

Ventilated Film Cans— Their Effect on the Diffusion of Decomposition By-products from Motion Picture Film

By Mick Newnham

One of the major issues in film preservation is decomposition of the cellulose ester polymers used as the film base. During decomposition acid by-products are formed that will catalyze and accelerate the decomposition reaction once a certain concentration of acid, the autocatalytic point, is reached. Apart from using controlled low-temperature and relative-humidity storage to slow the reaction, removing acid by-products from the decomposing film is an approach to slowing the rate of decomposition. Encouraging diffusion of the acids away from the film base is an effective control method. Film cans are comparatively well sealed and provide a buffering effect for the internal microclimate. This sealing also reduces the ability of the decomposition acids to diffuse from the film. Punching holes in the sides of film cans to allow ventilation of the diffused gases is often practiced. This paper examines the effect of ventilation designs of film cans as a strategy in the long-term storage of motion picture film assets.

Film cans are generally manufactured from a stable plastic or a metal, such as steel or aluminum. The lid is often a tight fit but does not seal a can completely, allowing a small degree of equilibrium between the external environment and the internal microclimate. Film cans have a buffering effect on the rate of change of the internal microclimate in relation to the storage conditions. Temperature is buffered less than relative humidity.¹

Critical Factors

One of the major issues in film preservation is the formation of free acids as a by-product of the decom-

position reaction of the cellulose ester polymers used as film base. Once a certain level of free acid has formed the reaction will become catalyzed.² Since the catalyst is produced by the decomposition reaction, the process is known as an autocatalytic reaction and the level of free acid where the reaction becomes autocatalytic is known as the onset or autocatalytic point. At acid levels beyond the autocatalytic point, the decomposition reaction progresses more rapidly at a given temperature than under conditions of low acid concentration at the same temperature (Fig. 1)

The most effective and commonly used means of controlling the rate of the decomposition reaction, and thus the amount of acid in the film, is low-temperature and low-relative-humidity storage. Even beyond the autocatalytic point, this has an effect in reducing the rate of reaction.

Establishing suitable vaults with effective insulation and moisture membrane sealing, air handling plants, and the associated ongoing running costs are very expensive and archives are typically poorly funded. Since the decomposition reaction is autocatalyzed by the acid by-product, another approach to reducing the rate of reaction is to remove or control the level of acid within the film.

Approaches to Lowering Acid Levels in Decomposing Film

Several methods have been proposed to reduce or remove the acid decomposition by-products:

Neutralization treatments using alkali baths to neutralize free acids in the film system (emulsion and base).

- Kodak/FPC Molecular Sieve-Acid Scavenger, which uses zeolites as a passive sorbent to capture acids in the film can microenvironment.

- "Dry Treatment" developed by the Vietnam Film Institute (VFI).³ Film is loosely unwound and placed in a high air exchange environment for 24 h; during this time the decomposition acids diffuse from the film.

These methods require relatively high levels of resources to carry out. Apart from those implications, other drawbacks limit the potential success of their application.

The neutralization bath involves a high degree of risk to the film materials. The acid by-product of the decomposition reaction increases the solubility of the emulsion gelatin to



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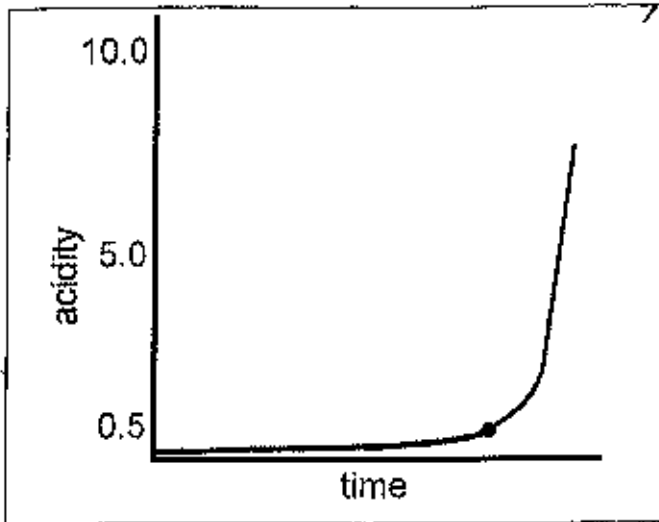


Figure 1. Time vs. acidity curve for cellulose triacetate at a constant temperature and relative humidity.

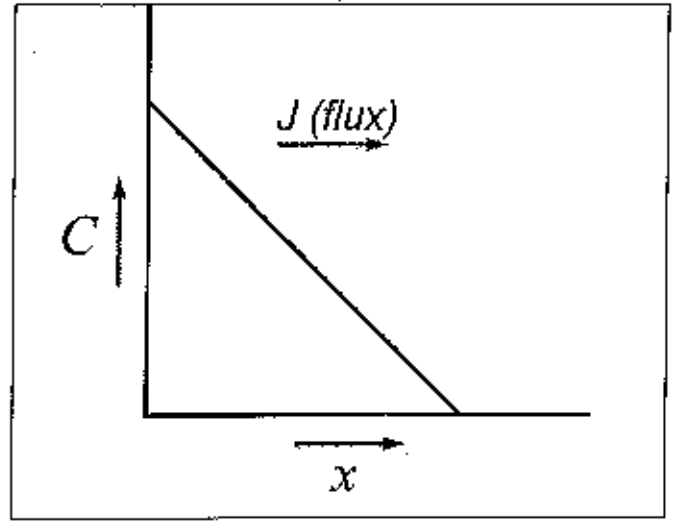


Figure 2. Fick's 1st Law of Diffusion.

such an extent that it becomes feasible for the emulsion to dissolve in the bath during treatment.

The kinetic energy of the vapors is very low and there is little energy to move the acid vapors into the sorbent. This requires a flow (positive pressure),⁴ significantly reducing the sorption potential of molecular sieves inside a film can where there is no air movement.

The Dry Treatment in its current form, as practiced in the VFI, or even with a higher degree of mechanization, has some risk of physical damage and time-out-of-storage considerations. Both the Molecular Sieve and Dry Treatment approaches use diffusion to lower the level of acid within the film; the acid is released from the surface of the film as a vapor that will flow from areas of high concentration to those of lower concentration.

General Theory of Diffusion

The diffusion of gases, in this case acetic acid vapor, is driven by their kinetic energy. Fick's First Law of Gas Diffusion describes diffusion as a response to a concentration gradient expressed as the change in concentration due to change in location (Fig. 2).

$$J = -D \frac{dC}{dx}$$

Where:

J is the gas flow ($\text{g cm}^{-2} \text{s}^{-1}$), perpendicular to the planes of equal concentration and points toward the regions of lower concentration, and D is the diffusion coefficient for that gas in air.

For maximum efficiency in removing the decomposition acids by diffusion from the film, the surrounding environment must have zero concentration. As the concentrations inside the film and the outside environment approach equilibrium, the emission rate reduces until at equilibrium the rate is zero.⁵ However, given that the decomposition reaction is continuing, there will always be a slightly higher concentration in the film.

The linear relationship between emission rate (ER) and concentration can be expressed:

$$ER = k(C_{eq} - C_{chamber})$$

Where:

k = the pollutant transfer coefficient

C_{eq} = the equilibrium concentration (g/m^3) when ventilation = zero

$C_{chamber}$ = the concentration in the chamber (e.g., film can) at time = zero

A steady-state concentration can be reached where the total mass of the

gas leaving the material equals the total mass of the gas leaving the film can.

This is shown in the Hoetjer Equation:

$$C_{st} = C_{eq} / (1 + N/Lk)$$

Where:

C_{st} = the steady state concentration

N = the ratio of air flow over the chamber volume

L = the loading or ratio of the object surface area over the chamber volume

In a film can a steady-state concentration will be reached when the concentration inside the film is equivalent to the concentration inside the film can. Any air movement through the film can will lower the steady-state concentration. If the flow of air through the film can is sufficient to maintain the concentration at zero then the rate of diffusion from the film will be maximized.

The wind tension under which motion picture films are stored has been shown to be critical in the rate of decomposition as measured by acid content. The effective surface area of the film is difficult to calculate.

The difference in the pack diameter of 700 ft of film between a tight wind under a tension of 350 g and a preser-

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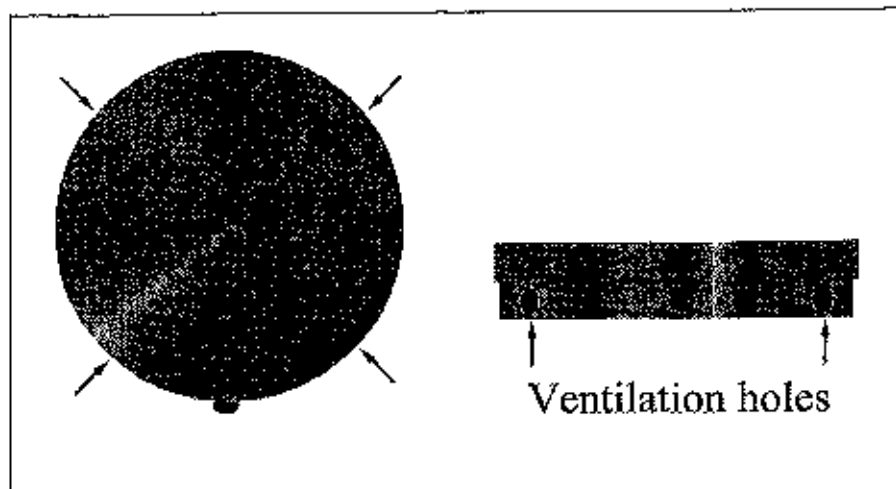


Figure 3. Ventilation apertures on test can 2.

vation wind with 200 g of tension is less than 1%. However the apparent effectiveness of preservation winds in reducing the acid content of the film is far greater than the slight increase in surface area based on pack diameter would indicate.

Experiments

Experiment 1

A series of experiments were undertaken to investigate whether positively ventilating a film can would have any effect on the on the free-acid level of a decomposing film. The first experiment looked for any change in free-acid concentration by comparing test films with a known free-acid content at the start. The test films were analyzed for free acid content using a water leach-free acidity test.⁶

Each film was then divided into two equal lengths, having the same acid content. The films were preservation-wound (approximately 200-gm tension) on a 75mm core. One film from each pair was stored in a non-vented can and the other film in a vented can.

The experiment was conducted in pairs of cans. In each pair:

- Test can 1 is nonvented and used as a control.
- Test can 2 is vented by 10mm diameter holes cut into the sides of

the can with aligned holes cut in the sides of the lid (Fig. 3).

• Each can has a neoprene grommet let into the side of the can. The detector tube makes a tight seal against the grommet ensuring that no air can enter around the grommet during sampling. The grommet is covered by polyester tape, except when readings are being taken.

A 2000-g weight was placed on each lid to simulate storage conditions in a stack. All acetic acid concentration measurements were taken at regular intervals through the grom-

met in the side of each can using a Kitegawa detector tube: 216S - Acetic Acid 1 to 50 ppm (parts per million).

The films were stored at 20°C/ ~50%RH in a constant airflow of 0.3 m/sec. Airspeed of 0.3 m/sec (approximately 1 km/h or 0.675 mi/h) was chosen as standard in a variety of vaults. After 12 months the films were again analyzed for their free-acid content. Average acetic acid concentration inside the film cans was >100 ppm for nonvented cans (this is above the resolution of the test equipment), 4 ppm for vented cans.

For the free-acid level, the head sample readings on vented cans showed approximately a 35% lower acid content than the nonvented. However, as samples were taken further into each reel, the difference in acid content decreased until the center of the reel was reached, where there was an imperceptible difference between vented and nonvented cans. The results are shown in Fig. 4.

Results

The lower steady-state concentration surrounding the film predictably

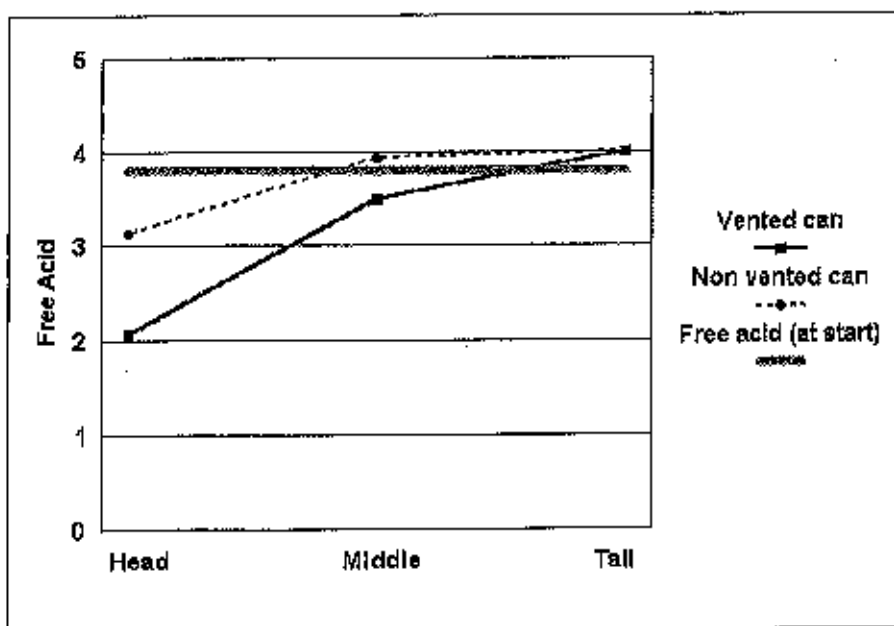


Figure 4. Acid concentration gradients across the film reels.

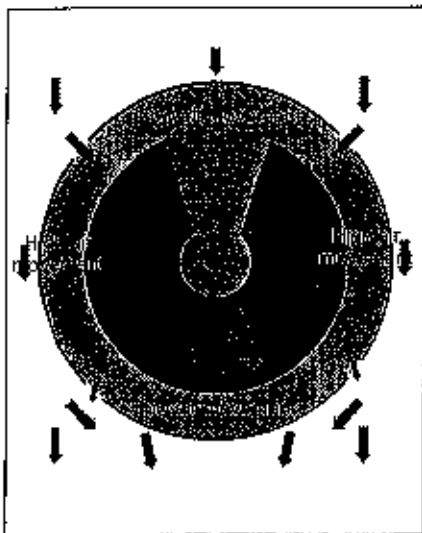


Figure 5a. Four apertures—oblique to the airflow.

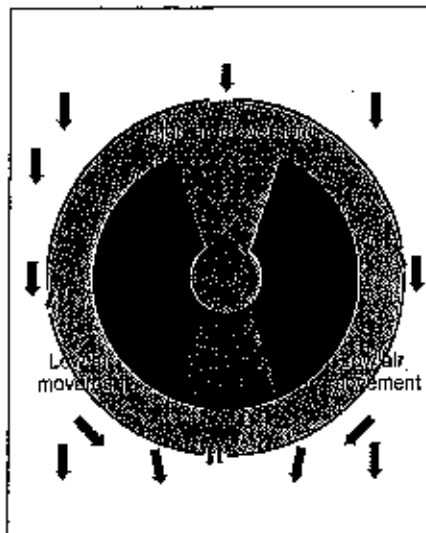


Figure 5b. Four apertures—aligned in the airflow.

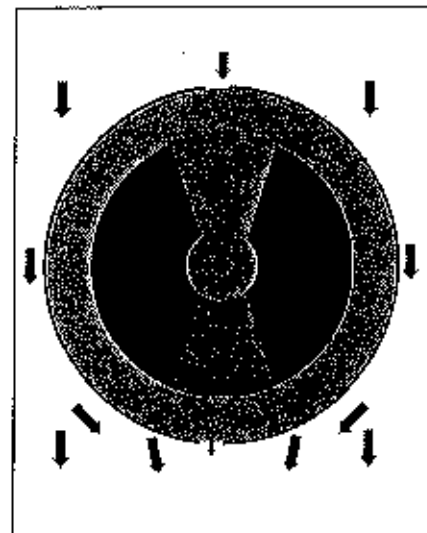


Figure 5c. Two apertures—coaxial to the airflow.

gave a lower free-acid concentration in the outer layers of the film. However, it would appear that the limited ability for air to move over the top and under the film within the can creates high local concentrations of acetic acid. These areas of high concentration reduce the ability of the acid to diffuse from the center area of the film reel.

The decrease in free acid at the head of the nonvented reels was surprising. Possible explanations are:

1. A degree of diffusion, either around the can lid or through the plastic walls;
2. Adsorption/absorption of acid by the plastic, in this case, high-impact polystyrene;
3. A reaction with some other component of the plastic, e.g., the pigment.⁷

Experiment 2

A second series of experiments looked at the way air flowed through a film can. Different combinations of number, shape, and location of the ventilation apertures were tried. The cans were placed in an airflow of 0.3m/sec, and using a Kitegawa Airflow Indicator, the movement of the air through the can was observed through a perspex can lid.

In the arrangement used for the first part (Fig. 5a), areas of low air movement occurred above and below the apertures. A high rate of movement occurred along the "sides" of the film. In Experiment 1 the air sampling location was unknowingly placed in an area of low air movement.

Figure 5b shows four apertures aligned in the airflow. This pattern created a low air movement area below the centerline of the can. There was a small degree of air movement at the trailing end of the can, observed as a "pulsing" in and out of it.

Figure 5c shows two apertures coaxial to the airflow. This arrangement produced an even airflow through the can. There were no observable eddy currents that impeded the airflow.

Conclusion

The round film cans used in the experiment behaved in accordance with Bernoulli's Principle. The "leading edge" of the can slows the airflow and increases the pressure and the "trailing edge," with higher airspeed, creates a proportionally lower pressure area. The air flows through the can to equalize the pressure differential. The simple arrangement of two holes aligned in the airflow proved to

be the most efficient location for creating the desired airflow through a film can.

Tests were carried out at a later date on different lengths of film and square film cans. Using the same arrangement of apertures gave very similar results. With square cans the two apertures aligned parallel to the airflow did show areas of low air movement in each of the corners, however, there was a continual airflow around the film.

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VENTILATED FILM CANS— THEIR EFFECT ON THE DIFFUSION OF DECOMPOSITION BY-PRODUCTS FROM MOTION PICTURE FILM

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Appendix

Other observations and optimizing the design for ventilated film cans:

It is most probable that the inability of air to flow adequately across the major diffusive surfaces of the film reel causes a major reduction in the effectiveness of positively ventilating film cans.

To design a film can that allows greater air flow over and under a film reel requires several changes in traditional design (Figs. A1 and A2).

1. The height of the film can needs to be increased slightly to allow more air space above the film.

2. Ridges to adequately support the film and permit airflow under the film need to be molded into the floor of the can (section X-Y) to direct the air through the can. Whether this parallels the axis of airflow or is at a slight angle needs to be determined. It is possible that similar air-directing

devices need to be molded into the top of the can well.

3. Pairs of ventilation slots should be located as low in the walls of the can as possible and also near the top of the lid (through the wall of the can and aligned slots in the lid). Slots appear to be preferable to round holes as they disperse the air more evenly around the film. By cutting slots low in the can wall, the air moves more freely across the bottom of the can and carries away the heavier decomposition by-products that tend to pool in the bottom of the film can.

Even with a design that maximizes airflow through the can, the storage

vault needs to be arranged so that a suitable airflow is directed through the stacks.

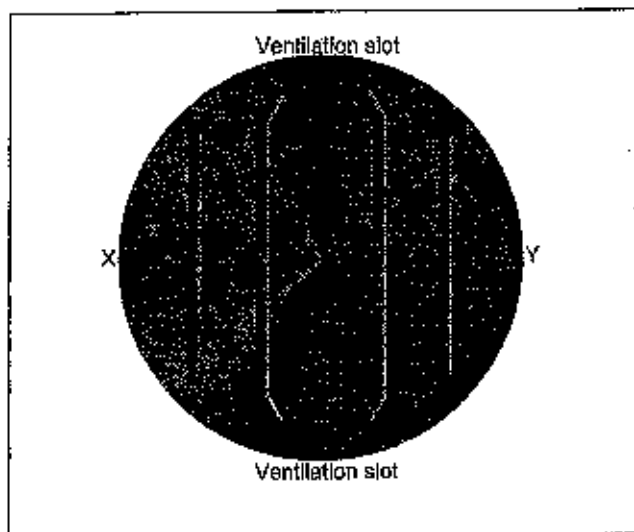


Figure A1. Molded ridges to support the film and allow air movement under the film.

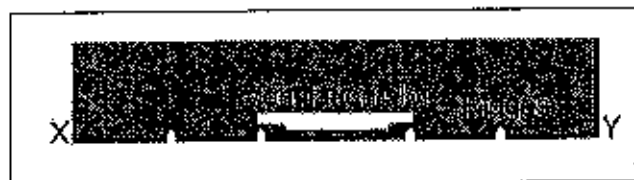


Figure A2. Cross section X-Y.

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Mick Newnham is a technical researcher with ScreenSound, Australia's Engineering and Research Group, Preservation and Technical Services Branch. His current research projects include examining the effect of cellulose triacetate film base decomposition on the modulation transfer function of the silver image and the efficiency of positively ventilating film cans as a low energy method of

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For the past few years, Newnham has been involved in film preservation training through-

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