THE EFFECTS AND PREVENTION OF "VINEGAR SYNDROME"

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The "vinegar syndrome" occurring worldwide due to the deacetylation of cellulose triacetate (CTA) support on processed motion-picture films under confined storage is extensively discussed in the literature. This paper describes the current research performed and the effects of vinegar syndrome through simulated aging of many motion-picture negative films under confined versus open incubation conditions. The results of hydrolytic degradation of CTA support at elevated temperatures and between 30 to 70% RH are extrapolated to simulate ambient or low temperature storage conditions. The data from confined storage suggest no difference in the degradation rates between the tin-coated versus the painted (iron) cans used in this study. A new methodology based on the results of this study is now recommended for preventing or minimizing the occurrence of acid-catalyzed hydrolysis of motion-picture films under confined storage.

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COLD STORAGE ENVIRONMENTS FOR PHOTOGRAPHIC MATERIALS

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INTRODUCTION

Recommendations appear in the literature as early as the 1950s to store color photographic materials at low temperature and low humidity.[1] Museums and archives began to seriously consider cold storage vaults after a key technical paper on the preservation of motion picture films was published in 1970 by Adelstein, Graham, and West.[2] The growing problem of acetate base deterioration[3] is raising the need to improve storage environments for black and white materials as well.

A test matrix of varying temperature and humidity levels readily shows that reductions in temperature and humidity slow major chemical degradation reactions such as chromogenic color dye fading and acetate base deterioration. Nevertheless, cold storage environments present a great challenge to many institutions. The challenge is not only a matter of capital equipment costs or restricted access. There is genuine concern about subjecting historical materials to low temperature and low humidity. The optimum storage environment for mixed material collections, and the physical risks to these materials when they are removed and later returned to storage, are not well understood. Bard and Kopperl investigated the mechanical properties of conventional photographic films before and after five hundred freeze/thaw cycles, and no significant changes were measured.[4] The results are reassuring about temperature, but the testing did not include humidity cycles. On the other hand, an emulsion coated on polyester base exhibited severe cracking after six months at room temperature when the relative humidity was changed between a low value of 10-20% and a high value of 60-70% in twenty-four hour intervals.[5] This result translates into approximately 180 cycles at relative humidity conditions not far from those that might be encountered between use and storage environments in a typical archive. It also suggests that there may not be an appropriate safety margin, especially for historical materials that already have weakened properties, and, when cold storage is meant to extend the use of a collection for centuries. Thus, the purpose of this paper is to examine the chemical benefits and the physical risks associated with the cold storage of photographic materials.

CHEMICAL STABILITY AND TIME OUT OF STORAGE

Figures 1 and 2 show the relative increase in stability that can be gained by lowering temperature and humidity. The response of chromogenic color dyes reported by Eastman Kodak Company[6] and acetate base degradation data from the Image Permanence Institute[7] are plotted. Although the chemistry of dye fading is distinctly different from acetate base degradation, the effect of temperature and humidity on the relative reaction rates is remarkably similar. A four-fold improvement is predicted by reducing the relative humidity from 60% to 20%, but ten-fold, hundred-fold, or even thousand-fold improvements are predicted when temperature is decreased. Conventional wisdom is that an optimum storage environment takes advantage of both parameters. Temperature and humidity effects combine in direct proportion, so more than one combination of temperature and humidity gives the same relative stability factor. This feature is best illustrated in Table I. Relative color dye stabilities are interpolated for a variety of temperature and humidity combinations. Additionally, the table includes the effect of time out of storage. An effective fading rate, R, is calculated as follows:

$$R = [(T_s \times R_s) + (T_u \times R_u)] \div (T_t)$$

where
T_s = time in storage
R_s = fading rate in storage
T_u = time in usage environment
R_u = fading rate in user environment
T_t = total time

One assumption is that aging mechanisms will revert to a rate governed by the temperature and humidity parameters of the work or display environment until the object is again returned to storage. The environment outside the storage vault was set equal to Kodak's standard condition of 24°C, 40% RH for the calculations presented in Table I, so R_u equals 1.

Table I reveals that small amounts of time out of storage dictate the ultimate limit to a cold vault's effectiveness. The table also shows that low relative humidity is significant primarily when temperature is not reduced much. When the temperature is lowered enough to establish a high relative stability factor, the added measure of low humidity has less significance due to the greater impact of the time out of storage.

STRESS CALCULATIONS

Reductions in temperature and relative humidity cause stress within the layers of photographic materials. Stress can be quantified if the individual material layer properties are measured, or in some cases, derived as a function of temperature, relative humidity, and time. Our approach to the problem was to model a multilayer photographic structure on a computer using the method of finite element analysis.[8,9,10] Actual dimensional changes were measured on test samples and compared to the calculated values. An accurate calculation of the dimensional change confirms the correct analysis of stress. The origin of dimensional change stems from each material layer's temperature coefficient of expansion and humidity coefficient of expansion. The internal stress arises from a mismatch in these properties and the inherent strength and stiffness of the layers at corresponding temperature and humidity levels.

Figure 3 shows the measured and computer calculated edge deflection in the corner of a 1 x 2 inch sample of Cibachrome print material as relative humidity is lowered from an initial value of 60% RH. Temperature was held constant at 21°C. The edge deflection at the corner is a sensitive indicator of the correct material properties in the computer model. Figure 4 illustrates the test fixture and how the deflection measurement was made. Cibachrome (now called Ilfochrome) was selected for the first computer modeling study because the emulsion layer is free of particles such as silver, dispersed resins, latex or oil color couplers, etc. From a mechanical point of view, Cibachrome can be modeled as a three-layer system consisting of the emulsion, polyester base, and a gelatin anti-curl layer. However, the anti-curl layer is loaded with glass (i.e., silica) particles that reside more at the surface. The glass particles imparted greater stiffness and a lower coefficient of expansion to the anti-curl layer and had to be considered. Their importance can be shown by modeling an anti-curl layer with no glass particles. The same layer thickness was programmed, but the material properties were set equal to the emulsion layer properties. (See also, fig. 3).

Figure 5 plots the stress in the emulsion and anti-curl layers due to decreasing relative humidity while figure 6 shows the effect of temperature. The stress levels are essentially additive when the sample is desiccated and cooled.

CONCLUSIONS

A significant decrease in relative humidity causes very high stress in the Cibachrome emulsion and anti-curl layers. Temperature reduction causes much less stress. Cibachrome is a unique photographic material, but other traditional silver-gelatin materials are expected to respond similarly to desiccation and cooling. Future research may establish limits for stress that provide a comfortable safety margin for old and new materials in a collection. Meanwhile, Table I clearly shows that excellent chemical stability can be achieved by selecting an appropriate storage temperature. It is not necessary to enforce the extra measure of low humidity. Therefore, it is recommended that chemical stability be managed by temperature while stress is minimized by maintaining more uniform relative humidity between the storage, work, and display environments. This recommendation invites the use of moderate humidity levels, but one should not expect low temperature to compensate for high relative humidity. At high humidity, the materials will be exceptionally free of stress, but they are then endangered by other problems such as mold growth and sticking of emulsion layers to other films or enclosure materials.

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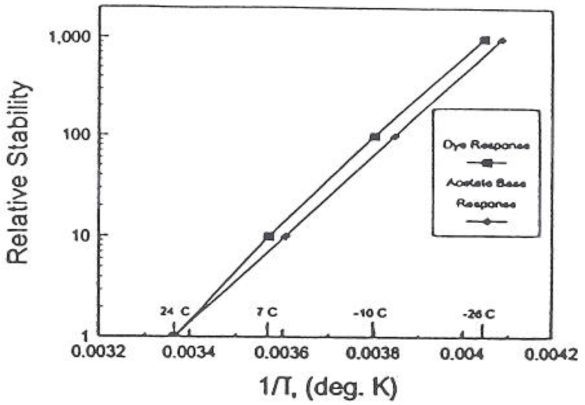

Fig. 1. The effect of Temperature on relative stability. Two common deterioration mechanisms are illustrated. The color Dye fading criterion is the amount of time required to reach a certain percentage of dye density loss. The criterion for acetate base degradation is the time required to reach a threshold value of free-acidity in the film base.

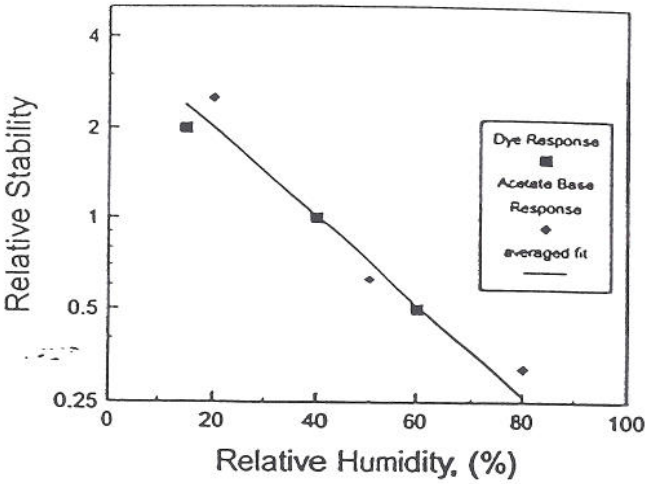

Fig. 2. The effect or relative humidity on relative stability. Criteria for deterioration as per figure 1.

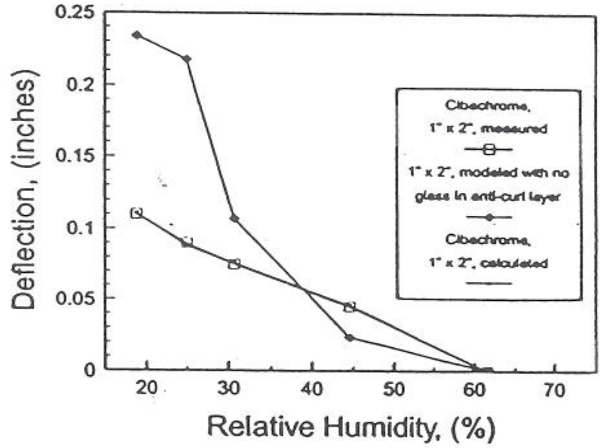

Fig. 3. Measured and Calculated edge deflection at the corner of a 1" x 2" sample of Cibachrome print film at 22°C as the relative humidity was decreased from an initial value of 61.5% to 18.8%. The effect of glass particles in the anti-curl layer can be seen by comparing the response of the normal Cibachrome to the calculated deflection of a Cibachrome structure modeled as if there were no glass particles in the anti-curl layers.

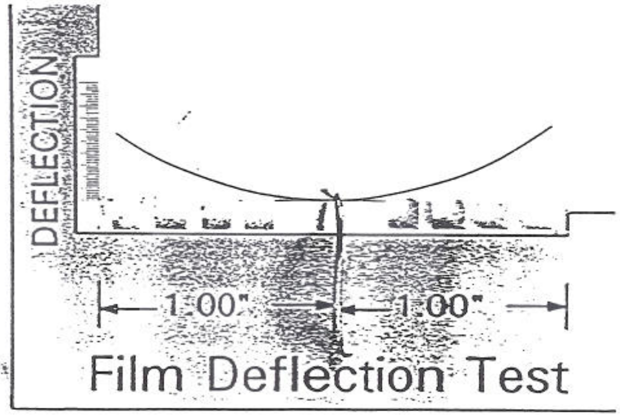

Fig. 4. Ruled test fixture used to measure the deflection in film samples subjected to changes in temperature and relative humidity. A 1" x 2" sample of Ektachrome 160T trimmed from 35mm film stock is illustrated. The sample was flat at 22°C when conditioned to 60% RH, but the edge deflected from the horizontal surface to 0.28" above the surface when the relative humidity was decreased to 20% RH.

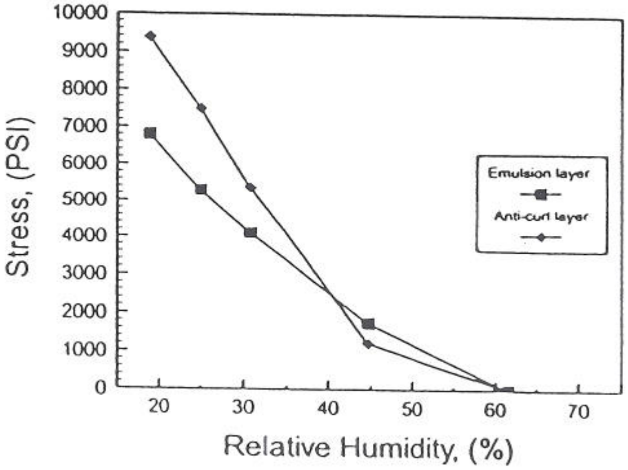

Fig. 5. The principal stresses developed in the emulsion and anti-curl layers of a Cibachrome print film at 22°C as the relative humidity is decreased from an initial value of 61.5% to 18.8%.

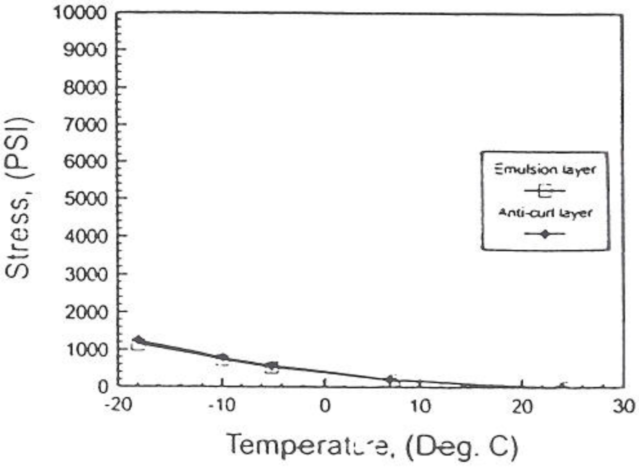

Fig. 6. The principal stresses developed in the emulsion and anti-curl layers of a Cibachrome print film at constant 50% RH as the temperature is decreased from 22°C to -18°C.

Storage Condition days Temp (°C)	RH	TIME OUT OF STORAGE (days per year) 0 days	1 day	2 days	5 days	10
24	60	0.5	0.5	0.5	0.5	0.5
24	40	1.0	1.0	1.0	1.0	1.0
24	15	2.0	2.0	2.0	2.0	1.9
15	50	2.3	2.3	2.3	2.3	2.2
15	40	3.3	3.3	3.2	3.2	3.1
15	30	4.3	4.3	4.2	4.1	4.0
7	50	7	7	7	7	6
7	40	10	10	10	9	8
7	30	13	13	12	11	10
2	50	14	13	13	12	10
2	40	19	18	17	15	13
2	30	25	24	22	19	15
-3	50	26	25	23	20	16
-3	40	37	34	31	25	19
-3	30	49	44	39	30	21
-10	50	71	59	51	36	24
-10	40	100	79	65	42	27
-10	30	132	97	77	47	29
-18	50	216	136	99	55	31
-18	40	305	166	114	59	33
-18	30	402	192	126	62	34
-26	50	707	241	145	66	35
-26	40	1000	268	154	68	35
-26	30	1319	286	160	69	36
"Perfect" Vault		∞	365	183	73	37

Table I. Average dark fading rates for chromogenic color dyes relative to an environment of 24°C, 40% RH. Table values are reciprocals to the effective fading rate. Underlined values correspond to rates and conditions listed in "Conservation of Photographs", Publication No. F-40, Eastman Kodak Co., 1985. Conditions equivalent to 24°C, 40% RH were assumed for the time that an object is out of cold storage. For example, 21°C, 50% RH gives the same dye stability as 24°C, 40% RH.