lt;sup>38</sup> Even here, *ISO 10356* is a bit of an exception: In yet another variation, Annex B refers to the powder stage as "acid." Because it is the only source to include pH in its description so far as I can tell, and because the more common adjective form is "acidic," I suspect this is a typographical error and that the authors intended to use the term "acrid" instead.

<sup>&</sup>lt;sup>39</sup> ISO, ISO 10356, Section 9.

<sup>&</sup>lt;sup>40</sup> Some sources, like Eastman Kodak, advocate automatic disposal once stage 3 has been reached. See Eastman Kodak, *Kodak Publication No. H-182: Safe Handling, Storage, and Destruction of Nitrate-Based Motion Picture Films*, (Rochester, NY: Kodak, 2006), 2, 6.

<sup>41</sup> NFPA, NFPA 40, 15.

<sup>&</sup>lt;sup>42</sup> ISO, *ISO 10356*, Annex B.

"shock sensitive."<sup>43</sup> On the one hand, the international standard maintains that nitrate powder is no more dangerous than an archival manuscripts collection; on the other, the domestic standard contends that nitrate powder is akin to gunpowder or nitroglycerine.

Anecdotes about the powder stage in the wider archival literature are equally contradictory. Some archivists clearly associate it with increased fire risk. Frank Holland (National Film Archive, U.K.), for example, associates flammability exclusively with powder decomposition products: "The 'dangerous stage' is when it's powder; that's when it can ignite from high temperatures or being near an open flame, something like that."44 Conversely, historian and preservationist Kevin Brownlow reminisces about running film in the powder stage through a projector (a cringe-worthy anecdote for many archivists, I suspect): "One could also see evidence of an interaction between the metal can and the celluloid. On a badly decomposed shot the film would jam in the gate and a pile of brown dust spread everywhere. But what amazed us was how little decomposition had taken place, and how smoothly the 65-year-old negative went through."45 For Brownlow, like Kula, fear of nitrate powder constituted a real threat to film preservation. He recalls with sorrow asking to view the last surviving print of the Louise Brooks film City Gone Wild at the Paramount vault: "the vault-keeper pulled the rusty cans from the shelf, noticed a little rust on the roll, and threw it and the other cans into a barrel of water."46

Whence all the confusion? The original sources for the information outlined above were, with few exceptions, published in *JSMPE* and *QNFPA* between the 1930s and 1950s. Therefore, a historical review of that literature and its limitations can inform an evaluation of contemporary information.

<sup>&</sup>lt;sup>43</sup> Kodak, *Photographic Films (Cellulose Nitrate Film Base) MSDS*, 1. Kodak's assertion that the brown powder is shock sensitive has no clear source, but it does seem to have been appended to Kodak's descriptions of nitrate decomposition relatively recently. As late as 1988, a summary article written by Kodak research scientists maintains only, "Cellulose nitrate support, unlike guncotton, is not explosive, but it is hazardous because it ignites easily, burns quickly, and gives off gases that are extremely poisonous." See William E. Lee and Charleton C. Bard, "The Stability of Kodak Professional Film Bases," *SMPTE Journal* 97 (November 1988): 912. The 1992 second edition of Eastman Kodak's *The Book of Film Care* also makes no mention of the brown powder being prone to explode when jolted. See "Storage and Handling of Processed Nitrate Film," in *The Book of Film Care*, ed. Edward Blasko, Benjamin A. Luccitti, and Susan F. Morris (Rochester, N.Y.: Eastman Kodak Company, 1992), 30–35.

<sup>&</sup>lt;sup>44</sup> Frank Holland and Catherine Surowiec, "You Always Treat the Film with Respect'," in *This Film Is Dangerous*, 335.

<sup>&</sup>lt;sup>45</sup> Notably, Brownlow attributes the powder stage to metal canning practice. See Kevin Brownlow, "Vault Farce," in *This Film Is Dangerous*, 540.

<sup>&</sup>lt;sup>46</sup> Kevin Brownlow, "Dangerous Stuff," in *This Film Is Dangerous*, 180. Of course, for another historian, the danger associated with the powder stage constituted a boon. Jay Leyda recalls wanting to buy a print for his own collection. Aware that he was competing with network buyers with much deeper pockets, "He took a look inside some of the film cans just the same. 'As I did so, out shot red dust—the sign the old nitrate film has gone to pieces and is dangerously inflammable'. 'Put our your cigarettes,' they yelled. And then they all went away thinking it was no good. So I bought the lot—200 cans—for a price that it's not fair to those big boys to mention'." Quoted in Roger Smither, "Fiery Tales," in *This Film Is Dangerous*, 518.

#### "The Stuff Just Goes...":47 A Historical Perspective on Nitrate Decomposition

In the early 1930s, about the same time that the first film archives began to appear,<sup>48</sup> the motion picture industry began to concern itself with the mechanism of nitrate film decomposition and its relationship to combustibility. The concern was probably spurred, at least in part, by a widely publicized May 1927 fire in a Cleveland Hospital that resulted in "125 deaths, mainly from the inhalation of toxic fumes given off in the fire and spread throughout the building by way of the elevator shaft and the network of risers used to carry the hospital heating system."<sup>49</sup> Though the fire was not attributed to moving image film (instead, it was sparked by construction in a basement that held 8,500 pounds of nitrate X-ray photographs), it nevertheless renewed interest in the safety risks associated with long-term nitrate storage. A follow-up report by the NFPA uses the word "decomposition" almost exclusively to refer to decomposition *caused by* fire, as opposed to decomposition *causing* fire. But the report clearly recognizes that the plastic's rapid decomposition once ignited was self-sustained and irreversible.<sup>50</sup>

In 1930, *JSMPE* began to make recommendations for the long-term storage of motion picture film. The first of these was to limit the exposure of nitrate stock to metals, which were believed to have a "corrosive" effect upon the film.<sup>51</sup> A year later, *JSMPE* republished a warning issued in Nuckolls's follow-up to the Cleveland fire:

There are three important reasons why nitrocellulose motion picture film needs special consideration, and why it differs from other ordinary combustible materials. These are:

- 1. Low ignition and decomposition temperatures;
- 2. Rapidity of combustion and resulting high temperatures;
- 3. Property of decomposing with little or no air supply, resulting in evolution of poisonous and inflammable gases.

<sup>47</sup> "A former film curator at the Library of Congress," quoted in Enticknap, "Nitrate's Still Waiting," 86.

<sup>&</sup>lt;sup>48</sup> The MoMA Film Library, the National Film Library of the U.K., and the Reichsfilmarchiv were founded in 1935; the Cinematheque Française and the International Federation of Film Archives were founded in 1936 and 1938, respectively. Most of the aforementioned institutions were first proposed in the late 1920s or early 1930s.

<sup>&</sup>lt;sup>49</sup> Smither and Surowiec, eds., "Calendar of Film Fires," in *This Film Is Dangerous*, 440.

<sup>&</sup>lt;sup>50</sup> See A. H. Nuckolls, "Cellulose Nitrate and Acetate Film," *QNFPA* (January 1929): 236–42.

<sup>&</sup>lt;sup>51</sup> See J. I. Crabtree and C. E. Ives, "The Storage of Valuable Motion Picture Film," *JSMPE* 15 (September 1930): 289–305. A 1936 report by the Committee for the Preservation of Film espouses similar concerns about metal cans and even goes so far as to propose Pyrex glass film cans. See Committee on the Preservation of Film, "Report of the Committee on the Preservation of Film," *JSMPE* 27 (August 1936): 153.

Wood and paper when heated rapidly do not ignite until a temperature in the neighborhood of 600°F to 700°F is reached, while nitrate film will decompose when exposed to temperatures around 300°F, and on prolonged exposure at temperatures as low as 230  $E^{52}$ 

Perhaps because Nuckolls greatly *over*estimated the flashpoint (or ignition threshold temperature) of nitrate film stock, it was only in 1933, to my knowledge, that the phrase "spontaneous combustion" was first linked to the material. A report by the newly formed Committee on the Preservation of Film observed, "There is considerable question, because of the comparatively recent development of nitrocellulose as a supporting base for photographic film, as to the danger of fire arising from spontaneous combustion."<sup>53</sup> No cases of fire had yet been definitively attributed to spontaneous combustion, however, and the authors conclude that low temperatures and low humidity in storage areas ought to prevent such an event. They recommend storage at 60 degrees Fahrenheit and 60 percent relative humidity (RH).<sup>54</sup>

In 1936, the Committee on the Preservation of the Film began to investigate the "character" of nitrate decomposition, reasoning, "Almost everyone realized that nitrocellulose film was unstable; but just how long it would last under optimum storage conditions, and what these optimum storage conditions were, no one knew."<sup>55</sup> The autocatalytic nature of nitrate decomposition, once initiated by ignition, was already widely recognized (and as such, the committee also strongly endorsed the use of storage cans that would automatically vent in case of fire<sup>56</sup>), but the initiating catalyst remained mysterious. Early hypotheses favored camphor, but tests on the levels of camphor present in decomposing nitrate led the committee to conclude that it was probably unrelated to nitrate decay. In the end, the body was only able to say, "Nitrate film is

<sup>&</sup>lt;sup>52</sup> E. W. Fowler and L. B. Newell, "Storage and Handling of Motion Picture Film," *JSMPE* 16 (June 1931): 775.

<sup>&</sup>lt;sup>53</sup> Committee on the Preservation of Film, "Report of the Committee on the Preservation of Film," JSMPE 20 (June 1933): 526.

<sup>&</sup>lt;sup>54</sup> Interestingly, the authors concede that "Early recommendations suggested a temperature of 40 to 50 and a relative humidity of 60 per cent," but say that recommendation was overturned since it required a film acclimatization room between the vault and the workroom. Committee on the Preservation of Film, "Report" (1933), 524.

<sup>&</sup>lt;sup>55</sup> Committee on the Preservation of Film, "Report" (1936), 148.

<sup>&</sup>lt;sup>56</sup> Iron clamps were designed that "permitted the lid to lift approximately one inch." Committee on the Preservation of Film, "Report" (1936), 152. Interestingly, the design of the experiment *might* suggest that the authors considered crystalline nitrate more flammable than noncrystalline nitrate.

at its best an unstable product, and anything which tends to increase its oxidation and hydrolysis will hasten deterioration."<sup>57</sup>

Beginning in December 1936, however, research into the mechanisms behind decomposition began to bear fruit. First, comparative research into the durability of nitrate and safety stocks led authors J. R. Hill and C. G. Weber to conclude that decomposition of the base plastic was the cause of decomposition of the silver halide emulsion.<sup>58</sup> Then, in June 1937, E. K. Carver published an article attributing the irregular decomposition of nitrate film stock to imperfect washing, suggesting that acidic residues triggered decay.<sup>59</sup>

The year 1937 would prove a watershed from a safety perspective, as well. On July 9, a nitrate fire ripped through a Fox storage facility in New Jersey, marking the first major nitrate fire attributed to spontaneous ignition. The event seemed to confirm reports of smaller fires resulting from spontaneous combustion that had been trickling in each summer over the course of a decade. The Fox materials ranged between five and twenty-five years of age, and a *QNFPA* article attributed all fires linked to spontaneous combustion to aging stock. Still, the NFPA shied away from strong causal claims linking combustibility to decomposition (emphasis below my own):

It is a well-known fact that scrap nitrocellulose material has a far greater fire hazard than the new material and that *some* nitrocellulose products tend to deteriorate with age, becoming less stable and more subject to decomposition after a *long* period of years. It is also possible that nitrocellulose film manufactured twenty or twenty-five years ago may not have been as well stabilized as the present American product and thus may be more subject to the possibility of spontaneous decomposition than the film in current use.<sup>60</sup>

That same month, the SMPE's Committee on the Preservation of the Film made fire safety a priority, acknowledging (rather reluctantly), "emphasis is shifting (temporarily, at least) from a consideration of preservation in terms of deterioration to a consideration of preservation in terms of film fires and film handling." Noting that "some recent and rather extensive film fires" partially spurred this shift, the committee agreed to "take cognizance of the fire problem

<sup>&</sup>lt;sup>57</sup> Committee on the Preservation of Film, "Report," (1936), 150. Because it failed to account for the tightly rolled structure of motion picture film, the committee's conclusion about camphor may have been premature. Later tests indicated that, in roll film at least, a significant amount of camphor could be retained over time. See M. Edge, N. S. Allen, M. Hayes, and P. N. K. Riley, "Mechanisms of Deterioration in Cellulose Nitrate Base Archival Cinematograph Film," *European Polymer Journal* 26, no. 6 (1990): 624.

<sup>&</sup>lt;sup>58</sup> J. R. Hill and C. G. Weber, "Stability of Motion Picture Films as Determined by Accelerated Aging," JSMPE 27 (December 1936): 688.

<sup>&</sup>lt;sup>59</sup> E. K. Carver, "The Manufacture of Motion Picture Film," JSMPE 28 (June 1937): 598.

<sup>&</sup>lt;sup>60</sup> Schedule Rating Office of New Jersey, "Fox Film Storage Fire," QNFPA (October 1937): 142.

as falling in the field of preservation, and render all possible service to those seeking help."<sup>61</sup>

By the end of 1937, then, it was clear that nitrate fire safety was an archival problem. Unfortunately, though, recognition of this fact seemed to have shifted attention away from research into the mechanisms behind nitrate decay. Though the Society of Motion Picture Engineers and the National Fire Protection Association both continued to publish nitrate fire safety recommendations, only one known article published between 1933 and 1950 addresses the mechanisms of nitrate decomposition, and it does so only indirectly. In a 1939 piece that explicitly targets moving image archival repositories, Gibson and Weber outline tests for indicators of decay (most notably acidity),<sup>62</sup> in very small samples taken from archival films. The article is an interesting one, because it describes early examples of minimally destructive tests for nitrate decomposition capable of detecting decay before the naked eye.<sup>63</sup>

But for many nitrate repositories (probably even for many of the repositories targeted by Gibson and Weber), the last word on decomposition management seems to be the committee's 1933 suggestion that "Periodic inspection of the original negative copies should be made at long intervals...of not less than one year or more than five years." Inspectors were instructed to "determine whether the film base is showing signs of deterioration, or whether the emulsion is adhering to the base," and "to determine the amount of shrinkage that has taken place." But only if "the film is showing marked shrinkage" should "a new master positive...be made at once so that the pictures contained on the film shall at all times be available for future use."<sup>64</sup> Despite the Fox fire, decay audits were not described as fire safety events until the following decade.

Another spate of fires attributed to spontaneous combustion in the mid-1940s renewed interest in the decomposition process, resulting in the 1950 publication of the seminal article, "Spontaneous Ignition of Decomposing Cellulose Nitrate Film." As its title suggests, the piece by James W. Cummings, Alvin C. Hutton, and Howard Silfin sought to prove the causal relationship between decay and combustibility. At the urging of the National Archives, the Fire Protection Section of the National Bureau of Standards designed an experiment meant to establish the flashpoint of decomposing nitrate film. The results

<sup>&</sup>lt;sup>61</sup> Committee on the Preservation of Film, "Report of the Committee on the Preservation of Film," *JSMPE* 30 (March 1938): 300–301. The committee meeting was held October of the previous year.

<sup>&</sup>lt;sup>62</sup> Gibson and Weber also outline tests for viscosity and residues left by sodium thiosulfate (more commonly known as "hypo"), a chemical used in photographic processing that is supposed to be removed during washing.

<sup>&</sup>lt;sup>63</sup> J. E. Gibson and C. G. Weber, "The Evaluation of Motion Picture Films by Semimicro Testing," *JSMPE* 32 (January 1939): 105–9.

<sup>&</sup>lt;sup>64</sup> Committee on the Preservation of Film, "Report" (1933), 529. Gibson and Weber do not mention fire safety either. See Gibson and Weber, "The Evaluation of Motion Picture Films," 105–9.

described in the article are now quite well known: the first roll of film ignited after an interval of seventeen days at 106 degrees Fahrenheit (less than half the number previously considered the material's flashpoint); the second ignited at 120 degrees Fahrenheit; no two rolls ignited at the same temperature.<sup>65</sup> Less well known, though, is the experiment's methodology, which is worth quoting at length:

Samples in various stages of decomposition were supplied by the National Archives for the purpose of simulating conditions which may have prevailed at the fire locations. These samples were stored in a special chamber, the temperature of which was controlled and recorded. The films were packed in individual cans with each wrapped in mineral wool to retain the heat of the exothermic decomposition reaction. The ambient temperature in the chamber was initially 95°F and, at intervals, was increased by small increments.<sup>66</sup>

Upon closer inspection, the experiment was shockingly poorly controlled. First, the choice to wrap the rolls in mineral wool may have been a necessary safety precaution in a room packed with other nitrate cans, but it seems to run in direct opposition to the experimenters' goal of "simulating the conditions which may have prevailed at the fire locations." Second, the article never gives the precise sample size. Apparently, however, it was not large, since the authors caution, "Because the number of samples investigated was small, it is doubtful whether this is the lowest temperature at which a reel of film can self-ignite."<sup>67</sup> Finally, and most importantly, the experimenters give little data in their report about the degree of decomposition of each experimental roll. They note only that the first roll to ignite was in "an advanced stage of deterioration,"<sup>68</sup> and that thus far, no film "in good condition has self-ignited," but these descriptions are imprecise, at best.<sup>69</sup> Were the most severely decayed films in Cummings et al.'s sample also the most combustible? We simply do not know.

Nevertheless, Cummings, Hutton, and Silfin go on to elucidate a five-stage decomposition process: First, "the photographic portion usually shows an amber discoloration with fading of the picture image." Second, "the emulsion becomes adhesive and the film convolutions tend to stick together during unrolling." Third, rolls develop "annular portions which are soft, contain gas bubbles, and emit a noxious odor easily recognizable." Fourth, "the entire film is soft, its

<sup>&</sup>lt;sup>65</sup> James W. Cummings, Alvin C. Hutton, and Howard Silfin, "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," *JSMPTE* 54 (March 1950): 269–70.

<sup>&</sup>lt;sup>66</sup> Cummings et al., "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," 270

<sup>&</sup>lt;sup>67</sup> Cummings et al., "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," 270.

<sup>68</sup> Cummings et al., "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," 269.

<sup>&</sup>lt;sup>69</sup> Cummings et al., "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," 270. The wording of the article also makes it impossible to discern whether the rolls in "good condition" were control samples of newly manufactured nitrate stock, or whether they were merely in a less "advanced stage of deterioration."

convolutions welded into a single mass and frequently its surface is covered with a viscous froth. A strong noxious odor is given off, unmistakable to inspection personnel when once identified." Finally, "the film mass degenerates partially or entirely into a brownish acrid powder."<sup>70</sup>

The authors explain that the entire image is "photographically reproducible" during the first two stages only. In the third stage, "only small portions of the film may be reproducible." Finally, during the last two stages, the film is "photographically worthless" and "should be destroyed at once without further consideration." At all stages of decomposition, the authors recommend disposal of the nitrate original, but (and despite, it seems, the poor controls of the original experiment) they also associate the final three stages of decomposition with increased fire risk: "Films of stages three, four, and five, designated for disposal, should be immediately submerged in water-filled drums. They should be carried in these drums to a remote, uninhabited area approved by fire authorities and destroyed by burning."<sup>71</sup>

Though the basis for the idea that later stages of decomposition pose greater fire risks is weakly established in "Spontaneous Ignition of Decomposing Cellulose Nitrate Films," the model of decomposition the article set forward proved to be very influential. In articles published for the projectionist, archivist, and amateur photographer communities, Kodak spokesperson John Calhoun disseminated the five-step process first elucidated by Cummings et al.<sup>72</sup> Still today, every major archival and safety standard cites the Cummings et al. piece (or a Calhoun derivative). Descriptions in archival manuals can also be traced to Cummings et al. (though they do not often cite it directly). In other words, archivists continue to revisit an inadequate experiment. Indeed, experimental methodology aside, Cummings et al.'s conclusions fail to describe the mechanisms behind decay, the relative duration of each stage of decay, or the precise pattern and rate of increase of fire risk.

Meanwhile, within the film archival community, only film preservation historians (like Enticknap and Grimm<sup>73</sup>) and image stability researchers (like Bigourdan) have tended to revisit the earlier pieces. Hypotheses about the roles of metal cans or acidic residues as catalysts for decomposition have persisted as archival folk wisdom, but have not been addressed in domestic or international

<sup>&</sup>lt;sup>70</sup> Cummings et al., "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," 271–72.

<sup>&</sup>lt;sup>71</sup> Cummings et al., "Spontaneous Ignition of Decomposing Cellulose Nitrate Film," 274.

<sup>&</sup>lt;sup>72</sup> See, for instance, John M. Calhoun, "Storage of Nitrate Amateur Still-Camera Film Negatives," *Journal of the Biological Photographic Association* 21 (August 1953): 674–78; John M. Calhoun "Old Nitrate Films Are Dangerous!," *International Projectionist* 37 (May 1962): 8–9, 17–18; and John M. Calhoun, "The Preservation of Motion Picture Film," *American Archivist* 30 (July 1967): 517–25. See also Robert A. Mitchell, "Common Sense: Best Film Preservative," *International Projectionist* 37 (May 1962): 4–6.

<sup>&</sup>lt;sup>73</sup> See Charles "Buckey" Grimm, "A History of Early Nitrate Testing and Storage, 1910–1945," *The Moving Image* 1, no. 2 (2001): 21–38.

standards. No sources seem to account for the diametrically opposed positions of *ISO 10356* and the Kodak *MSDS* on the brown powder stage.<sup>74</sup> Most disturbingly, standards and manuals continue to revisit literature from the first half of the century and ignore developments in chemical descriptions of nitrate decay that began to appear in the late 1980s.

### Temperature, Moisture, and Other Catalysts: Scientific Descriptions of Nitrate Decay

Recent experimentation in controlled settings suggests that nitrate decay is actually the result of several chemical reactions. The nitration process "grafts" nitrate groups<sup>75</sup> onto cellulose molecules,<sup>76</sup> creating a large compound that "By nature,...has the tendency to 'unmodify' itself and return to its native [cellulose] form by releasing the [nitrate] side-groups."<sup>77</sup> This reaction is externally catalyzed, usually by heat or moisture.<sup>78</sup> Actually, *all* substances decompose in the very long term, but the thermal sensitivity of the oxygen-nitrogen bond in cellulose nitrate is so acute that these bonds are, in the words of a team of European chemists, "almost readily cleaved."<sup>79</sup> The bonds are also very sensitive to moisture, which engenders hydrolytic reactions that accelerate the cleavage reaction. In fact, moisture is probably a more critical factor than temperature in nitrate decay.<sup>80</sup> Though its catalysts are external, its environmental threshold is so low that the primary decomposition reaction is inevitable in ambient conditions.

Happily, primary decomposition catalyzed by temperature and moisture is also very slow in ambient conditions, and slower still—indeed, virtually negligible—at the temperature and humidity levels recommended for long-term

<sup>&</sup>lt;sup>74</sup> This Film Is Dangerous includes a brief mention of an explosion attributed to impact in Scotland in 1982. It should be noted, however, that the fire occurred when nitrate was being transported in a trunk during the summer and that no description of this event is referenced in the Kodak document. See Janet McBain, "A Sobering Lesson," in *This Film Is Dangerous*, 566–67.

 $<sup>^{75}</sup>$  Nitrate is a negatively charged ion composed of one nitrogen and three oxygen atoms that can be expressed as the formula (NO $_{
m s}$ ).

 $<sup>^{76}</sup>$  Cellulose is a polysaccharide composed of hundreds to thousands of linked glucose chains that can be expressed in the formula  $(\rm C_6H_{10}O_5)_{n}$ .

<sup>&</sup>lt;sup>77</sup> Bigourdan, "From the Nitrate Experience," 55.

<sup>78</sup> UV radiation also catalyzes the reaction, though it is less relevant in a film archival setting.

<sup>&</sup>lt;sup>79</sup> Edge et al., "Mechanisms of Deterioration," 623.

<sup>&</sup>lt;sup>80</sup> N. S. Allen, M. Edge, C. V. Horie, T. S. Jewitt, and J. H. Appleyard, "The Degradation and Stabilization of Historic Cellulose Acetate/Nitrate Base Motion-picture Film," *The Journal of Photographic Science* 36 (1988): 106. Hydrolysis is also very harmful to the emulsion layer, a strong argument that low relative humidity should be prioritized in film preservation. See Edge et al., "Mechanisms of Deterioration," 623.

storage of nitrate film (2°C and 20–30% RH, respectively).<sup>81</sup> Unhappily, primary decomposition produces "volatile nitrogen oxide products," which catalyze secondary reactions in both the photographic base and emulsion. These reactions in turn produce more nitrogen oxides, creating an autocatalytic reaction loop.<sup>82</sup> Initially, secondary decomposition, like primary decomposition, is a relatively slow reaction. It increases at an exponential rate, however, and enters a very fast stage. For this reason, nitrate decomposition often appears to be very sudden— a film that has survived intact for decades may irrecoverably decay seemingly overnight. Once triggered, secondary nitrate decomposition can only be arrested by subfreezing temperatures.<sup>83</sup>

If temperature and humidity are the most omnipresent causes of nitrate decay, they are not the only ones. Almost all cellulose nitrate produced for moving image film stock was nitrated with a mixture of nitric and sulfuric acid. Although the sulfate groups created by the presence of the latter were theoretically removed in washing processes, in practice they could almost never be fully cleaned from the nitrate cellulose. Sulfate groups attract moisture and accelerate hydrolytic decomposition reactions.<sup>84</sup> Additionally, basic stabilizers, added to many batches of film stock with the intention of counteracting acid-catalyzed reactions, may have ironically themselves catalyzed decomposition reactions instead.<sup>85</sup>

Finally, research by Edge et al. demonstrates that iron catalyzes nitrate decay in at least two ways: first, iron cleaves the cellulosic backbone of nitrate cellulose; second, it reacts with nitrogen byproducts of nitrogen-oxygen cleavage to form basic compounds that attack more nitrogen-oxygen bonds, another autocatalytic reaction.<sup>86</sup> According to Edge et al., iron is a necessary catalyst for film to reach the final, powder stage. Though the precise composition, and therefore combustibility, of the powder itself remains unknown, analysis conducted by Edge et al. suggests that it contains nitrogen-oxygen functional groups, a fact that directly contradicts *ISO 10356*.<sup>87</sup> Although it is highly unlikely that the powder is shock sensitive, it is even more unlikely to be as inert as paper.

<sup>&</sup>lt;sup>81</sup> Bigourdan, "From the Nitrate Experience," 61.

<sup>82</sup> Edge et al., "Mechanisms of Deterioration," 623.

<sup>&</sup>lt;sup>83</sup> Bigourdan, "From the Nitrate Experience," 61. Still, this is an improvement, since it was long thought that *nothing* could arrest the secondary reactions.

<sup>&</sup>lt;sup>84</sup> Charles Selwitz, *Cellulose Nitrate in Conservation* (Marina Del Rey, Calif: J. Paul Getty Trust, 1988), 15. Selwitz's piece boasts an extensive review of scientific literature about cellulose nitrate, covering several decades of research.

<sup>&</sup>lt;sup>85</sup> Selwitz, *Cellulose Nitrate in Conservation*, 31. On this point, however, the Getty Conservation Institute provides no citation.

<sup>&</sup>lt;sup>86</sup> Edge et al., "Mechanisms of Deterioration," 629-30.

<sup>&</sup>lt;sup>87</sup> Edge et al., "Mechanisms of Deterioration," 628.

The full chemical sequence of nitrate cellulose decomposition was still only beginning to be theorized as late as 1995. Results published that year by Louvet, Lavadrine, and Flieder, however, confirmed that the molecule's weakest chemical bonds are those between oxygen (O) and nitrate (N) in the nitrate groups attached to its cellulose backbone. When the O-N bonds are broken, either by reaction with heat or moisture, they produce nitrogen dioxide (NO<sub>2</sub>), which in turn reacts with moisture to form nitric acid (NO). NO reacts with the O-N bonds in the cellulose nitrate molecules, producing still more moisture (itself a trigger for primary decomposition of the O-N bonds). NO also appears to react with the emulsion, fading the image by oxidizing the silver. In other words, we can be sure that the byproducts produced by primary decomposition of the O-N bonds are highly reactive and will sustain an autocatalytic reaction if they are not removed from contact with the film.<sup>88</sup>

The dominant byproducts of decomposition are acidic (even the basic catalysts produced in the presence of iron-release acidic molecules); thus, the degree of decay can be best predicted by acidity measurements. Indeed, as Gibson and Weber noted more than seven decades ago, acidity tests reveal the onset of decomposition long before it is possible to observe with the human eye.<sup>89</sup> This may cast some doubt on the value of the five-stage decomposition model; but unfortunately, even after seven decades, no nondestructive acidity tests for nitrate decay yet exist.

In practice, a suite of factors affected by the production and storage conditions of each print influence the decomposition process. Therefore, the decomposition process and its symptoms can also vary, undoubtedly a cause of the discrepancies in current descriptions of both for archival audiences. The largest cause for those discrepancies, though, must surely be the lack of communication between the archival and scientific communities. Only Jean-Louis Bigourdan has published his work in a source targeted primarily at archival audiences, and, though he cites the work of Edge et al. and Louvet et al., he does not cover all of their findings (nor should he necessarily be expected to).

#### Conclusion

Of course, the scientific literature also has significant gaps. Perhaps because research in the 1980s and 1990s was more concerned with image stability than with safety, it did not directly correlate decomposition to flammability. And,

<sup>&</sup>lt;sup>88</sup> A. Louvet, B. Lavadrine, and F. Flieder, "Size Exclusion Chromatography and Mass Spectrometry of Photographic Bases in Cellulose Nitrate Degradation," *The Journal of Photographic Science* 43 (1995): 30.

<sup>89</sup> P. Z. Adelstein et al., "Behavior of Nitrate Base Film," 368.

without full knowledge of the byproducts of nitrate decomposition, the archival and safety communities cannot easily extrapolate fire risk either. In addition, laboratory research has been sparse, sample sizes have been small,<sup>90</sup> and incentives for follow-up studies are low (after all, nitrate film stock is a discontinued product).

But the largest problem, in my opinion, is the minimal cross-talk among the archival, safety, and scientific communities. Archivists and safety officials have failed to follow developments in polymer science that affect their work, relying instead on outdated literature from their own fields. At the same time, the few scientists who have taken an interest in issues of nitrate preservation have failed to translate their findings into recommendations that can be readily understood by the communities to which those findings are most relevant.

So, what's to be done about all of this? Because I can hardly claim to be an expert in the field of polymer chemistry and because the citation tracking methodology I chose restricted the field of literature I reviewed,<sup>91</sup> this paper can only constitute a first step toward improved understanding of the cellulose nitrate

<sup>&</sup>lt;sup>90</sup> Edge et al. used a sample of four films in "Mechanisms of Deterioriation," 634. Adelstein et al. used a sample of five films in their influential article, "Stability of Cellulose Ester Base Photographic Film: Part IV—Behavior of Nitrate Base Film," 359. Louvet et al. drew their experimental "subjects" from a collection of four million sheet film negatives, a much larger sample, but one composed of still—rather than motion picture—film. Louvet et al., "Size Exclusion Chromatography and Mass Spectrometry," 30.

<sup>&</sup>lt;sup>91</sup> In researching this paper, I also reviewed the following historical sources (in alphabetical order, by author's last name): Henry Anderson, "Fire Prevention in the Motion Picture Industry," JSMPE 27 (December 1936): 662–76; Henry Anderson, "Paramount Studio Fire." ONFPA (April 1929): 438–41; John G. Bradley, "Changing Aspects of the Film Storage Problem," JSMPE 30 (March 1938): 303–17; John M. Calhoun, "The Physical Properties and Dimensional Behavior of Motion Picture Film," JSMPE 43 (October 1944): 227-66; "California Hospital X-Ray Film Fire," QNFPA (January 1930): 254-57; F. Carroll and John M. Calhoun, "Effect of Nitrogen Oxide Gases on Processed Acetate Films," JSMPTE 64 (September 1955): 501-507; Committee on the Preservation of Film, "Report of the Committee on the Preservation of Film," JSMPE 35 (December 1940): 584-606; "Consolidated Film Library Fire," QNFPA (January 1930): 243-51; "Film Exchange Fire Prevention Results," QNFPA (January 1926): 224-29; Charles R. Fordyce, "Improved Safety Motion Picture Film Support," ISMPE 51 (October 1948): 331-50; Charles R. Fordyce, "Motion-Picture Film Support: 1889-1976, An Historical Review," JSMPTE 85 (July 1976): 493-95; G. L. Hutchison, L. Ellis, and S. A. Ashmore, "The Surveillance of Cinematograph Record Film During Storage," *JSMPTE* 54 (March 1950): 381–83; "The Inflammable Picture Film," *QNFPA* (October 1922): 109–10; Ernest H. Lindgren, "Preservation of Cinematographic Film in the National Film Archive," SMPTE Journal 78 (October 1969): 876-79; Jac. R. Manheimer, "A Film Fire at Sea," QNFPA (April 1928): 337-38; Glenn E. Matthews and Raife G. Tarkington, "Early History of Amateur Motion-Picture Film," SMPTE Journal 64 (March 1955): 105-16; C. E. Kenneth Mees, "History of Professional Black-and-White Motion-Picture Film," ISMPTE 63 (October 1954): 134-37; Robert A. Mitchell, "The 35mm Projection Positive Film," International Projectionist 25 (February 1950): 7–9, 32–34; "A New Film Fancy," *QNFPA* (October 1925): 129; "Nitrocellulose Film Fires," *QNFPA* (July 1920); 108–109; A. H. Nuckolls and A. F. Matson, "Some Hazardous Properties of Motion Picture Film," *JSMPE* 27 (December 1936): 657–61; "The Pathé Studio Fire," *QNFPA* (January 1930): 220–26; A. J. Snow, "Salt Lake City Film Fire," *QNFPA* (January 1930): 252–54; Albert, F. Sulzer, "The Epoch of Progress in Film Fire Prevention," *JSMPE* 34 (April 1940): 398–408; Earl Thiesen, "The History of Nitrocellulose as a Film Base," JSMPE 20 (March 1933): 259-62.

The following image stability articles may also be of interest: P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and C. J. Erbland, "Stability of Cellulose Ester Base Photographic Film: Part II—Practical Storage Considerations," *SMPTE Journal* 101 (May 1992): 347–53; P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, C. J. Erbland, and J. L. Bigourdan, "Stability of Cellulose Ester Base Photographic Film: Part V—Recent Findings," *SMPTE Journal* 104 (July 1995): 439–47.

fire threat, one that I hope will be revisited, amended, and corrected in future publications. In the short term, archivists should continue to collect, review, and compile sources-both published and oral-on nitrate composition and decomposition. We should also begin to revise manuals, standards, and practice based upon the findings of published studies. Manuals and standards should no longer endorse copy-and-destroy policies as optimal solutions.92 The paramount catalytic functions of temperature and particularly humidity should be emphasized, and phrasing suggesting that rapid decay is inevitable and beyond our control should be eliminated. Iron's role as a catalyst should be officially recognized. The descriptions of the powder stage found in ISO 10356 and the Kodak MSDS should both absolutely be removed. One probably underestimates the threat of fire and exposure; the other probably panics shippers;<sup>93</sup> both are very likely erroneous. More generally, the utility of the five-stage decomposition description should be reconsidered. In the last analysis, it may not provide much information beyond the obvious fact that a film or photo's historical value fades with its images.

In the medium term, moving image archivists should consider changes in practice, as well. Certainly, we should follow the advice of Jean-Louis Bigourdan and develop acid testing strips for nitrate inspection.<sup>94</sup> Ideally, moving image archivists should also begin to compile information about their films and storage conditions, in an effort to begin to answer residual questions with practice-centered data. For example, should we continue to house materials in cans containing iron that might catalyze decomposition? Has storage in cans made of other materials (e.g., plastic and aluminum) had any observable effect upon films? Should we store films with stabilizing chemicals? Edge et al. suggest that a "tris stabilizer," uniting a metal deactivator, a hydroperoxide decomposer (a thermal stabilizer), and hindered piperidine (a very stable basic compound), could as much as double the lifespan of a nitrate print even under ambient conditions<sup>95</sup>—but what are the practical costs and benefits associated with such

<sup>&</sup>lt;sup>92</sup> Adelstein et al. note that "nitrate films in storage *do* represent a distinct fire hazard; duplication may be justified for this or other curatorial reasons." Adelstein et al., "Behavior of Nitrate Base Film," 360. Risk analysis might also better inform recommendations about copy-and-destroy policies in cases where fire hazards are elevated.

<sup>&</sup>lt;sup>93</sup> FedEx and UPS now refuse to ship nitrate by air unless it is packaged according to code for HAZMAT class 4.2, though it is officially classified in the less hazardous 4.1 class.

<sup>&</sup>lt;sup>94</sup> Bigourdan, "From the Nitrate Experience," 61. Such strips have been developed for cellulose acetate already. See P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and C. J. Erbland, "Stability of Cellulose Ester Base Film: Part III—Measurement of Film Degradation," *SMPTE Journal* 104 (1995): 290.

<sup>&</sup>lt;sup>95</sup> Edge et al., "Mechanisms of Deterioration," 630.

a strategy, and is it effective in cold storage?<sup>96</sup> Finally, we need to properly assess and quantify the fire risks associated with nitrate storage, rather than continuing to rely on anecdotal evidence—and we might begin to do the same for other nitrate-related safety issues, including potential health risks from exposure to nitrocellulose material and the off-gases it produces.

As a long-term goal, we need to work to improve communication lines among archivists, the National Fire Protection Association, and nitrate chemical researchers so that future findings and concerns are properly disseminated. Significant barriers to communication exist, and one major reason that the moving image archival community has not engaged with scientific publications is technical language. A possible solution is the addition of a stronger chemistry component in moving image archival education programs, closer to the model of conservation schools than to that of library schools.<sup>97</sup> Smaller steps, such as inviting chemists to archival conferences, or publishing updated white papers on nitrate conservation,98 should also be taken. Practicing archivists should participate as much as possible in future scientific research. Ideally, this participation would include donation of films and storage materials to laboratory experiments, expanding the size and diversity of future research samples. Archivists should also play to their own strengths and gather as much contextual information as possible about extant motion picture prints, seeking to identify patterns in survival rates. On a simpler, but arguably more urgent level, communication lines to the general public should also be improved. Nitrate film stock is desperately in need of an advocacy campaign that emphasizes its assets rather than its liabilities.

The nitrate moving image archival community is small—there are probably no more than a dozen archivists employed full time in the highly specialized field of nitrate preservation. Though the small size of this community may at first appear to be a stumbling block to the kind of widespread reform suggested in this paper, it is quite the opposite: it means that the largest collections of nitrate motion picture film are relatively centralized, a favorable condition for future research opportunities. Reforms targeted at repositories with smaller volumes of nitrate holdings will probably follow the policies adopted first at larger institutions such as the Library of Congress, George Eastman House, the

<sup>&</sup>lt;sup>96</sup> A review of literature conducted by Berkeley's Bancroft Library on the storage of flat film (an excellent source, incidentally, for archives looking to implement cold nitrate storage) found that sieves were ineffective and even harmful in low temperature conditions. See Loren C. Pigniolo, "Low-Temperature Storage of Nitrate Still Film: A Case Study and Model," in *IS&T's 2004 Archiving Conference, Proceedings*, ed. F. Frey and R. Buckley (San Antonio, Tex.: Society for Imaging and Technology, 2004), 207.

<sup>&</sup>lt;sup>97</sup> Technical skills will probably be necessary for long-term digital preservation as well.

<sup>&</sup>lt;sup>98</sup> AMIA's new publication, AMIA Tech Review, might be an ideal venue for such publications. See http:// www.amiatechreview.com/, accessed 2 April 2010.

Academy, or UCLA.<sup>99</sup> And, in the meantime, the Association of Moving Image Archivists and the Society of American Archivists can alleviate the more quotidian costs of shipment and disposal through the organization of regular HAZMAT training sessions for members (the societies' annual conferences would be ideal venues).<sup>100</sup>

Though the number of nitrate motion picture film archivists is small, the lessons of this study impact a far wider group (and not least the still photographic archivists whose flat film collections are now included in the scope of *NFPA 40*). Despite the fact that archivists are often accused of an overly empiricist outlook, we may fail to interrogate and test our field's received wisdom. Just as many archival scholars have begun to ask, "Who are our users?," we might also remember to ask, "What are our materials?"—even, perhaps especially, when the answer seems obvious.

<sup>&</sup>lt;sup>99</sup>Larger institutions like these might consider publishing white papers that clearly outline best practices for smaller institutions without staff members specialized in film or photographic preservation.

<sup>&</sup>lt;sup>100</sup>AMIA's Nitrate Film Committee has already arranged for moving image archives to share the cost of an emergency response telephone number service. For more information about the Nitrate Film Committee, visit http://www.amianet.org/groups/committees/nitrate/nitrate.php, accessed 2 April 2010.

After completing this piece for publication, I learned about an article by Greg Hill, "New Nitrate Film Storage for Library and Archives Canada," in *Topics in Photographic Preservation* 10 (2003): 74-85. It documents research LAC conducted in preparation for its new building, including two collaborative efforts: one with the Canadian Explosives Research Laboratory (CERL) on cold storage and explosive venting, and the other with health inspectors on human sensitivity to exposure to nitrate holdings. The CERL found that "the rate and temperature of combustion of nitrate was significantly reduced" at -20°C (p. 80), while the health inspectors measured levels of nitric oxide and nitrogen dioxide well below the accepted safety thresholds, but nonetheless high enough for "several employees working on the nitrate segregation project for extended periods" to develop "chronic sensitivity to it" (p. 83). Hill's paper is an important example of the research called for in my article, and I highly recommend it not only for the data it provides, but also as a model for continuing investigation into nitrate material by the archival community. I am indebted to Kathleen Mullen, Preservation Coordinator at the Wisconsin Historical Society, for giving me this article and demonstrating the importance of yet another body of literature, that of conservators.