

A National Cellulose Acetate Search?

A paper by Angeletta Leggio¹, Hilary Berthon² and Colin Webb² Preservation Services, National Library of Australia - presented to the First National Symposium, Book and Paper Group, AICCM, Canberra, March 2000

Good morning. This paper really belongs to Angeletta Leggio and Hilary Berthon from our National and International Preservation Activities section, and I'll very shortly sit down and let Angeletta talk about cellulose acetate, a subject which she is far better equipped to discuss than I am. However, I wanted to take just a few minutes to tell you where this paper came from, and some of the more general things we are putting in place to try to address our problems with cellulose acetate.

We've been worried about acetate in our collections for some time. There are places where we store photographic negatives and microfilm where we get that faint whiff of vinegar that tells us something is amiss. In other collections I have seen negatives from the 1950s that looked a bit dodgy one year, and were unprintable a year later. For a collection like ours at the National Library of Australia, the potential for information loss is immense. We hold something like xxx photographic negatives, many from the 1920s to the 1960s – classic acetate stuff. We hold something like xxx microfilms, including many produced from the 1940s to the 1970s – we even know that some microfilms we hold from the 1980s were produced on acetate. In our Oral History collections we know we have a lot of tapes on an acetate base – although like everyone else we have never seen any of them with vinegar syndrome.

So we're sitting on something of a time bomb. Everything we know about other libraries and archives in the country suggests that they almost certainly have similar potential problems.

Now it's easy to say there are reliable solutions to this. In the world of conservation research this one looks like something that was settled some years ago. People like the Image Permanence Institute, Kodak, and others have been studying this for a long time. We know some things we could do. We know that when we find an acetate neg we can put it into cold storage and put off the day when it will be unprintable. We know when we find an acetate microfilm that we had better copy it as soon as we can. In that way it's an easy thing. The researchers move on to the next problem.

But the preservation managers know that they aren't dealing with a single neg or a single roll of microfilm. We're dealing with hundreds of thousands, they're scattered through our collections, and we don't have the resources to find them, we don't have the resources to

store them properly, and we don't have the resources to copy them. Not all at once, anyway, and not without a lot of help.

I've already said that we have been aware of this problem for some time. We have been dealing with the immediate problems, by doing exactly the things I just mentioned. We've already copied a lot of acetate microfilm, including a lot of the camera masters of the Australian Joint Copying Project (which will mean something to people working in libraries and archives – the AJCP was one of the first great international microfilming projects that Australian libraries undertook, filming unique records about Australia in UK record offices and archives – virtually all AJCP microfilm masters were made on acetate). So we haven't been idle. But frankly, we know we've barely scratched the surface (probably an unfortunate term in this context).

For the past couple of years we've been focused on getting our nitrate material under some kind of control. We can recognise that our acetate problems are going to make our nitrate problems look very insignificant, but there have been good political reasons why we had to concentrate on the nitrate.

We've also been hoping that the magic solution would come along to solve our acetate problems. Every time someone publishes something about acetate we look in hope. But we've finally concluded that this is a vain hope. While the options are available, no-one is going to design a workable, cost-effective strategy that will tell us exactly what to do. (Or maybe they will – we just haven't read the right literature, or spoken to the right people yet.)

So this is where we are – looking at the options and trying to work out what is going to work for us, knowing that we're going to have to go begging for resources to implement it. And at this stage assuming, emphasise assuming, that others are in the same position. We want to test that assumption, to see if there is value in working on these implementable, politically sellable strategies together.

Now I'll hand over to Angeletta to get into the interesting parts.

Cellulose acetate has been a widely used carrier for photographic still negatives, movie film, microfilm and audio. However, it is subject to slow deterioration, releasing acetic acid: this phenomenon is known as the 'vinegar syndrome'. Accompanying this degradation are many visible signs of physical deterioration – shrinkage, channelling, buckling, the appearance of crystals and bubbles on the surface of the film – and ultimately, loss of the information carried on the film. The vinegar syndrome poses a serious threat to a large portion of our twentieth century documentary heritage. In response to this threat, the National Library of Australia (NLA) has launched a project which will investigate the range of strategies available for dealing with the problem of cellulose acetate degradation in collections. It will scope the extent of the problem nationally and plans to use this information to develop recommendations for cost-effective national action.

The cellulose acetate project is one of a number of preservation projects which the NLA is keen to undertake in partnership with others. It is being coordinated through the newly formed National & International Preservation Activities (NIPA) section of Preservation Services Branch. The Library is keen to draw upon the collective experience of institutions

around Australia in handling cellulose acetate and seeks comments or information about the cellulose acetate problem from others engaged in managing cellulose acetate collections. To assist it in obtaining information about the condition of collections within Australian institutions, and current practices, strategies, attitudes and resources available to deal with this problem, the Library has produced a questionnaire which will be sent to Australian institutions holding cellulose acetate collections. The Library will also be contacting these institutions to discuss their requirements and experience with managing cellulose acetate collections to ensure that any proposed solutions reflect the needs of the various institutions. The website which the NLA has established for this projectⁱ provides background information about the project, contact details and an online version of the questionnaire.

Cellulose acetate is the generic term used to describe a variety of acetylated cellulose polymers, including cellulose diacetate, cellulose triacetate and the mixed esters of cellulose acetate propionate and cellulose acetate butyrate. Both cellulose diacetate and cellulose triacetate may be acetylated on one, two or all three of the available sites on each glycopyranose ring. Cellulose diacetate usually has a degree of substitution of 2.3 and triacetate close to 2.7ⁱⁱ. The mixed esters usually have degrees of substitution of about 1.8.

While cellulose acetate was first produced in 1869ⁱⁱⁱ, it wasn't used in the photographic and film industries until 1909. Eastman Kodak Company produced small quantities of sheet film in the hope that it would replace unstable cellulose nitrate. However, due to limitations with the manufacturing technology at the time, it wasn't until 1923 that an adequate process was found. This was used to produce 16mm amateur motion picture film (home movie) on a large commercial scale.^{iv}

This material, known as cellulose diacetate, became brittle and shrunk within a short period, so modifications were made to increase its stability. In the early 1930s mixed esters, such as cellulose acetate propionate and butyrate, were used to produce 16mm and 8mm motion picture film, sheet film and x-ray film. In the late 1940s, 35mm film and microfilm were produced on cellulose triacetate. By 1951, production of cellulose nitrate had stopped and motion picture film, microfilm and negatives were being produced on triacetate film. At last, many believed a stable carrier had been found. However, in the early 1950s, a large number of deteriorating triacetate films were found in India. This resulted in further changes to the production, but deteriorating cellulose acetate collections continued to be found throughout the 1970s until today. Since the early 1980s, research has been conducted to determine why cellulose acetates deteriorate, and how the mechanism can be reversed, slowed or stopped.

The factors responsible for the hydrolysis of the acetyl side groups from the main cellulose chain appear to be numerous and are typically difficult to fully identify. Anecdotal accounts abound of widely varying rates of cellulose acetate deterioration which cannot be attributed to differences in storage conditions. However, the presence of moisture, acids and elevated temperature have all been shown to be crucial factors in controlling the rate of deacetylation.

Deacetylation of cellulose acetate requires the presence of water. While removal of water would effectively prevent hydrolysis of the acetyl side group from occurring, some water is necessary to prevent the acetate film from contracting and becoming brittle. Therefore, while it is recommended that relative humidity be kept in the low range to slow

deacetylation, a relative humidity of at least 20% is required to ensure physical damage to the film does not occur. As well as humidity control, low temperature storage has been demonstrated to result in very significant reductions in the rate of cellulose acetate deterioration.^v

Acetic acid generated on deacetylation gradually diffuses to the surface of the film. Initially, the free acid is generated slowly, the rate of reaction being governed primarily by temperature and relative humidity. However, after the autocatalytic point has been reached, the levels of free acid rapidly increase as the presence of free acetic acid catalyses further deacetylation and the reaction rate is influenced mainly by the presence of the acidity. High levels of free acid result in visible signs of deterioration such as shrinkage (through chain scission and loss of plasticiser and solvents), embrittlement (through chain scission); channelling (see Figures 1 and 2), crystals and bubbles on the surface (caused by migration of the plasticiser) and oxide shedding on reels of film. The well-known vinegar odour also occurs.

Other factors which have been suggested to play a role in cellulose acetate degradation include: the presence of iron^{vi}; the nature of the plasticiser^{vii}; the presence of pollutants in the storage environment or residual chemicals from the manufacturing process^{viii}; and the gelatin emulsion^{ix}. Finally, it should be mentioned that, while the vinegar syndrome is the major problem affecting cellulose acetate collections, this material is subject to other forms of deterioration, which may need to be taken into account when managing these collections.

The strategies for dealing with cellulose acetate deterioration fall broadly into the categories of: slowing down the deterioration; and transferring the information held on the cellulose acetate film to new carriers. Slowing down the deterioration of cellulose acetate may be achieved by controlling the temperature and humidity of the storage environment, and by the removal of the generated acetic acid through ventilation or actively, through use of molecular sieve acid scavengers. Effective monitoring, with indicators and other passive types of monitoring can assist in the management of cellulose acetate collections by identifying the degree of deterioration which has occurred and the urgency with which action may be required. Rescue treatments, such as emulsion transfer, may be considered to be an option for valuable material which has degraded. Finally, copying, for example through photographic duplication, or digitisation, may be considered.

In its cellulose acetate project, the NLA will investigate the feasibility of the strategies mentioned above. The project will have a national focus which takes account of the potential for cooperation and the cost-effectiveness of the proposed solutions. The NLA looks forward to sharing the results of this project with other Australian institutions and working with them to find solutions which will ensure that our heritage on cellulose acetate film survives.



¹ State Library of Victoria

² National Library of Australia

ⁱ National Library of Australia. *Cellulose Acetate Project A National Strategy for Dealing with Deteriorating Cellulose Acetate Collections*. Online. Available:

<http://www.nla.gov.au/preserve/ca.html>. 16 March 2000.

ⁱⁱ Edge, M. (1995) *The Decay of Polymers in Information Storage Carriers. Technology and Our Audio-Visual Heritage: Technology's Role in Preserving the Memory of the World. Fourth Joint Technical Symposium, Jan 27-29 1995, National Film Theatre, South Bank, London, UK*. Technical Coordinating Committee: London. pp 20-30.

ⁱⁱⁱ Aubier, D. et al. (1996) *Degradation Caused by Cellulose Diacetate: Analysis and Proposals for Conservatin Treatment*. Restaurator Vol.17 No. 2. Munksgard: Copenhagen pp130-143.

^{iv} Fordyce, C.R. (1976) *Motion-Picture Film Support, 1889-1976: An Historical Review*. Journal SMPTE Vol. 85, pp493-495.

^v Reilly, J.M. (1993) *IPI Storage Guide for Acetate Film*. Image Permanence Institute: New York.

^{vi} For example, see: Allen, N.S. et al. (1988) *Acid-Catalysed Degradation of Historic Cellulose Triacetate, Cinematographic Film: Influence of Various Film Parameters*. European Polymer Journal Vol. 24 No. 8, pp 707-712.

Allen, N.S. et al. (1988) *The Degradation and Stabilisation of Historic Cellulose Acetate/Nitrate Base*. Journal of Photographic Science Vol. 36 No. 3, pp 103-106.

Allen, N.S. *et al.* (1988) *The Nature of the Degradation of Archival Cellulose-Ester Base Motion Picture Film: the Case for Stabilisation*. Journal of Photographic Science Vol. 36 No. 2, pp 34-39.

Allen, N.S. *et al.* (1992) *Degradation and Stabilisation of Cellulose Triacetate Base Motion Picture Film*. J. Imaging Science and Technology, Vol. 36 No. 1, pp 4-12.

Jacobsen, M. Determining New Standards for Long Term Storage of Film. Online. Available: <http://www.dancan.dk/standards.html>

Edge, M. *et al.* (1988) *Cellulose Acetate: An Archival Polymer Falls Apart. Preprints of Contributions to the Modern Organic Materials Meeting. Edinburgh 14-15 April, 1988*. Scottish Society for Conservation and Restoration: Edinburgh. pp 67-79.

^{vii} For example, see: Lee, W.E. and Bard, C.C. (1988) *The Stability of Kodak Professional Motion-Picture Film Bases*. SMPTE Journal Nov. 1988. pp 911-914.

Shinagawa, Y., Murayama, M. and Sakaino, Y. *Investigation of the Archival Stability of Cellulose Triacetate Film: the Effect of Additives to CTA Support*. In: Allen, N.S. *et al.* (1992) *Polymers in Conservation*. Royal Society of Chemistry: Cambridge.

^{viii} Reilly, J.M. (1993) *IPI Storage Guide for Acetate Film*. Image Permanence Institute: New York.

^{ix} For example, see: Edge, M. *et al.* (1988) *Cellulose Acetate: An Archival Polymer Falls Apart. Preprints of Contributions to the Modern Organic Materials Meeting. Edinburgh 14-15 April, 1988*. Scottish Society for Conservation and Restoration: Edinburgh. pp 67-79. Allen, N.S. *et al.* (1988) *Acid-Catalysed Degradation of Historic Cellulose Triacetate, Cinematographic Film: Influence of Various Film Parameters*. European Polymer Journal Vol. 24 No. 8, pp 707-712.