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Crystalline Deterioration on Glass Cinema Slides

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Abstract

Glass cinema Slides are similar to glass lantern slides. The slides are photographic images either created on an emulsion coated onto a glass plate or a section of photographic film sandwiched between two glass covers. The slides are intended to be viewed by projection onto a screen. The slides were used in many ways, such as advertisements and “sing-a-longs”, during cinematographic performances from the dawn of cinema until the late 1970’s.

Typically slides are robust, with physical damage the most common form of deterioration. However the National Film and Sound Archive (NFSA) collection contains examples of slides with significant crystalline growths that have formed within the slide.

Four slides from the 1930’s, both black and white and hand colored, were made available to be deconstructed to closely examine the nature of the growths. The slides were deconstructed by removing the paper binding tape and separation of the glass plates. This was done in a way that permitted the slides to be reassembled with the original tapes intact.

Raman Spectroscopy identified the substance as sodium sulphate. Further testing using FTIR Spectroscopy proved inconclusive. Previous research by Ishikawa had determined that the adhesives used were unlikely to be the source of the sodium sulphate.

There was little technical information found on the paper used as the binding tapes. However based on the physical characteristics of the material required it was thought that kraft paper was possibly used. The limited information also indicated that kraft paper may be the source of the sodium sulphate. However, since the information is scant, further research is being conducted to follow this suggestion through.

The simplest approach to removing the sodium sulphate by gently swabbing with water was followed. However due to the water soluble nature of the color dyes great care was needed, as was the requirement to avoid drying marks.

Introduction

Glass Lantern or Cinema Slides are positive transparent images on glass designed to be viewed by projection onto a screen. The process for manufacture of a lantern slide required a negative to be exposed onto a photographic glass plate to form a positive image for projection. Later processes used a gelatin plate process to develop the image and photographic manufacturers used plates coated with silver chloride or silver bromide plus other organic compounds for the process. The photographic image was produced in monochrome and could be tinted, chemically toned or hand colored. As the 20th century moved on, lantern slides were also made on film supports that were then sandwiched between glass.

Figure 1: Typical glass slide structure.

Once the photographic image was produced on glass it was sandwiched with a cover glass and then sealed around the edges with binding tape. Binding tapes made of paper with the adhesive already applied were sold commercially. The adhesive was activated by moisture and was usually gum based.

Research Aims

The National Film and Sound Archive (NFSA) hold a large collection of Glass Lantern and Cinema Slides. Within this collection there were a small number of slides exhibiting a white crystalline deterioration. As the most common type of deterioration for lantern slides is usually breakage of the glass support or damage to the photographic image layer, the deterioration on these slides was uncommon.

The aim of this research project was to identify the nature of this white crystalline deterioration. Once the nature of the crystalline substance had been confirmed, the information was to be used to develop a hypothesis of how and why this deterioration process occurred and to develop a treatment plan for the safe treatment of the deteriorated slides.

Four glass cinema slides, two colored and two black and white, were chosen for testing. No provenance or documented history was found to provide information on the age, usage or the storage conditions of these particular slides prior to their acquisition by the National Film and Sound Archive of Australia.

Investigation into the printed information on the paper binding tape of the pink colored glass slide, stating the glass slide manufacturer's name and address (Fig. 2), suggested that this slide was made in the early 1930's by Gunn's Slide, 9 Collins Place (Melbourne, Australia), between 1926 and 1938.

Figure 2: Binding tape showing the name and address of the slide manufacturer.

This information, as well as research into the song lyrics reproduced on the slides, indicates that it is probable that the slides were made around the same time that the songs were released. This would date the slides to be around 70 to 80 years old.

Methodology

It was essential that all testing techniques conducted on the glass cinema slides had to be non-destructive. A treatment was sought to remove the aesthetically blemishing and potentially pernicious substance. It was also important that once the research had been conducted and any appropriate treatments carried out, the slides could be reconstructed and the original paper binding tapes re-adhered to the glass.

Microscope Examination

A microscopic examination of each glass cinema slide being used in the research was carried out using an Olympus SZX9 microscope. Images were taken at several locations on each slide to examine the physical characteristics of the crystalline formation. Examples of these are shown in Figure 3.

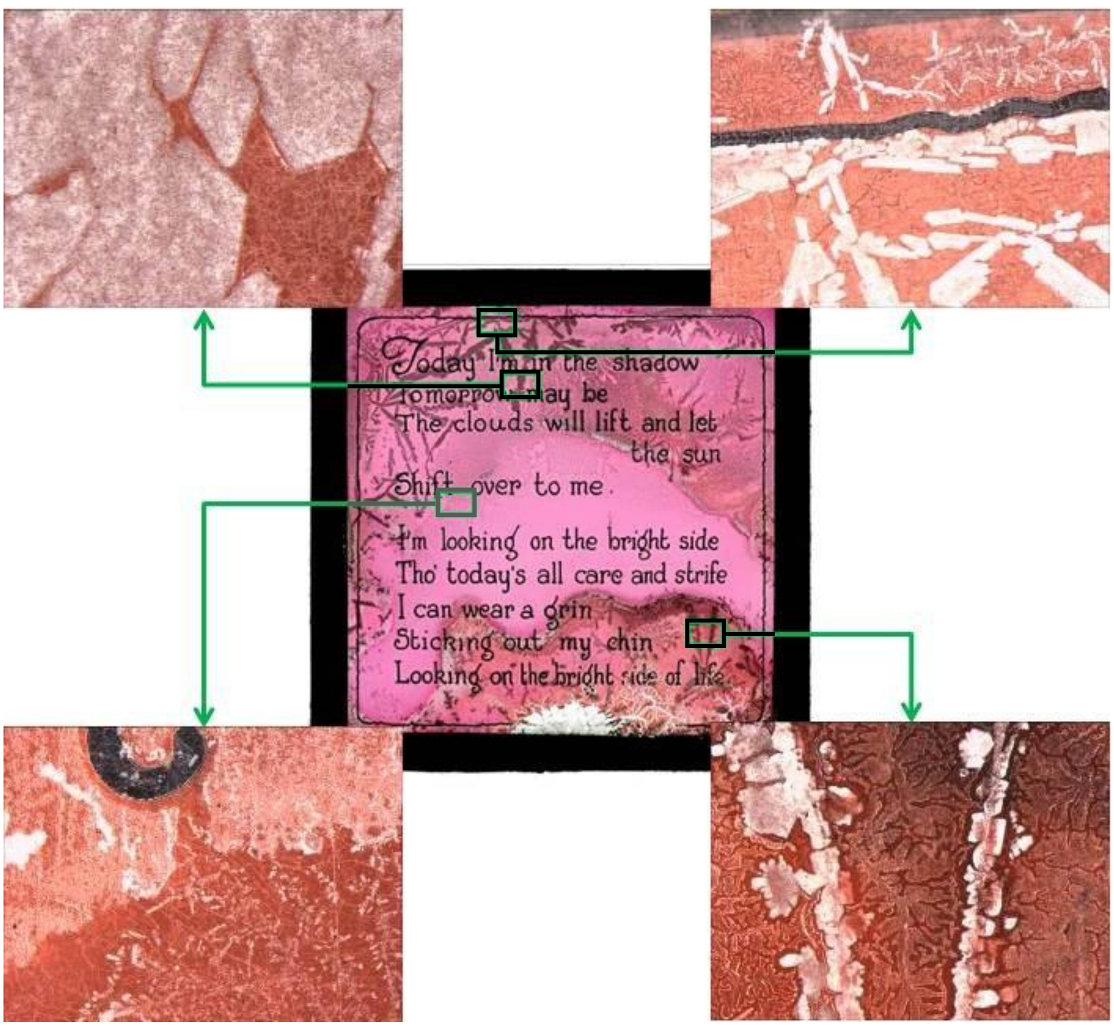


Figure 3: Photomicrographs of deterioration.

Slide Deconstruction
To access the white crystalline deterioration, the cover glass on each slide had to be removed.

The paper binding tape was detached from the glass slide on one side only, leaving the tape adhered to the other side of the glass slide. This was accomplished using a preservation pencil to relax the adhesive and soften the paper tape. It was then possible for a septum lifter to be guided under the edge of the paper tape and the paper lifted up to detach it from the glass.

This method of removal was generally straightforward except in a few areas which had an excess of adhesive. There were also some places where the tape was better adhered onto the vertical sides of the glass; it was hypothesized at the time that this may have been due to the deterioration process.

Once the paper tape was removed, the cover glass of the cinema slide was separated using a scalpel to pry the edges of the slide apart and break the seal. After separation, the crystalline formation was evident on both parts of the deconstructed slide.

Raman Spectroscopy
Raman Spectroscopy was chosen as a testing technique because of its non-destructive quality and minimal sample preparation requirement. It was serendipitous that the cover glass of the cinema slides fitted perfectly onto the Raman microscope stage eliminating the need to remove samples from the glass.

The Raman Spectrometer was set for testing using a 785 nanometer laser. This laser being closer to near infra-red, has lower energy than the alternative 653nm laser, thus reducing the potential for fluorescence in the test sample. Raman Testing was undertaken at the University of Canberra with the assistance of Alana Treasure, Paintings Conservator at the Australian War Memorial.

The testing was carried out in two separate locations on each cover glass. Initially, two visibly different areas of deterioration were chosen. However the finer thread like deterioration was not picked up by the Spectrometer and results showed peaks only for glass in these areas, possibly because the deterioration was too thin. Therefore each testing area was chosen for its solid white appearance (see figures 4a & 4b).

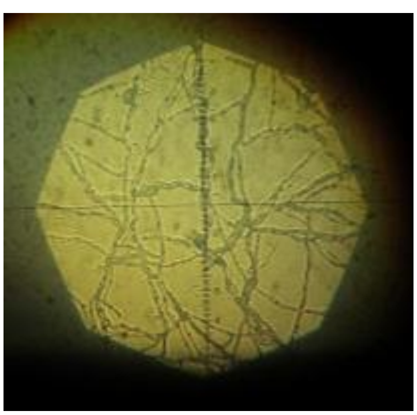


Fig. 4a: Threadlike deterioration.

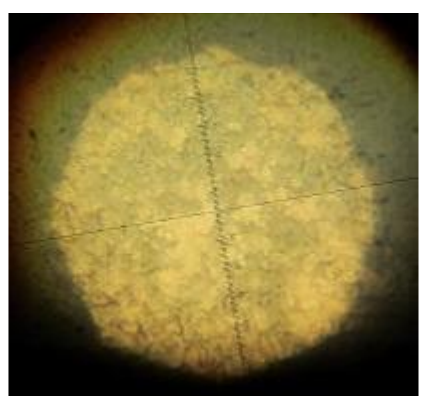


Figure 4b: Solid white deterioration as seen through the Raman microscope.

Binding Paper Test

The initial examination of the slides indicated that the crystalline deposits appeared to have started at the edges of the slide and progressed towards the centre of the slide. This suggested that the source of the crystalline substance was possibly external to either the glass or photographic image.

A test was conducted to see if any deterioration products could be extracted from the paper binding tape using a simple water extraction. A section of binding tape was removed from the black and white slide titled "My Shining Hour" (1) and the blue tinted slide titled "I'm Saying Goodbye with a Sigh" (2). Two test tubes were set up and the binding paper placed in the test tubes with 5mls of distilled water.

After a week, the water in test tube 1 was slightly cloudy while test tube 2 was less so.

The water from each test tube was qualitatively transferred to small beakers and the water was evaporated by heating (65-90^{o}C). After the liquid had evaporated a brownish residue remained in the bottom of each beaker. A sample of each residue was analyzed by FTIR Spectroscopy.

Fourier Transform Infra Red Spectroscopy (FTIR)

As a complimentary test and to confirm the Raman results, FTIR testing was undertaken at the National Archive of Australia.

With the assistance of the Archives' Conservation Chemist, Ms Rajani Rai, analysis of samples of the crystalline substance was carried out using a Thermo Nicolet Nexus FTIR spectrometer in attenuated total reflection (ATR) mode.

Samples from each of the cover glasses from the four cinema slides were tested individually and samples of the residue from the extract of the two binding papers were also tested.

Crystal Growth Experiment

The morphology of the crystals as observed under the microscope showed that the growth was probably from the edge of the slide inwards and that the parent substance was located outside the slide microenvironment.

To test this hypothesis a simple experiment to observe the growth of salt crystals within the slide microenvironment was conducted.

Two glass plates of the same dimensions as typical glass slides were bound together on all sides with paper tape and held with metal spring clips (Figure 5). The entire apparatus was placed in a sealed vessel and left for 48 hours.

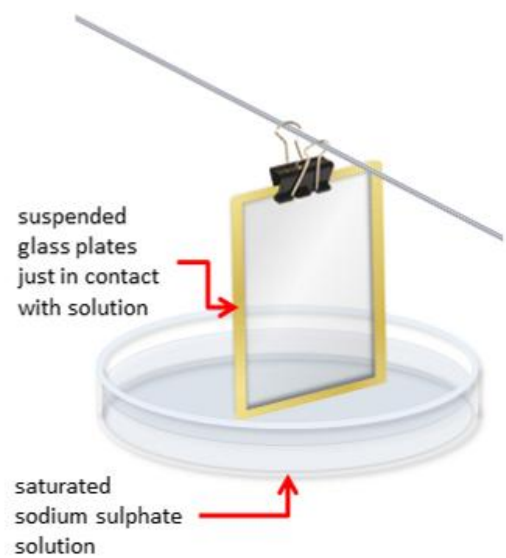


Figure 5: Crystal growth experiment.

The glass plates were removed from the vessel and left to sit under room conditions for several weeks until all the liquid that had been drawn between the plates had appeared to have evaporated and crystal growth had commenced.

Results

Raman Testing

The samples from all four glass cinema slides showed identical peaks, Figure 6 shows the typical spectrum. The peaks on the sample spectra substantially matched sodium sulphate (Na_2SO_4).

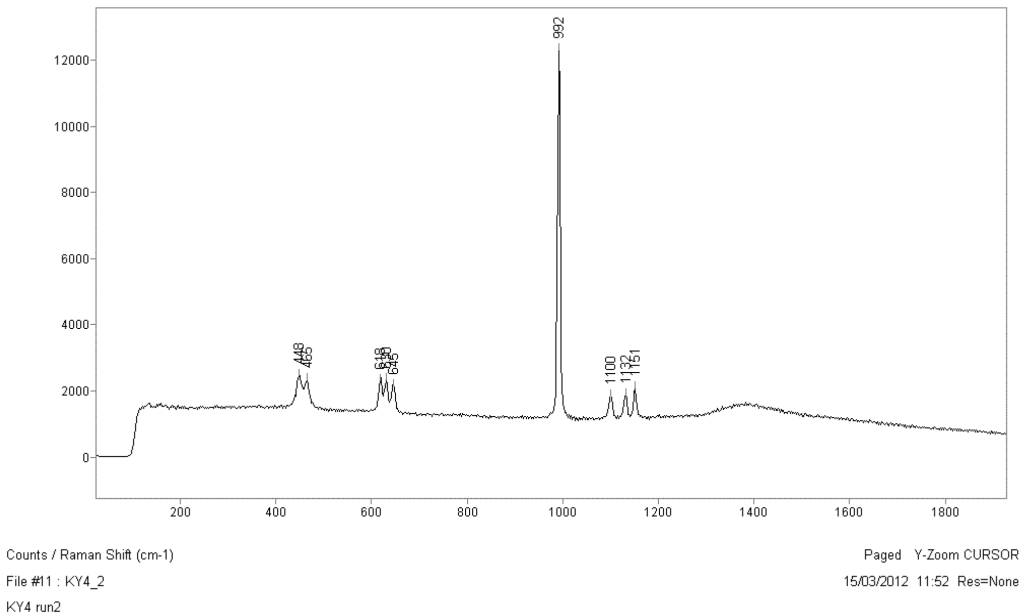
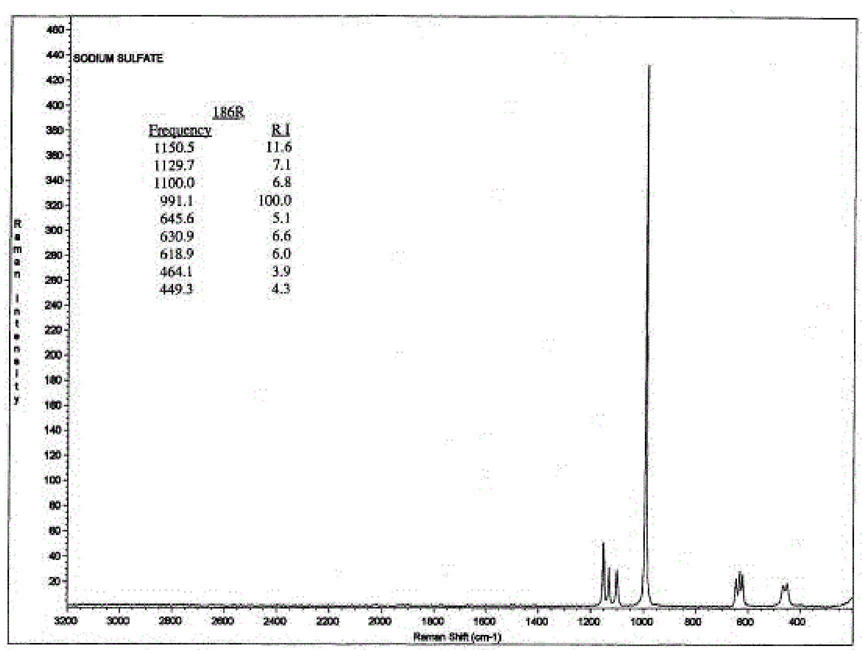


Figure 6: Raman analysis spectrum, typical from cover glass samples.



186 Sodium sulfate Na_2SO_4

Figure 7: Sodium sulphate Raman spectrum.

FTIR Results (Cover Glasses)

FTIR results from samples from all four cover glasses showed that there were strong peaks at 610-640 cm^{-1} and also at 1098-1110 cm^{-1}. Small peaks at 1633-1637 cm^{-1} and at 3274-3301 cm^{-1} was also noted on all four samples.

Research indicates that sulphates show two characteristic frequencies, one at 610 to 680 cm^{-1} and the other at 1080 to 1130 cm^{-1}. The area around 1633-1637 cm^{-1} is also an indicator for Na_2SO_4. These results confirmed the presence of sodium sulphate in the crystalline substance.

However, the Spectral Library at the National Archive of Australia returned the nearest match for the cover glass spectra results as Logwood Extract (Figure 8).

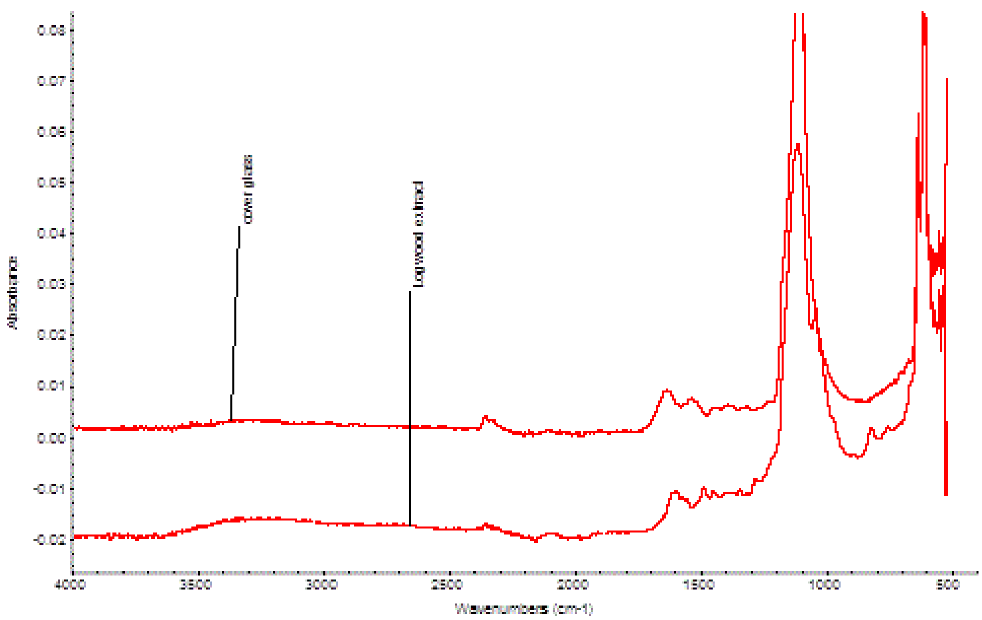


Figure 8: Overlayed spectra, cover glass sample and Logwood extract

Logwood extract is a dye which originates from the heartwood of the Logwood tree. This dye was used in the early 1900s to dye paper pulp and it was also used as a component of some inks. Further research is needed to determine whether this is a feasible match.

FTIR Results (Paper Extracts)

The FTIR results for the test sample from the paper extract contained strong peaks in the 1100 and 600 regions indicating a probability for sodium sulphate in the test sample. However, the National Archives Spectra Library showed the closest match for the paper extract was kaolin (Aluminum Silicate). Kaolin is used as filler in paper though it is insoluble in water.

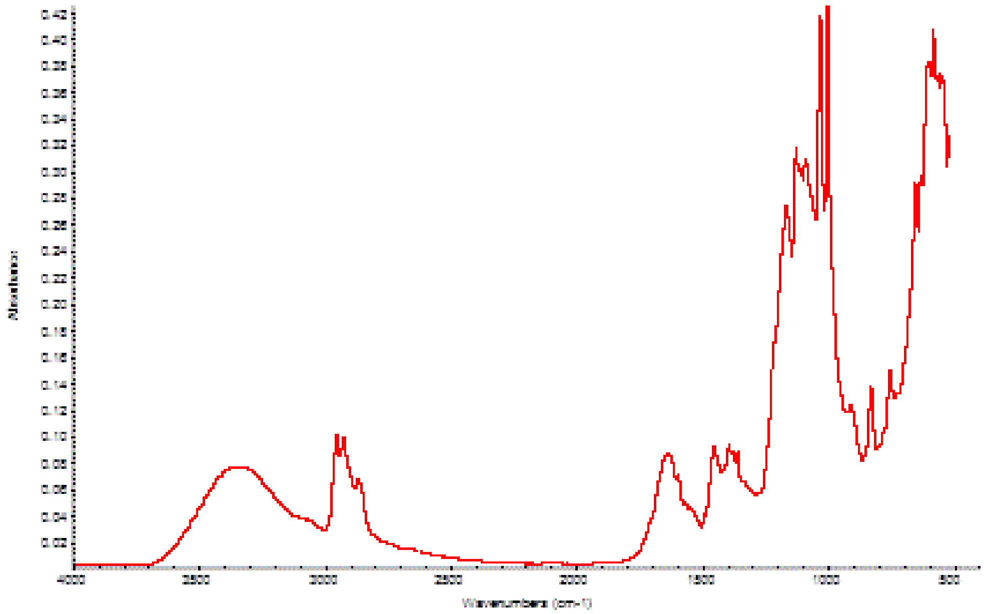


Figure 9: Paper extract 1.

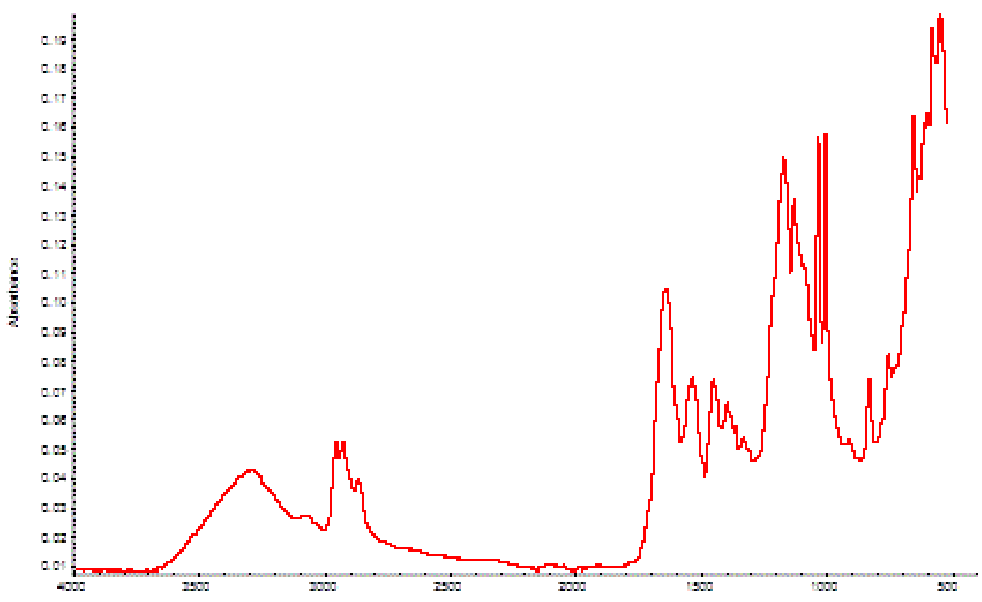


Figure 10: Paper extract 2.

Analysis of adhesives used on the binding paper tape from lantern slides held in the NFSA collection was conducted in 2010. The spectra result from this analysis showed a match for vegetable gum (Fig. 11) and it is considered highly probable that the slides used in this investigation used the same or a similar adhesive.

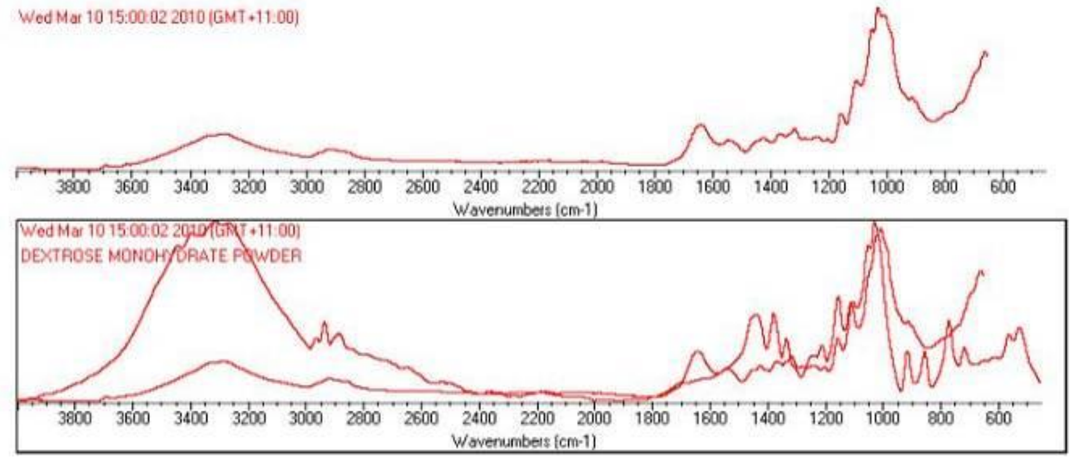


Figure 11: Binding tape adhesive FTIR (NFSA 2010).

Crystal Growth Experiment

Between the two plates a number of crystals had formed that were similar to the structure observed in the original glass slides under examination. (Fig 12). The nature of the crystal growth so closely followed the pattern in the experiment that it indicated that there may have been a great deal of water present at some time in the slides life, such as a water based disaster. A second close examination for signs of such a disaster was undertaken and clear signs of water damage found.

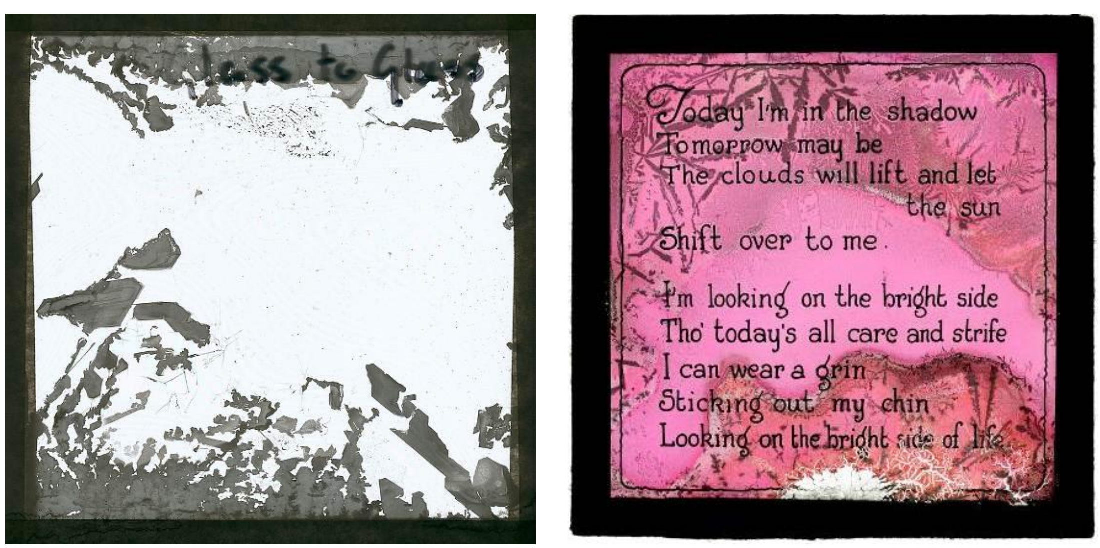


Figure 12: experimental analogue (left), original deterioration (right).

Hypotheses as to the Source of Sodium Sulphate

The Raman spectra clearly show that the predominant species in the crystalline substance is sodium sulphate. However the primary source of the sodium sulphate remains unclear as the FTIR Spectroscopy did not provide sufficient information.

The sodium sulphate present on the lantern slides may have come from a number of sources including the binding paper, glass and residual photographic chemicals or possibly even a combination of these sources.

Paper
Literature searches on the paper used for lantern slide bindings have not provided conclusive information. Physical examination shows the paper to be comparatively robust.

Sodium Sulphate is used by the pulp and paper industry in the production of cardboard and brown paper. It is also used in the manufacture of kraft paper. The Kraft process for paper manufacture was developed in 1883. This process produced a stronger paper pulp by the addition of sodium sulphate to the paper making process and by the early 20th century it was the most important pulping process.

Residual Chemicals
Glass cinema slides follow the typical photographic development process. From this era there were various formulations for fixing solutions, however "hypo" or sodium hyposulphite ($Na_2S_2O_3$) is predominant in all the formulations. Other chemicals commonly used in fixing solutions included potassium metabisulfite ($K_2S_2O_5$) and sodium sulfite (Na_2SO_3).

After fixing, the slide was washed. A washing regime described in contemporary literature (hypo) to be sufficient to remove the fixing solution recommended 2 minutes agitation in water repeated 7 times with fresh water for each wash. Depending on the efficacy of the washing procedure, residual fixer may have been present within the gelatin layer within the slide.

Glass
Sodium sulphate is used in glass making as a firing agent. The percentage is less than 1% w/w. The glass showed no obvious signs of deterioration.

Conservation Treatment
Due to inconclusive FTIR results it was decided to remove the deterioration from only 2 of the 4 slides so that if further research was to be conducted there would still be samples of the deterioration product available for testing.

Sodium Sulphate is soluble in water and therefore preparation and application for removal of the white deterioration product was straightforward. To test how the slides and the deterioration would respond to cleaning, the cover glasses were cleaned first using cotton swabs dipped in deionised water. Black pigment/color that had delaminated from the painted border (mask) of the slide was picked up by the swabs along with the sodium sulphate. It was not expected that the delaminated black color would be water soluble. The cover glasses cleaned up very well with all traces of the deterioration being removed.

Cleaning of the gelatin based side of the slide was conducted with extreme caution as it was not certain whether the text and colored tint on this side of the slide was also water soluble. Damp cotton swabs were lightly rolled across the surface of the gelatin emulsion. Black pigment was picked up by the swab but this was only around the outer edges of the slide. The text did not appear to be water soluble. Some faint color from the blue slide was picked up but this did not seem to have an effect on the appearance of the slide. The sodium sulphate was removed from the gelatin layer however crevices left by the deterioration product in the gelatin were still visible once the sodium sulphate had been removed in this area.

Due to the natural reaction of gelatin swelling when moisture is applied to its surface, the slides were left overnight to give the gelatin layer time to return to normal and to make sure there were no other problems prior to the reconstruction of the slides and re-adhesion of the paper binding tapes.

New binding tape was applied to the black and white slide on three sides as this slide had only one binding taped side prior to deconstruction. The original binding tape was re-adhered to the blue colored slide. All original binding tapes were re-adhered to the slides using methyl cell paste with deionised water.

The pink colored slide and the other black and white slide were also reconstructed but without any conservation treatment to the deterioration.

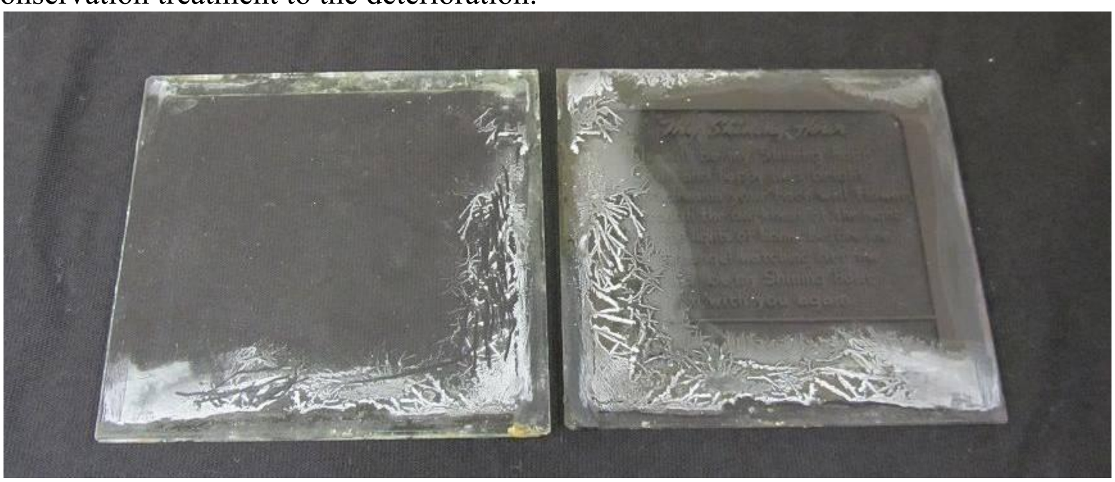


Figure 13: Before Cleaning (30.4.2012).

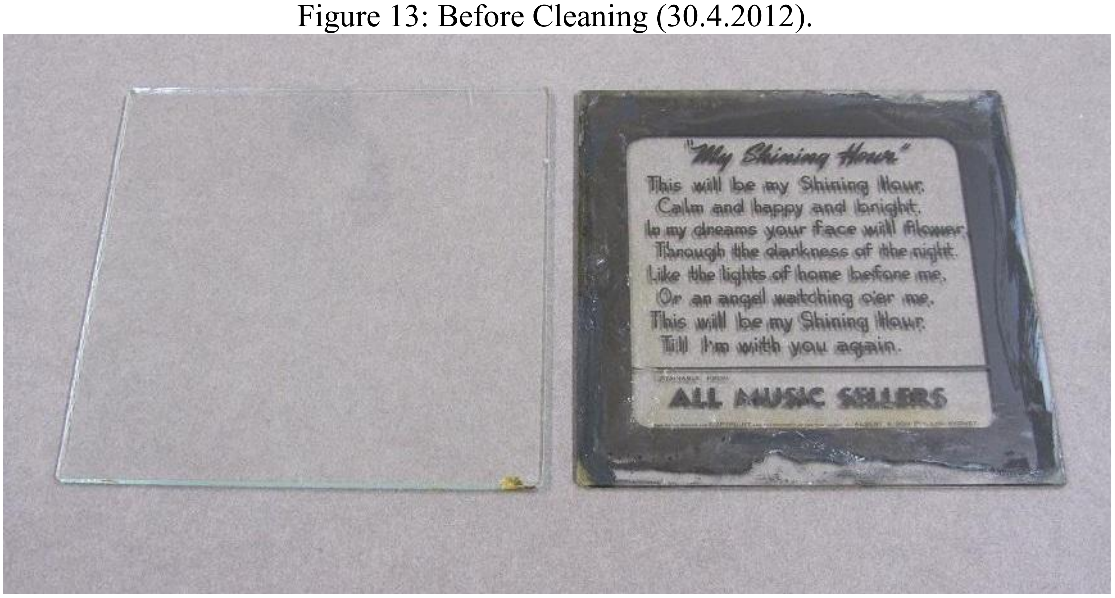


Figure 14: After Cleaning (14.5.2012).

Figure 15: Before Cleaning (30.4.2012).

Figure 16: After Cleaning (14.5.2012).

Conclusion

With the positive Raman test results it was possible to identify the crystalline substance as sodium sulfate, devise a treatment plan and remove the deterioration product from the glass cinema slides.

A definitive result was not obtained from the FTIR spectra results and this would have been helpful in establishing where the deterioration product had originated.

However, the location and direction in which the deterioration product had formed within the glass slide indicates that the deterioration initiated at the outer edges of the slide. This would suggest that the paper binding tape as a result of a water based disaster was the catalyst in the formation of the deterioration.

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