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Photographic Conservation Research at ScreenSound Australia

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ABSTRACT

ScreenSound Australia supports a section dedicated to researching many aspects of audio visual media conservation and preservation. This includes photographic media such as motion picture film, (stills, negatives) and photographic prints.

Much of the research has been focussed on the behaviour of photographic objects during long term storage. Given the nature of ScreenSound Australia's core passive preservation strategy, areas such as fluctuating environmental conditions, the interaction with enclosures and microclimates have been a priority for research. However recovery treatments have also been researched and several novel treatments have been developed based on the study of the behaviour of photographic gelatin.

This paper presents an overview of the research projects and summarises the findings on the behaviour of gelatin as it relates to the conservation of photographic materials.

INTRODUCTION

ScreenSound Australia's conservation research started in the early 1990s. At this time ScreenSound Australia was known as the National Film and Sound Archive. The impetus for the initial research program was as a result of an unreported failure of an air-handling plant that resulted in extreme relative humidity in one of the major stores for several weeks.

A condition reporting program, on the films that had been stored in the affected vault identified mould and ferrotyping as major blemishes on a significant percentage of the films examined. Ferrotyping on motion picture film is a surface blemish that occurs when the emulsion layer, which is

normally matt, takes on a glossy surface characteristic. This can occur over either, part or the entire surface and creates a noticeable effect upon the projected image.

A serious condition, known as blocking where the layers within a film pack adhere together making unwinding of the film impossible without serious damage and possibly tearing, was also identified.

While it was known that rewashing the film and swelling the gelatin emulsion may help in removing surface blemishes, it was unknown whether this treatment would remove the more severe effects of mould damage and ferrotyping. A second unknown related to the paucity of published information on the long-term effect of rewashing treatments on the stability of colour photographic dyes.

To make matters worse there was no treatment for blocking and consensus was that the problem was unsolvable.

From this beginning the Research and Conservation Group (RCG), as it is now known, has developed and now employs three people full-time to research issues surrounding the preservation of audio-visual materials.

PROJECTS RELATING TO THE BEHAVIOUR OF PHOTOGRAPHIC GELATIN

Colour Acetate Restoration Project (CARP)

This project initiated conservation research and laid the ground work for future research projects by focusing on the gelatin emulsion. Phase one examined methods of swelling gelatin to remove surface blemishes and investigating the long term effects on colour dye stability of each component in the traditional rewash formulations.

Phase two focussed on reducing the adhesion that occurred between film layers in the blocked packs. Emulsion swelling was also the pathway examined using the various swelling solutions examined during phase one.

Kodak (Aust) Pty Ltd and especially Kodak's Motion Imaging Technical Centre (MITC) in Melbourne provided invaluable assistance in this project.

The new techniques developed for dealing with the problems of surface blemishing are now practiced in several countries. These techniques also form the basis of the revised motion picture film disaster recovery procedures advocated by ScreenSound Australia.

Although successful treatments were developed, the mechanism of adhesion and the subsequent release were not adequately determined.

Unblocking Decomposed Cellulose Triacetate Motion Picture Film

ScreenSound Australia was instrumental in the formation of the South East Asia Pacific Audio Visual Archives Association (SEAPAVAA). One of the seminal events in SEAPAVAA's formation was a workshop held in Canberra under the auspices of ASEAN. Participants, who arrived from many countries in South East Asia and the Pacific, were invited to bring along a preservation problem to discuss during the technical sessions. Participants from the Philippines brought a film that had severely blocked. This blocking was not the result of tight wind and high relative humidity during storage, but as a result of decomposition of the cellulose triacetate (CTA) film base, commonly known as Vinegar Syndrome.

Microscopic examination showed that a crystalline substance cemented the layers of film together. Analysis showed the crystals to be mainly tri-phenyl phosphate (TPP), a common additive in the manufacture of cellulose triacetate film base.

TPP is very soluble in ethanol so a simple treatment was developed to dissolve the cementing layer allowing the film to be unwound. Over the intervening years this has been refined by using varying concentrations (depending upon the degree of adhesion) of ethanol in a 3M Specialty Fluid HFE-7100.

Further Investigations into Unblocking Decomposed Motion Picture Films

It was the mechanism of the adhesion of TPP to the gelatin that allowed an insight into the behaviour of gelatin.

Gelatin swells as a result of two main mechanisms, one is due to a change in the charge on the strand surface and the second due to lyotropic effects with certain ionic and non ionic solutes (Rose 1977).

Since the salt components of the rewash solution were limited in the lyotropic effects they could instil in the emulsion, closer attention was paid to the pH induced changes.

The main clue was that TPP would not adhere unless the gelatin was acidified.

At the iso electric point, the amine and carboxylic groups are in balance and there is no net charge on the gelatin strands. This enables the strands to exist tightly interwoven and in close proximity to other strands which gives gelatin many of the photographically desirable characteristics. As the pH is lowered the amine groups protonate and develop a positive charge, (NH^+). It is to this positive charge that the TPP was attracted.

Applying this charge change characteristic to the aqueous unblocking treatment developed by CARP shows that at the pH range of the aqueous unblocking solution, ~pH 8.5, there is a predominance of negatively charged carboxylic groups (COO^-). The theory relates to the net negative charge repelling other adjacent strands and may even causing a weakening of any connection between strands that have cross linked between adjoining layers of film in the pack.

Investigation into the Mechanism of Maintaining a Lower Free Acid Level Inside CTA Motion Picture Films During Long Term Storage Using a Low Tension Preservation Wind

Motion picture film that has been stored tightly wound is far more likely to decompose at a faster rate than more loosely wound film (Bigourdan 1997).

As the acidic decomposition by products autocatalyses the reaction, it was hypothesised that increased potential for the diffusion of the by products from loosely wound films may be reason. However the difference in area of the major diffusive surfaces of a film pack between loosely and tightly wound is a fraction of a percent and would not account for any measurable differences.

Examining the pressure that may occur within a film pack at various wind tensions and the effect this may have on the diffusion potential from a film pack were the prime areas of research for this project.

Not surprisingly it was found that there was a much greater potential for the diffusion of gas in more loosely wound film packs. The results indicated a very sharp inflection point occurring between a tension of 250 grams and 300 grams. Above and below this range there was little change, see Figure 1

However, it is well known that motion picture films will shrink over time due to diffusion of manufacturing solvents. Shrinkage in the order of 1.5-2% is common after several years. To examine the effects that shrinkage might have on a film pack, pressure strips were inserted into a film that was artificially shrunk by extracting the plasticisers and allowing the wound film to stabilise during a drying process. The increase in internal pressure at 1.5% went beyond the resolution of the test equipment indicating that even moderate shrinkage can have a profound effect on the diffusion from even loosely wound films over time.

It is debated whether diffusion alone, which is a very slow process, is sufficient to account for the differences in rate of deterioration between tightly and loosely wound films.

Edge (1990) theorised that the gelatin emulsion was capable of acting as a sponge for acidic by-products. Using the analogy of a sponge we developed a model of the role that gelatin may play in the superior stability of loosely wound films. When a sponge is under no pressure it will absorb far more than a sponge under pressure. Similarly, the gelatin emulsion may absorb more acetic acid when it is under no pressure. It is also

possible that when the gelatin structure is pressurised the diffusion pathway is somehow obstructed further trapping the catalysing acids within the film base.

The Effect of Vinegar Syndrome on the Modulation Transfer Function of a Silver Image

It is understood that the gelatin emulsion will absorb acidic by-products from the CTA base decomposition, it is also understood that there will be physical changes in the emulsion due to swelling and that gelatin is soluble in acetic acid. However, it was a general assumption that Vinegar Syndrome did not have any affect on the silver image. This assumption was predicated by the nature of acetic acid as a weak acid and lacking the potential to attack the silver metal that forms a black and white photographic image. The vulnerability of the emulsion had not been considered.

Normally any investigation into the micro characteristics of a photographic image requires access to a microdensitometer. While a microdensitometer was made available courtesy of the RAAF, the analysis of changes in the image structure was made using test tones on an optical sound track printed onto CTA base film.

The sound track approach was preferred, as ScreenSound Australia has well equipped audio studios with very good equipment and skills for the analysis of sonic signals. Minute changes in the edge structure could be simply identified and measured.

Test materials were prepared and placed under accelerated aging conditions. At various intervals the image and acid content were measured.

The tests were run until the gelatin emulsion started to suffer from gross deformities (Figure 2), however up until this point there was no significant change in the test signals due to a change in the image structure (Figure 3). What was discovered were localised deformities that appear to have been caused by TPP migrating from the film base and possibly hydrolysing to form strong acids such as phosphoric acid. Around these local irregularities were strong patterns that significantly disrupted the image structure.

DISASTER RECOVERY

The two most commonly thought of disasters are fire and flood. Both these events may be devastating for photographic materials. But between ‘no effect’ and ‘total loss’ lies a range of problems, largely related to gelatin. Both types of disaster may cause the gelatin emulsion to block.

Fire

On several occasions people who have had their photographic collections damaged by fire have approached ScreenSound Australia for assistance. The softening of the gelatin has caused the emulsion to adhere to adjacent objects, in the case of motion picture film causing blocking (Figure 4). Depending upon the length of time the emulsion has been softened and the degree of desiccation of the emulsion, the film can be unblocked by the same treatment mechanism as for routine unblocking.

Flood

The ubiquitous stabilisation procedure is to: “… place the film in cold water and arrange a rewash”. This advice dates back to 1963 and comes from the Federal Fire Council (Washington DC) and has been widely accepted since. For small motion picture film collections this may be an adequate approach, depending upon how accessible rewash facilities are. However, the time limit for this stabilisation is dependant upon the rate of biological attack on the emulsion and, especially in the case of decomposing films, the solubility of the emulsion.

In a project to determine the best method of stabilisation, RCG examined the rate of absorption of a wound film pack and the effect of sub-zero storage on a film after immersion for 24 hours.

An interesting discovery was that a film pack would absorb very little water even after 24 hours total immersion at 20^{o}C. Prolonged immersion will cause the water to progressively diffuse through the film pack dependant upon factors such as:

- Wind tension
- Emulsion thickness
- Emulsion hardening during initial processing
- Temperature

In most cases the water had barely penetrated beyond the perforations on 35mm film.

The formation of ice crystals within the emulsion is often a reason cited for not freezing wet films. However, even at temperatures of –22°C there were no ice crystals noted inside the film pack and there were no measurable image dislocations or surface effects that may have been attributed to ice crystals.

The only caveat suggested by this research was that wet films should be packed inside freezer bags and as much air as possible drawn out before the bags are sealed and placed in a freezer. If this practice was not followed there was an increased risk of adhesions being formed in the water logged section of the film pack due to freeze drying effects.

SUMMARY

Since the early 1990s ScreenSound Australia has actively researched many aspects of the behaviour of emulsion gelatin in regard to the preservation and conservation of photographic materials.

Areas of significance for long term storage have been the effect of extended period of high relative humidity and decomposition on the emulsion.

The pH related change in the surface charge of gelatin has been a crucial key to understanding the behaviour of gelatin during treatments.

Wind tension plays a significant role in the diffusion of decomposition by-products from decomposing films. Pressure within the film pack influences the ability of gelatin to absorb acid by-products.

Gelatin retains the image structure of a decomposing black & white film until such time as gross deformities occur. Tri-phenyl phosphate leaching from the film base may cause the gelatin to alter sufficiently to affect the image structure.

In motion picture film format (as film wound into reels) flood affected films can withstand freezing if the film is packaged in a sealed plastic bag from which most of the air is removed.

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AUTHOR BIOGRAPHY

Carey Garvie is an Assistant Conservator in the Research & Conservation Group at ScreenSound Australia. Carey has qualifications in cultural heritage studies and the conservation of cultural materials specialising in works on paper. For the past two years Carey has been involved in audio-visual media preservation research, most recently studying the effects of cellulose triacetate decomposition on a photographic silver image.

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