Stabilizing treatment of decaying cellulose acetate film base attacked by vinegar syndrome

Karin Bonde Johansen [1] & Jesper Stub Johnsen [2]
[1] Film Archivist, Danish Film Institute, Copenhagen, Denmark
[2] Head of Department of Conservation, National Museum of Denmark, Copenhagen, Denmark.

Abstract

An overview of previous research and description of recent experiments of washing of fresh and decaying motion picture films are addressed in this paper. The objective is to investigate whether treatment methods can be a supplement or an alternative to cold and dry storage for cellulose acetate films. Despite some experiments showing positive treatment results, none have led to a perfect or even useable method as an alternative to good storage conditions.

Introduction

Since the mid 1980s, many experiments have been performed to investigate the degradation pathways of cellulose acetate films and to find ways to slow them. Degradation of cellulose acetate is known as the vinegar syndrome due to a distinct smell of vinegar. The most dominant results suggest that long term stability depends on storage at low temperature and low humidity [1].

What of the alternatives? Is active treatment possible to reduce decay of cellulose acetate films? As indicated in a survey by the Netherlands Film Museum [2] there are still many unanswered questions. Some researchers claim that using molecular sieves to reduce the vinegar syndrome is a benefit others do not. Rewashing may have a temporary benefit and in India this technique has been used systematically in order to reduce the vinegar syndrome.

Overview

This overview concerns research both on the microclimate around the film and treatments of the film. The benefit of good storage environment is described well in other papers [3][JSJ1].

The microclimate around film has also been investigated; buffered cardboard cans with an alkaline reserve or interleaves of buffered paper to adsorb generated acetic acid delay degradation of the film [4]. However, the effect was only limited. In 1988 it was found that cans of iron increase the degradation of cellulose triacetate [5].

Ventilation of cans was investigated. Ventilation may avoid accumulation of decomposition of acid by-products from the film. Newnham found that two holes aligned seemed to give the best airflow in the can [6], but Bigourdan & Reilly [7] found that even if the cans were ventilated effectiveness at preventing the vinegar syndrome was minimal. Airtight cans are not recommended.

Molecular sieves, silica gel and zeolites are all desiccants, which can adsorb gases including acetic acid or water vapour. These desiccants have been investigated for their abilities to adsorb acetic acid in film cans and thereby keeping the degradation rate of cellulose acetate low. In 1994 it was found that molecular sieves were an effective way to reduce acids and recommended for long term storage [8]. In 1998, molecular sieves and silica gel were found to be effective at lowering acidity levels in motion picture films, if 5 %wt based on the mass of the film were used [9]. Ligterink investigated zeolite in 2002 [10] and he found that only large amounts of zeolites were effective in reducing the acidity level in motion picture films if water vapour was present. Water competes with acetic acid for adsorption sites in zeolites.

Besides changing the microclimate in order to reduce acidity of the film, several different methods have been tried with the film itself. At the Vietnam Film Institute, ventilation of an unwounded film supported on a grid before washing reduced the acid level considerably. There were on the other hand problems with shrinkage of the film using this method [11].

Experiments performed by Newnham and Garvie in 2003 showed that using low tension wind (less than 300 g of hold back tension) of 35 mm film reels before long-term storage were recommended [12].

Chemical treatments of film are poorly described in the literature. Allen et al (1990) describe experiments using baths of weak bases (aqueous solutions with calcium stearate and nickel stearate, and also ammonium and magnesium acetates), but none of these experiments stabilized decayed films [13]. In the same paper experiments with several different stabilizers are described [14]. Despite some positive effects on acidity, the experiments have not been mentioned again.

To date, no treatment has been identified which might supplement or replace cold and dry storage. This led to the research project described in the next section.

Experimental

There were two goals for these experiments:

1) During the lifetime of a film, the film is washed several times. We do not know the long-term effect of water on film, except that high humidity accelerates degradation. The film is of course washed after developing, prints might be rewashed several times to reduce scratches and original negatives are often rewashed more than once before the first copy is made. No experiments have been published which have investigated the long-term effect on washing.

2) The experiments described here investigated whether it was possible to wash the acetic acid from decaying films and thereby decrease the decaying effect of the vinegar syndrome. The experiments also include wash in an alkaline bath to investigate if it was possible to incorporate an alkaline reserve in the film, to neutralize acid accumulated later. This is inspired by paper conservation where deacidfication is a well documented procedure to improve the long term stability [15].

Thirty-five mm black and white motion picture films of cellulose triacetate, ORWO Positive Motion Picture film PF2 (FilmoTec GmbH, Germany), were used as test material for the experiments. The test material was wound around polypropylene cores with 30 m of film in each roll. To obtain test material with different degrees of degradation, one third was not pre-aged, one third was slightly pre-aged and one third was highly pre-aged. The pre-ageing was performed at 90°C. After pre-treatment, the rolls were washed in either tap water or in an alkaline solution of 0.1 M sodium acetate (CH_3COONa). The wash was carried out in a processing machine for microfilm (called COPEX FP500), and the speed at the machine resulted in total immersion of the film in the aqueous solution for 1 ½ minutes.

After the aqueous treatment the rolls were conditioned to 50 % relative humidity for three weeks, sealed tightly in bags and afterwards exposed to accelerated aging at 60°C for up to 10 months.

Measurements

The Water-Leach Free Acidity Test [16] was the main test method for monitoring the results of these experiments. Attenuated Total Reflection-Fourier Transform Infrared spectroscopy was also used. For more details, see Shashoua & Johansen, 2005 [17].

For the Water Leach Free Acidity Test small pieces of film are soaked in water, stirred at 38 °C for 24 hours and the mixture filtered. The solution is titrated against 0.1 M NaOH and the acidity value is expressed as millilitre 0.1 M NaOH. Duplicate measurements are made for each sample.

Results and discussion

Films that not have been pre-aged (called new films) benefited from washing after accelerated ageing. The untreated sample has generated more acid after 10 months of incubation, than the samples washed in water and 0.1 M sodium acetate (see figure 1). Therefore, according to these experiments it seems that various aqueous treatments performed on new films do not increase the rate of degradation; in fact it seems that aqueous treatments improve the stability of the film. There is no difference in the effect of the treatments between washing in water and in 0.1 M sodium acetate.

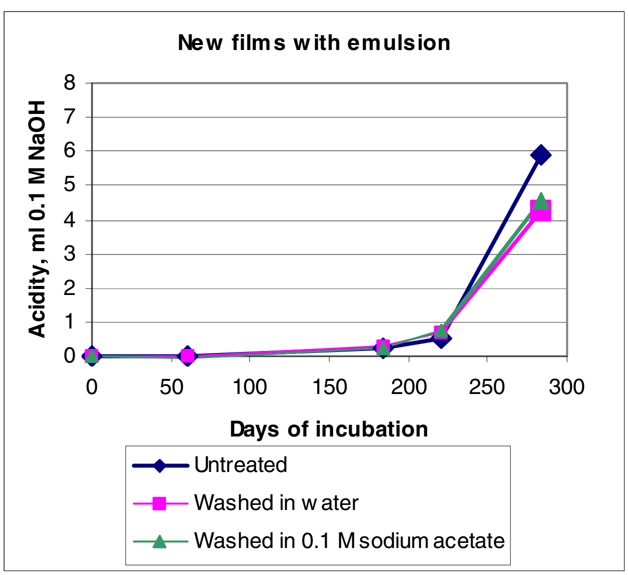

Figure 1. *Acidity in new cellulose triacetate films after incubation at 60°C.*

By contrast, the effect of washing slightly and highly pre-aged films is negative. The samples washed in water and the samples washed in 0.1 M sodium acetate generated higher amounts of acid after incubation than the untreated samples (see figures 2 and 3).

For the slightly pre-aged samples the negative effect occurred after 88 days of incubation, whereas the negative effect for the highly pre-aged samples can be seen after 35 days of incubation. This means that washing slightly degraded films might increase the degradation of the film, not immediately after the wash, but after some time. Washing highly pre-aged film will, according to these experiments, increase the degradation of the film soon after treatment.

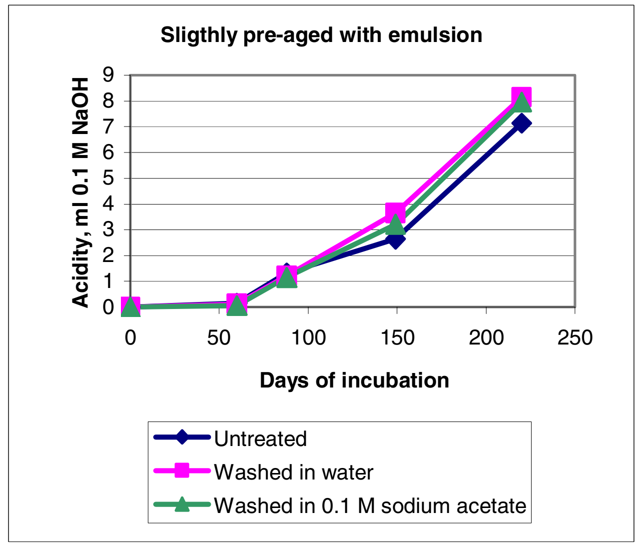

Figure 2. *Acidity in slightly pre-aged cellulose triacetate films after incubation at 60°C*

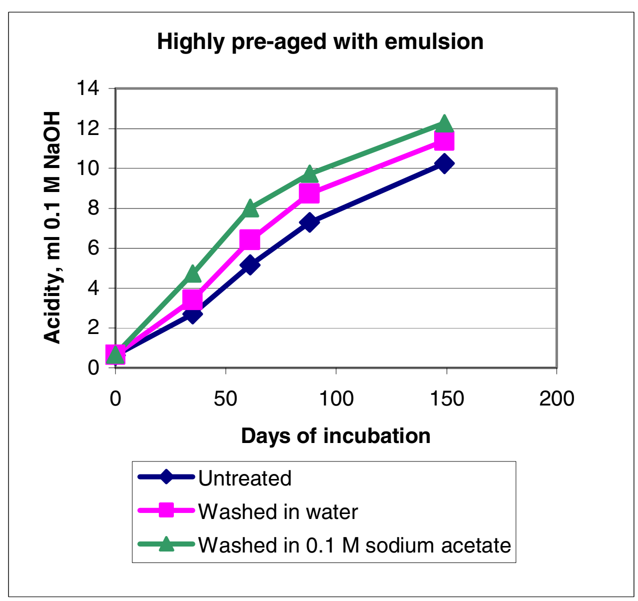

Figure 3. *Acidity in highly pre-aged cellulose triacetate films after incubation at 60°C.*

Conclusions of the experiments

The results of our experiments show that treatment of new films in water (forexample rinsing after developing) have no affect on the rate of degradation of the film.

On the other hand, aqueous treatment of decaying motion picture films may accelerate the degradation. This mean that treatment in water cannot be used in order to “wash away” acidity and it has not been possible to incorporate an alkaline reserve in or on the film. Based on these results rewashing old film in order to reduce scratches may accelerate the decay caused by the vinegar syndrome. For more details, see Johansen, 2004 [18].

General conclusion

Over the past 20 years the degradation of cellulose acetate still and motion picture films has been an issue of intensive research. The overall conclusion so far is that there is no alternative chemical treatment, special packing or ventilation procedure that is a realistic alternative to cold and dry storage if long term archiving of the film is important.

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Author Biography

Karin Bonde Johansen is film archivist at the Danish Film Institute since 1999. She is Master of Science from The Royal Danish Academy of Fine Arts, School of Conservation in 2004 with the thesis: Effect of Washing of Cellulose Triacetate Films with Different Degrees of Degradation. From 1992 to 1999 she worked among other things with Middle Ages manuscripts.

Jesper Stub Johnsen is Director of Conservation at the National Museum of Denmark. From 1999-2003 head of the Film Archive at the Danish Film Institute. He is PhD. from the University of Göteborg with a thesis on conservation management on photographic collections. 1982-1999 he worked as a photograph conservator at the National Museum of Denmark.