

Chapter 11

The Physical Properties of Photographic Film Polymers Subjected to Cold Storage Environments

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The photographic record of the twentieth century is rapidly being lost. The gelatin of the image emulsions is relatively stable, but the silver salts and dyes that form the image, and the principal photographic film bases, cellulose nitrate and cellulose triacetate, have been found to be chemically unstable within the time frame of historical significance. In an effort to save these photographic records, several strategies to enhance their useful life have been developed. These involve low relative humidity (RH) and/or low temperatures. The ability of the polymeric film bases to sustain these lower temperatures has been examined. The data indicate that these materials can safely tolerate storage at low temperatures, easily to -20 C, and that cycling of the film bases within the range +25 C to -25 C has no adverse effect on the mechanical stability of the film bases.

The long term preservation of photographic materials must of necessity consider the adverse effects of light, relative humidity (RH) and temperature. Storing the film in the dark is almost axiomatic but the optimal values or ranges of RH and temperature have been the subject of much discussion. Previous research has described the benefits and tradeoffs between RH and temperature (1). From the chemical point of view (Arrhenius considerations), it is clear that any long term storage of photographic materials would benefit more from strategies involving low temperature than low RH. However, it was necessary to demonstrate that there are no structural hazards involved in the low temperature approaches. A number of questions require answers. What are the dimensional changes and thermal coefficient

mismatches associated with lowering the temperature? Are significant stresses developed and do these stresses represent a potential for damage to the film? Finally, how often can the films be cycled through temperature changes in order to provide user access?

Dimensional Response to Thermal Changes

Studies of the mechanical properties of the photographic film bases, cellulose triacetate (recent origin) and nitrocellulose (50 years old) were conducted. For stability during storage it is required that any temperature related dimensional changes of the cellulose nitrate and cellulose triacetate polymers be such that there are no severe stresses induced in either the image or film base layers. The basic criterion for damage is that the stresses in any of the photograph materials should not exceed the yield point, the point beyond which permanent deformation occurs. For a large class of organic polymers the yield point has been found to be at a minimum strain value of 0.004. This was also found to be true for both the image emulsions and the different film bases. Figure 1 illustrates the full stress strain plot for 50-year-old nitrocellulose film stock base. The 0.004 yield point is a conservatively low value and allows one to set a specific limit to the minimum temperature change required to cause permanent deformation in a fully restrained specimen. It is important to note that the breaking stress and strain for the material far exceed the yield stress and strain used to calculate the allowable environmental limits and permit considerable leeway in handling films.

Figure 2 shows the dimensional changes of both cellulose triacetate and cellulose nitrate over the temperature range +40 C to -40 C and at a relative humidity of 50%. Similar curves have been developed at other relative humidities with the same general response. What is particularly interesting is that the dimensional response of both motion picture film bases is quite similar at the ambient temperature ranges expected in movie theaters, which is around 18 to 25 C. Perhaps this was the intent of the manufacturers since both films must fit the projector sprockets equally well. This physical match also extends down to about -20 C, the storage temperature of most modern single stage freezers.

Another interesting effect is the raising of the yield point on lowering the temperature. Further mechanical testing at low temperatures revealed that the yield point (strain) for nitrocellulose rose to as high as 0.011 at -20 C. The yield strains for this material over a wide range of temperatures are shown in Figure 3. All are above the 0.004 value used as the damage criterion. Damage by our definition is permanent deformation, not failure. Much greater strains are required to cause actual failure. Similar measurements have been made for gelatin, the principal component of the image layer, and have been reported elsewhere (1,2). Within the RH range of 30% to 60% gelatin also has yield points in excess of 0.004.

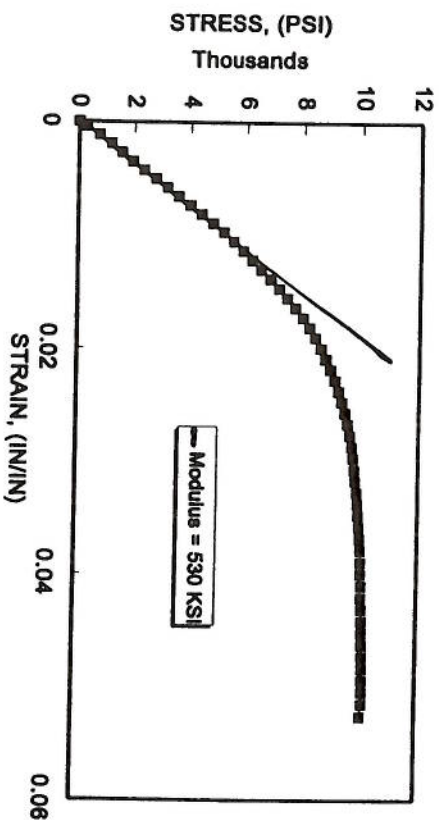


Figure 1. The full stress-strain plot for a 50 year old nitrocellulose film stock base.

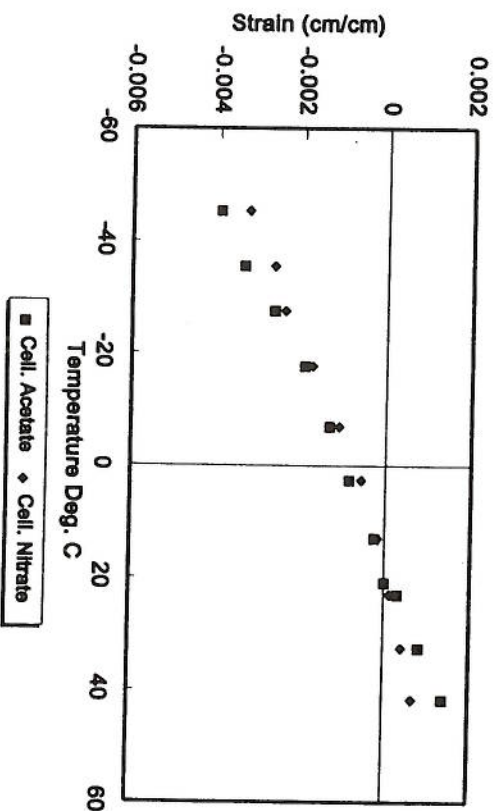


Figure 2. The dimensional response to temperature, as strain, of modern cellulose triacetate and 50 year old nitrocellulose film stock base. The RH is 50%.

Thermally Induced Stress and Strain Development in Restrained Films

Cooling a restrained photographic film will cause the development of both stresses and strains in the various layers of the film. That there are stresses developed in a material restrained from shrinking is intuitive. But strains are also developed. If a material of length L_1 is allowed to freely shrink on cooling to a new length, L_2 , the material is stress free. If, at the lower temperature, the material is stretched back to its original length, L_1 , the material has both stress and strain. The values of stress and strain are identical to those developed if the material had been fully restrained and not allowed to shrink when cooled. It can be shown that the magnitude of the dimensional change of a material freely contracting during cooling is the same as the mechanical strain developed when the material is restrained during cooling. Further, the stresses developed during restrained cooling are identical to those developed when a material is stretched back to its initial length after freely shrinking during a temperature reduction (4). In the case of motion picture film, the worst case assumption is that the film is fully restrained from shrinking when it is spooled on the reel. Full restraint is the worst possible condition though no structure is actually fully restrained. If the fully restrained material can safely tolerate thermal change under these conditions, then it can tolerate cooling under all other conditions of lesser constraint.

Assume that the film in question has a film base of cellulose triacetate. Figure 2 shows that when this material cools from 20 C to -20 C the magnitude of the free swelling strain is 0.002. If the material had been restrained, the magnitude of the mechanical strain would have been 0.002 also. This is only half the lowest permissible strain of 0.004 used as a criterion for damage. The film base can safely be lowered to -20 C. But is the gelatin emulsion layer also safe?

The thermal coefficient of expansion (the slope of the strain versus temperature plot of an unrestrained material) for the cellulose triacetate is approximately 0.00005/°C in the region of interest. For the gelatin image emulsion, the thermal coefficient of expansion is 0.000030/°C. If the emulsion were to be considered as an independent material alone and restrained, the same temperature drop, from 20 C to -20 C, would induce mechanical strains of only 0.0012, less than the film base. If the film is restrained, all layers are restrained and the response of each layer can be considered independently.

Cut film is normally stored unrestrained in sheets of different sizes. What is the response of the combined film base and the gelatin image layer during cooling? The mechanical strain developed in the different layers of a film when it is cooled unrestrained is easily approximated. The film base tends to contract (thermal coefficient of 0.00005/°C) at a greater rate than the gelatin emulsion layer (thermal coefficient of 0.00003/°C). The response of the composite is intermediate between the layers (if they were acting independently) with the actual response dependent on the relative thickness and stiffness of the different layers. For film, the base is so much thicker than the image layer that it essentially determines the response of the composite. Thus, the strains developed in the gelatin layer are approximately the temperature change times the difference in the two coefficients. In this case the

thermal change is -40 C and the difference in coefficients is $0.00002/^{\circ}\text{C}$, so the emulsion layer develops a mechanical strain of 0.0008 in compression. This is well within the elastic range of the material. It would take a more sophisticated analysis to calculate the exact resulting strains but the answer would be less than computed above.

Thermal Cycling of Materials

The number of times that photographic materials can be cycled between ambient and cold storage temperatures also needs to be determined for an adequate storage strategy. If the strain values encountered during the cycling stay below the yield point, then no permanent deformation of the object takes place, regardless of the number of cycles it experiences. Since the changes in temperature produce strains that are within the elastic region (strain less than 0.004) then the concept of fatigue need not enter into consideration. Since it can be shown rigorously that mechanical and thermal cycling are identical (4), then any mechanical cycling to strains of 0.004 would reflect thermal cycling from 22 C to -40 C . Lower values of strain would correspond to a smaller temperature drop. Figures 4 and 5 show the mechanical cycling or unload compliance curves of nitrocellulose film and gelatin for selected points over a range of 5000 cycles. No plastic deformation was observed. Since the deformation exceeded the 0.004 value slightly, it is evident that this value is conservative for both materials. Similar results were obtained for the cycling of cellulose triacetate.

Discussion and Conclusions

Twentieth century photographic materials suffer from several different mechanisms of degradation, including the hydrolysis of cellulose acetate ("vinegar syndrome") and dark fading. In fact, they are often less stable than 19th century photographic objects. What these mechanisms have in common is that their rates are more sensitive to change in temperature than RH. Photographs at room temperature should be kept at a RH between 35% and 65% in order to avoid damaging stresses and strains produced by differential dimensional responses of the photographic layers to RH changes. The possibility of mold growth or going above the glass transition temperature, T_g , of the gelatin emulsion layer further reduces the preferred upper limit to 60% RH. Reducing the RH within the stated range can increase the chemical stability by a factor of 2 to 4, but this is not enough to ensure the survival of photographic collections. Lowering the temperature can produce orders of magnitude increases in chemical stability.

Truly long-term preservation efforts must consider factors that minimize the effects of several decay mechanisms and will invariably use strategies that lower storage or exhibit temperatures. The important question then is whether the photographic materials can survive the effects of cold temperature and of cycling into and out of storage environments for study or exhibition.

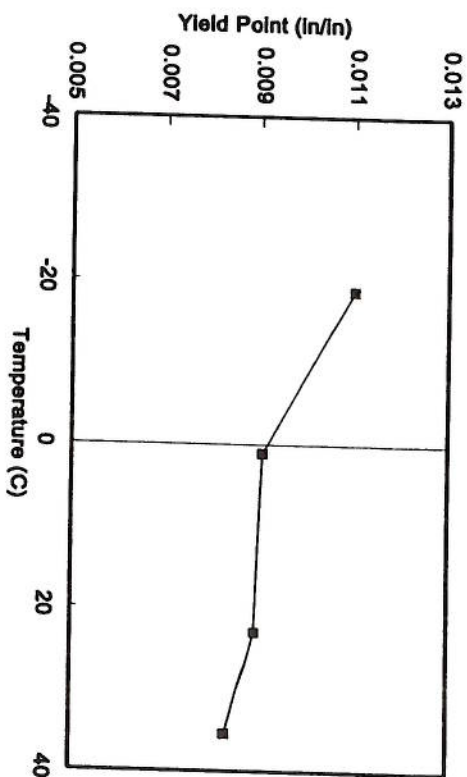


Figure 3. Variation in yield point with temperature for 50 year old nitrocellulose film stock base. The RH is 50%.

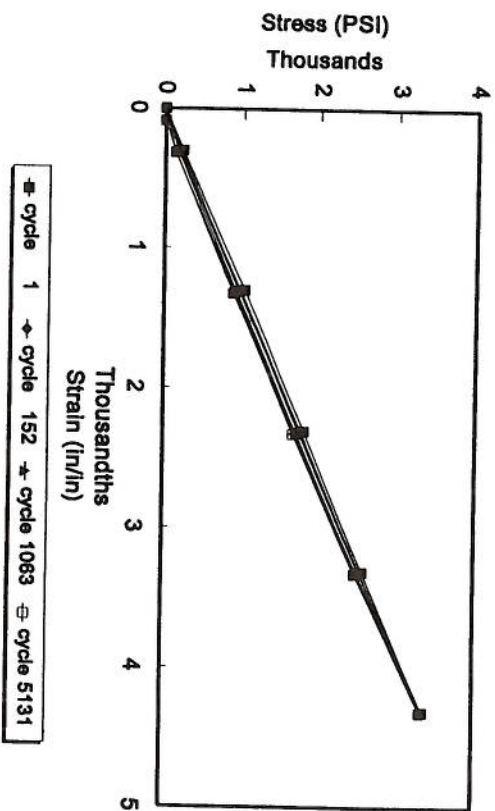


Figure 4. The unload compliance curves for nitrocellulose film stock base at various times during 5131 cycles to a strain level of 0.004.

The data presented here indicate that the dimensional change induced by lowering the temperature to that of a single stage freezer, i.e. -20 to -30 C, is considerably less than that which would induce plastic deformation in either the polymeric base or the gelatin layers. The assumption that one or more layers in the photographic materials are fully restrained is conservative. In fact, all materials will be contracting together, with different coefficients of thermal expansion, so that relative strains will be even less than the data for individual materials indicate. Other objects such as glass plate negatives are a special case and are not being considered here although the same principles apply. The data also complement previous studies (2-4) that have shown that cycling within the ambient to -25 C range is benign.

The choice of -20 C for a storage temperature is an optimized value based on two independent principles. First, -20 C is a temperature easily attained in commercial freezers using single stage compressor systems. Second, if the collection is used to any extent during the year, then the effects of the colder storage must be time averaged with the effects of the ambient conditions of use. As the time of use increases, the degradation occurring during use becomes much greater than that during cold storage. The time-out-of-storage becomes the dominant consideration and the benefits of further improvement in stability by temperatures below -20 C during the time in cold storage become limited (1).

The data described above and similar data for other materials allow certain general conclusions to be drawn. As a practical matter photographic materials typically contain a gelatin image-bearing layer adhered to various substrates (e.g., cellulose nitrate or triacetate, glass, paper). The chemically and physically safe environment for these common objects can be summarized in a simple plot such as Figure 6. This figure shows the boundaries of RH and temperature, A, B, C, and D, which represent the limits of safe storage and exhibition. Point A is 35% RH, B is 60% RH, both at 25 C, while point C is 40% RH and D is 20% RH, both at -25 C.

The contour lines labeled 2, 4, 10, 30, 100, etc. denote the improvement in expected lifetimes compared to a room temperature environment of 21 C at 50% RH. The benefits of a preservation strategy that utilizes a lower RH, i.e., moving horizontally on the graph, has a maximum effect of increasing the expected life by a factor of 2 to 4. A strategy of lowering the temperature to sub-zero values, i.e., moving vertically on the chart, has a much more significant impact.

Hazards do exist with any storage or user environment that is beyond the glass transition of gelatin (as indicated in the graph). Procedures should be used to ensure that cold stored objects are returned to room temperature in such a way that the microclimate at the surface of the object does not condense water or otherwise exceed the recommended RH limits.

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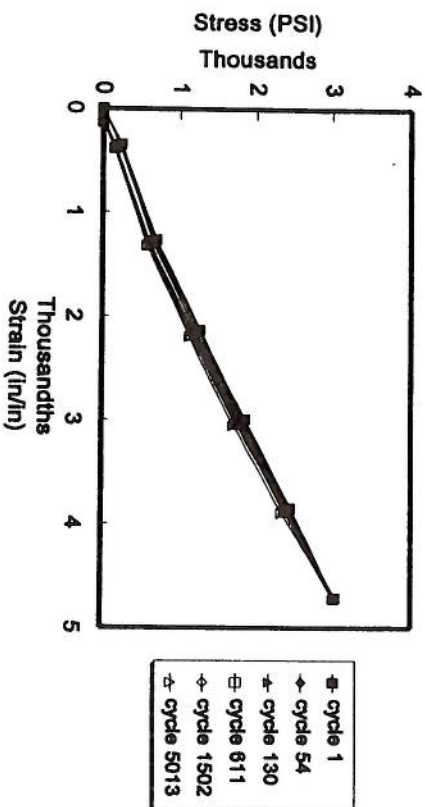


Figure 5. The unload compliance curves for gelatin at different times during cycling to a strain level of 0.0048. No yield is measurable.

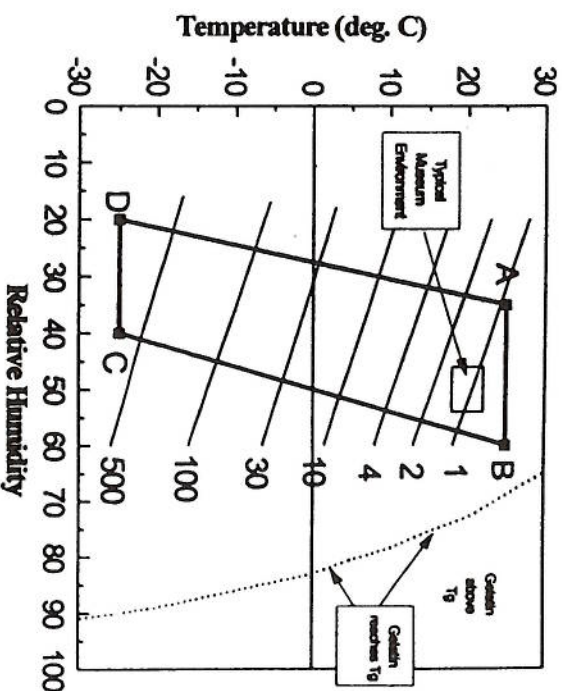


Figure 6. Range of allowable relative humidity and temperature for materials containing gelatin films.

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Chapter 12

Probing the Factors That Control Degradation in Museum Collections of Cellulose Acetate Artefacts

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Cellulose acetate artefacts in museum collections cover a period from the early 1900's to the present day. Conservators have observed that certain of these objects are showing signs of warping, crazing, cracking, discolouration and shrinkage accompanied by a strong smell of acetic acid. Previous studies on cellulose nitrate artefacts show a correlation existed between the residual sulfate from manufacture and subsequent susceptibility to degradation. A parallel study of the accelerated ageing of modern samples of cellulose acetate and also selected artefacts dating from the 1940's has been carried out. The tests involved exposure of the objects to temperatures of 35 °C, 50 °C and 70 °C and relative humidities of 12 %, 55 % and 75 % for extended periods of time. The samples were monitored for changes both in their visual appearance, mass and chemical composition. Chemical analysis was carried out using micro FT-IR spectrometry and ion chromatography. The changes in the molar mass distribution were studied using gel permeation chromatography. Naturally aged samples have also been studied to help validate the accelerated ageing studies.

Plastics have had an increasing influence on human activity since the early years of the 20th century and as such are becoming an increasingly important part of

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