That Smell in the Vaults

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THAT SMELL IN THE VAULTS: THE DEGRADATION OF POLYMERS IN AV MATERIALS

VINEGAR Syndrome[(1)], *Rancid Butter Syndrome*[(2)], *Rotten Fish Syndrome* -- evocative but accurate descriptions of the pervasive killers of our sound and moving image heritage. Leaving aside the well-known problems of nitrate film we are faced with the stability problems of our polymer-based supports. All polymers are subject to decay; and the cellulose nitrate, cellulose diacetate, cellulose butyrate, cellulose propionate and cellulose triacetate bases are no exception. The problem is not limited to film -- audiotape, videotape, computer tape, computer disk and other formats are subject to the same inevitable decay and destruction.

Over the last few years it has come to the attention of archivists around the world that the life expectancy of our audio-visual heritage is not what we once thought it should be. Storage conditions naturally have dramatic impacts on life expectancy. We used to think that black and white film and magnetic tapes could be safely preserved at a temperature of +12C and a relative humidity not exceeding 60%. For colour film the recommended ranges were -5C and a maximum of 30% relative humidity (RH). As early as 1954,[(3)] in India, it was known that acetate based film had stability problems. At that time it was thought that the extremes of temperature and humidity prevalent in that country were the problem. Since then it has been discovered that it is a much more widespread phenomenon and extensive research has been made in determining its causes and methods to ameliorate its destructive effects. Now, before we dabble in the shallows of polymer chemistry, it is a good idea to establish a common base of terminology.

35mm Motion Picture Film

First let us look at the structure and composition of a typical piece of 35mm motion picture film. A film is composed of multi-layered materials consisting of a base or support, a very thin adhesive layer, and one or more layers of emulsion, filters and varnish.

The base of old, pre-1950 era standard 35mm film was generally nitro-cellulose (nitrate film). Acetyl-cellulose film is commonly known as safety film. Both film stocks have equally good physical characteristics but have very different reactions to the environment around them because of their chemical compositions. An antihalation coating may be applied to the back of the base or incorporated into the base itself.

The adhesive layer is a very thin layer of gelatin. Gelatin is an animal albumen[(4)] that is very susceptible to moisture. It swells and becomes sticky in humid (over 60% RH) conditions and it is an excellent nutrient for fungus and bacteria.

The emulsion layer of black and white film consists of a suspension of very fine particles of silver halogens in gelatin. Colour films have multiple layers of emulsion, one for each of the subtractive colours (yellow, magenta, and cyan) as well as one or more filter layers. Each layer of colour emulsion contains a different suspension of dyes depending on the process used. These dyes are generally members of either the Azomethine or Indoaniline classes. Dyes in film are naturally quite unstable and react negatively to temperature and humidity faster than the silver image.

The varnish layer is a protective coating sometimes applied to the blank side of the base to prevent physical damage.

Videotape

Videotape is also made up of various layers. Beginning at the bottom is a protective or tarnishing layer designed to provide smooth mechanical transport while preventing static electrical buildup.

The next layer consists of polyester foil and comprises the bulk of the videotape structure. It provides the physical support for the magnetic layer. Between the magnetic layer on top and the support layer is an intermediate coating that acts to bind the magnetic and support layers together. The uppermost layer is the magnetic layer that consists of metal particles in an organic bonding agent. Most metal particles are now coated to reduce the migration of metallic ions into the other layers. Audiotape is similarly structured.

Optical Disc

Optical Discs such as CD-ROMs, Audio CDs and Videodisks also consist of several layers. Most commercial CDs have a polycarbonate support, although there are CDs manufactured with PMMA and glass supports. A reflecting layer made of chromium, aluminum, or gold/platinum. A protective layer or varnish covers the reflective layer and the labeling ink goes on top. The weak link in a CD is the fact that the information is stored on the side with the thinnest protection.

All these layers contain polymers of various types and, although I will refer to film while discussing the chemistry, the processes apply to all polymer materials. If film is a polymer, just what is a polymer and how does it degrade?

A polymer is a series of organic molecules linked in long chains. These molecules may have attached pendant groups. The base of motion picture film consists of a backbone of hydroglucose molecules chained together in long strings with additional chemical groups included; nitrate in cellulose nitrate, or acetate in cellulose acetate, cellulose diacetate or cellulose triacetate film. The chemical formula of the cellulose triacetate film is (C6H7O2-(O-CO-CH3)3; the first group is the cellulose backbone and the second group is the acetate pendant, the final subscript indicates there are three pendants to each cellulose group.

From this point, the chemistry becomes complicated. Basically the process consists of polymers reacting with moisture and this causes the pendants to break free from the backbone. In the case of acetate pendants, these combine with the moisture to form acetic acid that produces the tell-tale "vinegar" smell. These reactions produce more water; they also produce enough heat to make the reaction process self-sustaining. As the process continues the backbone itself begins to break down as the chain of molecules undergoes a series of scissions. Complicating the process are the added effects of degradation caused by ultra-violet light and chemical reactions caused by impurities in the film and metal ions from the environment (i.e., metal film cans). All of these processes remove Hydrogen atoms from the molecules causing them to break and form new compounds. Metal ion concentrations of as little as ten parts per million accelerate the degradation by acting as catalysts. Since videotape contains large quantities of metal particles in comparison to the amount of polymer, this becomes a major problem. Videotape manufacturers have attempted to reduce this problem by applying a coating to the particles.[5]

The by-products of these reactions can themselves react with the other components of the film structure. The gelatin layer is hygroscopic and absorbs the newly created water, swelling and becoming sticky in the process. The silver particles in the emulsion also react with the water and disassociate causing images to fade and loose definition and eventually to disappear.

Polycarbonate requires higher energy inputs to degrade, however ultra-violet light provides this, and makes CDs vulnerable. The protective layer's resin, besides being vulnerable to mechanical damage, has reacted very badly to contacts from inks, and adhesives in labels, as well as metallic ion catalyzed polymer degradation.

What to do?

The presence of one of these "syndromes" becomes apparent whenever a container holding infected film is opened. There are few instruments as sensitive as the human nose and the most cost efficient method to survey a collection is to have the vault staff sniff. Unless the storage history of a particular piece of film is known, inspections should be made once every two years. Suspect film is then set aside for further examination and determination of the proper course of treatment or copying and disposal. Film that is not exhibiting signs of degradation requires storage conditions which will reduce the inevitability of the onset of degradation.

Current research seems to indicate that storage conditions should generally be "cooler and dryer" with temperatures stable at around +10C or lower for b/w film and <+2C for colour film. Relative humidity should be in the 15 to 30% RH range for both. New industry standards are being developed for both temperature and relative humidity.

Research by Dr A. Tulsi Ram and others at the Eastman Kodak Company into the use of molecular sieve zeolites to extract the products of the degradation process have been quite interesting. A molecular sieve functions both as a desiccant (like the familiar silica gel) and as a scavenger. The sieve's molecular geometry allows it to capture and retain vapours like acetic acid. These molecular sieves work best in confined environments such as film cans and polyethylene bags.(6)

There are polypropylene film cans equipped with vents available that allow the degradation products to escape to the atmosphere. This reduces the concentrations in the immediate environment of the film and helps slow the reaction rate. Combined with effective air handling systems in the vaults, the vented vapours offer no further danger. Unfortunately it is becoming increasingly difficult to purchase small quantities of these cans. Recently a manufacturer reportedly refused any order of less than 40,000 cans.

It becomes clear that to enhance the life expectancy of our audio-visual heritage strict adhesion to archival storage standards is imperative. It is also clear that it is impossible to expect chemical inertness in the materials and that all will degrade. We can only hope to retard the degradation and preserve what we have as long as possible. The main problem with this scenario is that only archives with specialized facilities and collections are currently able to provide this environment. However for every specialized moving image and sound archive there are hundreds of other archives, many very small, which have these materials. These archives are all beginning to collect audio-visual materials in increasing quantities.

In a survey of the counties of Waterloo and Wellington in southwestern Ontario, Canada, over 350 archival repositories were identified. Of these repositories, I have identified only four with storage facilities for audio-visual materials that even came near the environmental conditions required for b/w film. I have yet to find even one archive that did not have audio- visual materials. In speaking with colleagues throughout the Province of Ontario I am lead to believe that this is the normal situation and I suspect that it is the same for other jurisdictions. While we now have structures in place to preserve theatrical feature film materials, the enormous mass of non-theatrical production is, by default, being left to rot and disappear. The "pat" solution is to copy everything onto digital media and keep recopying as the signal carrier degrades. There are many problems with this solution. It costs enormous amount of money. There are unimaginable amounts of material to be copied (30 seconds of 35mm Academy aperture colour motion picture film uncompressed takes about 70 Gigabits).(7) All compression technologies lose some information in the process. None of the proposed storage media has as long a life expectancy as properly processed and stored b/w motion picture film.

Perhaps the greatest problem is that while we attempt to provide the digital technology solution, the existing materials are disappearing daily. What is needed now is a system of vaults and "triage" centres to provide for the immediate rescue of endangered materials now held by small archives and companies. We are looking at a cultural disaster on an epic scale. A century of the world's visual and aural history lost.

Notes

1. Vinegar Syndrome - describes the odor given off by the decomposition of the cellulose triacetate base.

2. Rancid Butter Syndrome - describes the odor given off by the decomposition of the cellulose butyrate base.

3. Ram, A. Tulsi, et al. "Simulated Aging of Processed Cellulose Triacetate Motion Picture Films ." *Archiving The Audio-Visual Heritage Third Joint Technical Symposium* FIAF Technical Coordinating Committee and UNESCO, 1992 52-60.

4. Eaton, George T. "Photographic Chemistry." Morgan and Morgan (New York 1957) 15-23.

5. Nakamura, Tokio, et al. "Archival Stability of Metal Video Tape as Used for Beta-CAM SP," *Archiving The Audio-Visual Heritage Third Joint Technical Symposium* FIAF Technical Coordinating Committee and UNESCO, 1992 61-69.

6. Ram, A Tulsi, et al "The Effects and Prevention of the "Vinegar Syndrome"." *Journal of Imaging Science*

and Technology 38 No.3 (May/June 1994) 249-261.

7. Swinson, Peter R., "Resolution-Independent Film Scanning: How Independent is Independent?," SMPTE Journal 104 No.2 (February 1995) 82-84.

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