

The Vinegar Syndrome. Early warning improves the occupational health and the preservation of the collection of films

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1. Introduction

Photographic and film materials held in collections run the risk of degrading. An infamous problem is known as Vinegar Syndrome (Wilhelm 1993; Catalina and delAmo 1999). This is a chemical process in which the cellulose acetate base film degrades and since this type of film has been in use since about 1950, the scale of this problem is significant. As well as attacking film-base materials, the aggressive acids released in the syndrome damage film emulsion. These acids, primarily acetic acid, are also harmful to health. Eventually the entire film is lost. This process may be accelerated and aggravated by poor storage conditions. The early detection of deteriorating materials is essential if a film collection is to be conserved. The current methods to determine the degradation state are based on time-consuming acidity strips or subjective visual observation. It will be helped enormously by a new fast objective method for locating film in an early stage of degradation and measuring the extent of the degradation.



Figure 1. An example of a cellulose acetate base film, severely affected with the Vinegar Syndrome (photo by Hadassa Koning, used with kind permission).

The current methods to determine the degradation state are based on time-consuming acidity strips or subjective visual observation. It will be helped enormously by a new fast objective method for locating film in an early stage of degradation and measuring the extent of the degradation. Near Infrared Spectroscopy (NIR) has been proven being a suitable, fast and non-destructive method for the identification of cellulose based materials (Michell 1995; Havermans and Aziz 2005). Therefore we dedicated this work for developing a management tool for film identification and degradation based on NIR.

2. Experimental

Classification of the origin of films

The films were originally classified by a) the description of the manufacturer or b) the preservation worker or c) testing according to ISO 18901 into the three groups cellulose acetate, cellulose nitrate or polyester carrier (Anonymous 1999; ISO18901 2002).

Degradation

A reference set of naturally aged cellulose acetate based films was created. This was based on the degree of degradation using A-D strips film base deterioration monitors, Image Permanence Institute, Rochester (Anonymous 1998). For a quantitative determination of the degree of degradation, a free acidity test was performed, according to ISO 18901, 2002 (ISO18901 2002).

Artificially aged set

Known cellulose acetate film materials were subjected to artificially ageing to establish a certain degree of degradation (Bigourdan, Adelstein et al. 1998). The ageing conditions applied were $(90.0 \pm 0.5) ^\circ\text{C}$ and $(50 \pm 1)\%$ relative humidity for a maximum of 800 hours.

Measuring the NIR-spectra of the film samples

The artificially aged samples were combined with naturally aged samples to create the final reference set of test specimen. From each sample the NIR spectrum was recorded from $4000 - 9000 \text{ cm}^{-1}$ using a Buchi NIRFlex N-400 equipped with a NIRFlex Horizontal Sample Desk connected to a personal computer with NIRCAl software. All the film samples were positioned on the NIRFlex Horizontal Sample Desk in such a way, that the light enters the film from the anti-halo layer or the carrier. Subsequently two basic calibration sets were developed using the 450 samples.

3. Results

The first calibration set was the classification on the origin of the film carrier. Discrimination was made between cellulose acetate, cellulose nitrate or polyester films. The second calibration set was the prediction of the degree of degradation of the cellulose acetate film. The degradation levels were expressed in three levels according to the used reference methods.

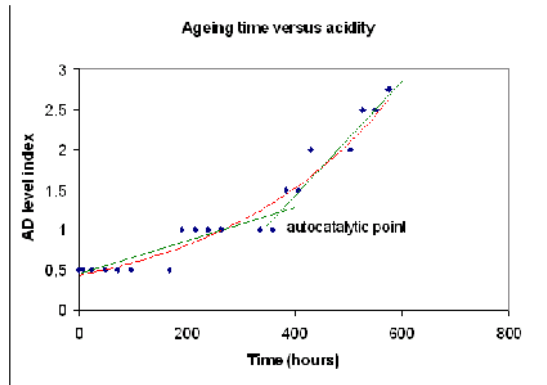


Figure 2 presents the result of the artificially aged cellulose acetate films. Based on these results, it is obvious that the degradation follows an exponential curve. This is in agreement with other researchers as the reaction follows an autocatalytic second order acid catalysed hydrolyses (Feller 1994). At A-D level 1-1.5 (380 hours) the autocatalytic point is reached. From this point on the degradation of the film accelerates. According to the A-D Strips Manual, three deterioration groups for cellulose acetate films have to be considered. These groups were confirmed by means of the results from the Free Acidity Test. It was remarkable, that the Free Acidity Test as measured volumetrically, gave no linear relation with the A-D strips method.

Figure 2. A-D level index. The x-axis shows the time of the materials subjected to the artificial ageing, and the y-axis shows the A-D level index.

Based on the absorption of dedicated organic groups present in the films, a classification model for distinguishing the raw material of the film material was established using 50 samples per known origin. The validation was carried out using 15 samples per origin. Grouping of the film materials was applied. Based on the clustering methods, we were able to make a cluster of the used origin of the materials: cellulose acetate; cellulose nitrate and polyester. Subsequently the NIR spectra of the Cellulose acetate films with different known ageing level were correlated with the results of the A-D strips method and the Free acidity Test.

4. Conclusion

Based on the results, a simple user interface was concluded, enabling the user of the interface to characterise the origin of the film and the degree of the film. This user interface is simple following the tree shown in Figure 4. Based on the answer of the user interface, the film can be stored under the correct storage conditions and if needed further action can be taken for preventing the film and the collection for further deterioration. Also by selecting out the materials that are in a highly degree of deterioration, a positive contribution to the indoor air quality of the storage will be given, as less acetic acid emitting materials are left in the store location.

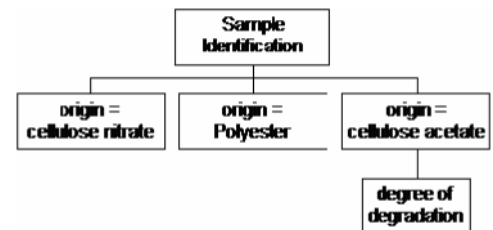


Figure 3. The user interface. After placing a sample, the answer will follow within a second.

5. References

- Allen, N. S. and M. Edge (1992). Degradation and Stabilisation of Cellulose Triacetate Base Motion Picture Film. *Journal of Imaging Science and Technology* **36**: 4.
- Anonymous (1998). User's Guide for A-D Strips. Film Base Deterioration Monitors. The Safe and Accurate Way to check Film for Vinegar Syndrome. Rochester, Image Permanence Institute.
- Anonymous (1999). Appendix M: Management of Cellulose Nitrate and Cellulose Ester Film. *NPS Museum Handbook, Part 1*, Museum Management Program. **I**.
- Bigourdan, J. L., P. Z. Adelstein, et al. (1998). "Use of Micro-Environments for the Preservation Cellulose Triacetate Photographic film." *Journal of Imaging and Technology* **42**(2): 59-66.
- Catalina, F. and A. delAmo (1999). *Los soportes de la cinematografía 2*. Madrid, Ministerio de education y cultura.
- Feller, R. L. (1994). "Accelerated aging: photochemical and thermal aspects, Research in conservation." (4): 23-27.
- Havermans, J. B. G. A. and H. A. Aziz (2005). "NIR as a tool for the identification of Paper and Inks in conservation research." *Restaurator* **26**: 172-180.
- ISO18901 (2002). ISO 18901: Imaging materials - Processed silver-gelatin type black-and white films - Specifications for stability. Geneva, Switzerland, ISO: 1-22.
- Michell, A. J. (1995). Near-Infrared Spectroscopy - A Valuable Tool For Pulp And Paper Research? *49th APPITA Annual General Conference*, Hobart, Australia, Appita, Australia.
- Wilhelm, H. (1993). The Permanent Preservation of Color Motion Pictures. *The Permanence and Care of Color Photographs: Traditional and Digital Color Prints, Color Negatives, Slides, and Motion Pictures*. Iowa, Preservation Publishing Company: 299-345.