Moisture Content Isolines and the Glass Transition of Photographic Gelatin; their Significance to Cold Storage and Accelerated Aging

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Abstract

Constant moisture content in a photographic gelatin can be established experimentally by sealing the gelatin in a vapor tight container with little free air volume compared to the volume of gelatin. Moisture content isolines can then be determined by varying the temperature and measuring the relative humidity in the free space after thermal and vapor phase equilibrium is reached. Surprisingly, the moisture content isolines reveal the glass transition temperature of the gelatin and its strong dependence on moisture content. The glass transition is correlated with the Flory-Huggins interaction parameter for a gelatin-water system, and the effects of water on the physical properties of the gelatin-water system are presented. Finally, the relationship between moisture content, relative humidity, and temperature is discussed with respect to accelerated aging tests of photographic materials and long term storage in cold temperature environments.

Introduction

The relationship between moisture content, relative humidity, and temperature is fundamentally important to the preservation of photographic materials. Gelatin, paper, and cellulose acetate are hygroscopic polymers, and their moisture content plays an important role in chemical and structural stability. The relationship between temperature, relative humidity, and moisture content can be measured by more than one method and also plotted on more than one graphical coordinate system. When moisture content versus relative humidity at constant temperature is plotted, the resulting graph is customarily called a moisture absorption isotherm. On the other hand, if relative humidity versus temperature is plotted while the moisture content is held constant, then a moisture content isoline is expressed.

The moisture content in a hygroscopic sample can be experimentally held constant by sealing the sample in a vapor proof container and ensuring that the moisture buffering capacity of the air inside is negligible compared to the moisture buffering capacity of the hygroscopic material. The moisture content of the sample is determined by traditional gravitometric techniques. Then, by measuring the relative humidity at different temperature levels, moisture content isolines can be determined. One advantage of this experimental approach is that data can be obtained at low temperatures without having to wait for long periods of time for thermal and moisture equilibrium to occur.

Moisture content isolines for photographic gelatin have previously been measured, and they easily reveal the glass transition temperature of the gelatin (1). The glass transition temperature (T_g) of gelatin is highly dependent on moisture content, and its importance to photographic conservation has been largely overlooked. The glass transition of an amorphous material is defined as a discontinuity in the rate of change of specific volume with temperature. Both inorganic and organic amorphous materials undergo glass transitions and the T_g values often help to characterize the materials. In descriptive terms, when photographic gelatin is below T_g it is hard, more brittle and "glass like" in nature. Above T_g it turns "rubbery" or "gel like". Hygroscopic polymers possess the additional feature that T_g can vary with the amount of moisture in the material. The variation of gelatin's T_g with moisture content has been measured by analytical techniques such as dilatometry or differential scanning calorimetry, and data has been compiled from various sources in the literature (2). It will be shown that the glass transition temperature of gelatin can also be determined from moisture content isolines. To summarize, the relationship between moisture content, relative humidity, temperature, and the effect of these variables on the glass transition of gelatin helps to explain how photographic materials behave in a sealed package or ventilated space when the temperature changes. The behavior is amplified during accelerated aging tests and also with respect to cold temperature storage due to the magnitude of the temperature change experienced under these conditions.

Moisture content
Isolines and the Glass transition

The moisture content isolines of an unhardened photographic gelatin are shown in figure 1. Five moisture content levels were tested: 11.1%, 13.0%, 14.4%, 16.6%, and 18.2%. These moisture content levels produced equilibrium relative humidity levels at 25°C of approximately 30%, 46%, 59%, 68%, and 75% RH, respectively. No other hygroscopic materials were present to influence the results. The data in figure 1 indicated that the relationship between moisture content, relative humidity, and temperature (at standard
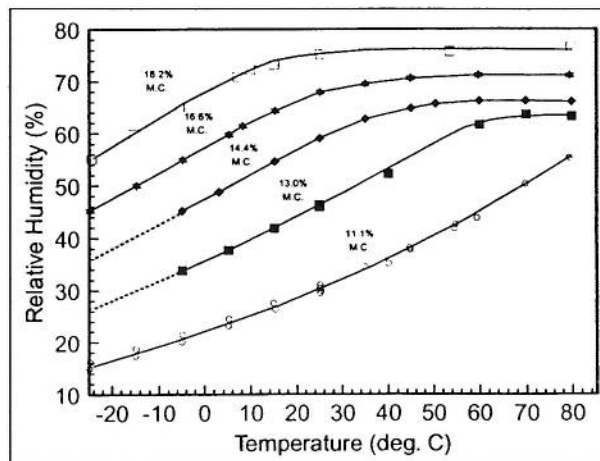

Figur 1. Moisture content Isolines for unhardened photographic gelatin.

atmospheric pressure) is not simple. Under ventilated conditions (e.g., an environmental test chamber where make-up air is introduced and the samples are freely hung), the data show that changing the temperature while maintaining a fixed value for relative humidity will also cause the moisture content of the gelatin to change. The moisture content isolines may be interpreted similarly to the reading of the contour lines on a topographic map. At fixed coordinates for temperature and relative humi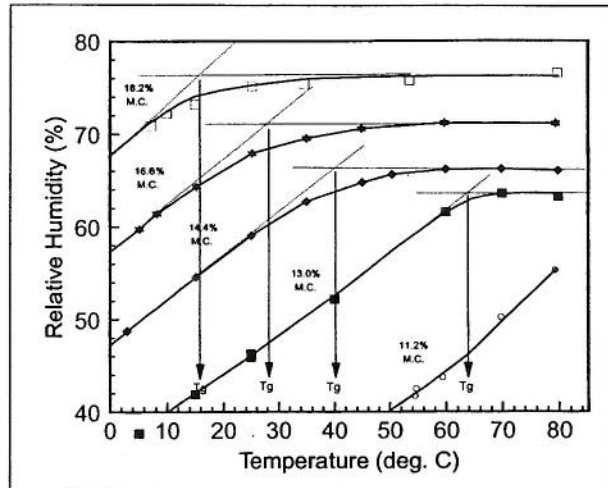dity, the equilibrium moisture content can be interpolated between the marked contour lines. The situation is even more complicated for photographic materials stored in sealed packages (e.g., photo materials sealed in moisture proof bags). Gelatin has the capability to "over buffer" the package. In an over buffered microclimate, decreasing the temperature will decrease the relative humidity while increasing the temperature will increase the relative humidity. However, as can be seen in figure 1, at a certain temperature level which varies with moisture content the rate of change in the relative humidity with respect to increasing temperature drops off to essentially zero. The gelatin no longer possesses the ability to over buffer the sealed environment, and the relative humidity remains constant as temperature is further increased. This bifurcation in the slope of the moisture content isoline marks the glass transition of the gelatin. Figure 2 illustrates how the bifurcation of the data can be used to determine the glass transition temperature of the gelatin. Figure 3 is a plot of the very same data shown in figures 1 and 2, but the data are now plotted in the graphical coordinate system used to report moisture absorption isotherms. The glass transition is then hidden by the selection of the different coordinate axes.

Whereas the data in figure 1 can be used to estimate the moisture content in the gelatin for free hanging environmental test and storage conditions, an estimate of the gelatin moisture content and relative humidity conditions inside a sealed package is complicated by the introduction of additional hygroscopic materials. Film base, paper products, and other hygroscopic materials can compete with the gelatin to varying

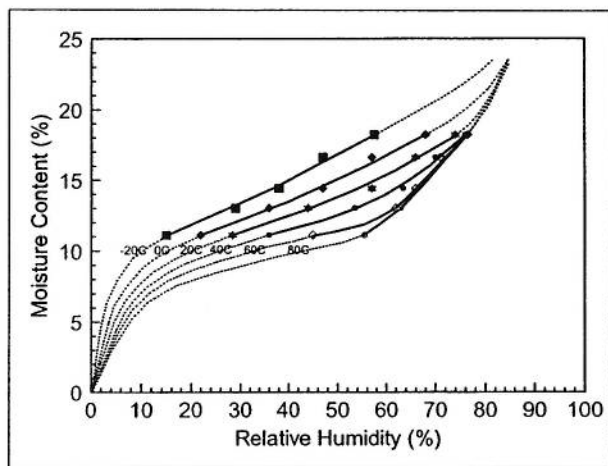Figur 2. Glass transition temperature of gelatin determined by moisture content isoline.

Figur 3. Moisture absorption isotherms for unhardened photographic gelatin. (Dashed lines illustrate curve shape outside measured data range).
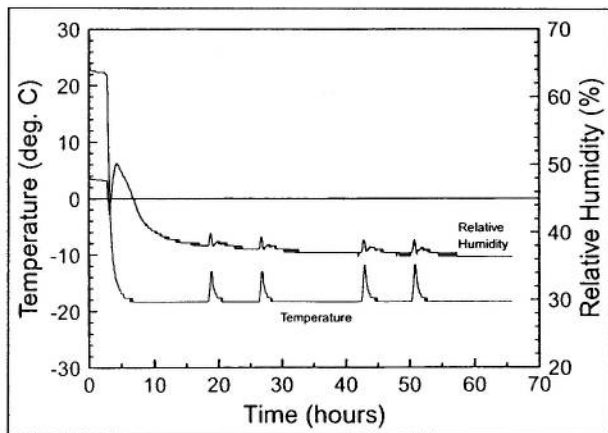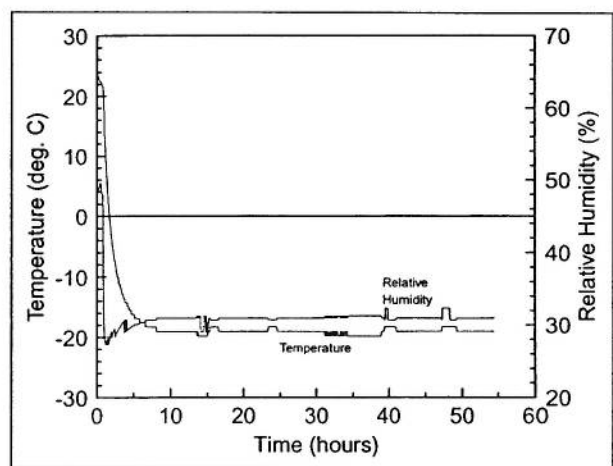

Figur 5. Microclimate response of letter-size document box, 75% filled with slides in plastic sleeves and paper folders, cooled to -18°C.

Figur 4. Microclimate response of motion-picture film roll (500ft. length, triacetate base), enclosed in polyethylene bag, then cooled to -18°C.

degrees and cause a moisture redistribution and an equilibrium RH that may differ from the value established solely by gelatin. Additionally, the other materials will not match the gelatin's glass transition behavior and its subsequent influence on relative humidity. Nevertheless, the general tendency of photographic materials to over buffer a sealed package when the gelatin binder is below T_g can easily be demonstrated. Figure 4 illustrates a roll of motion picture film that was inserted into a sealed plastic bag and allowed to cool to sub-zero temperature. An ACR "Smartreader" data logger was also enclosed in order to measure the microclimate response inside the package. Figure 5 shows the results of cooling a package comprised of a document box (acid-free conservation board construction) filled with slides in polypropylene sleeves and further housed in paper folders. The data in figures 4 and 5 confirm that the RH shift can be very

significant when large temperature reductions are involved. Similar microclimate effects for vapor barrier wrapped paintings subjected to cold temperatures during transit have been reported by Richard (3).

Discussion

Relative humidity is defined as the ratio of the water vapor pressure, P_w, to the saturation vapor pressure of water, P_{Wsat} (the fractional value is then multiplied by 100). In the sealed package microclimate used to measure the moisture content isoline data shown in figures 1 and 2, the water in the gelatin is more than ample under all test conditions to saturate the air inside the package if it was released to the air as water vapor. The presence of the gelatin causes vapor pressure lowering that is evident because the sealed system is unable to reach 100% RH. This vapor pressure behavior can be further understood by considering the colligative properties of a gelatin-water polymer system. Raoult first observed the phenomena of vapor pressure lowering, boiling point elevation, and freezing point suppression in 1887 when small amounts of solute were added to a solvent. However, the gelatin-water system is complex, and will not follow ideal binary system behavior necessary to conform to Raoult's law. The Flory-Huggins theory considers a polymer-solvent lattice model and accounts to some extent for the fact that long molecular chains of polymers will occupy the lattice structure differently than solvent and solute species having similar molecular sizes (4). Although the theory does not completely predict the thermo-dynamic behavior of polymer solutions, it is valuable because equations for colligative properties such as osmotic pressure have been derived. These equations have been found to be very useful in the molecular weight determination of polymers using measuring methods such as osmotic pressure, vapor pressure lowering, light scattering, etc. The Flory-Huggins theory incorporates an interaction parameter, χ. To paraphrase Flory, " χ represents the difference in energy of a solvent molecule immersed in pure polymer compared with one surrounded entirely by other solvent molecules". However, gelatin interacts with water in more than one way so all water molecules in the gelatin water matrix cannot be represented by a constant value for χ. Using an empirical modification of Flory-Huggins theory, Yapel, Duda, Lin, and Meerwall have evaluated the interaction parameter as a function of solvent volume fraction and modeled the mutual and self-diffusion of water in photographic gelatin (5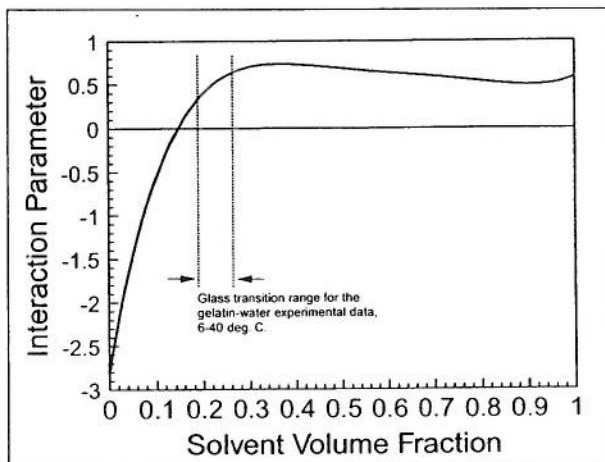). The interaction parameter was calculated from water activity/sorption data of Bull taken at 25°C and 40°C and these results were combined with other values for χ measured by Busk for dilute gelatin solutions at 6oC (6,7). The compiled results were then fitted with a 5th order polynomial, $Y = 2.795 + 31.422X - 107.331X^2 + 176.995X^3 - 143X^4 + 45.379X^5$ where Y is the interaction parameter and X is the solvent volume fraction. This equation has been used to plot the response in figure 6. The large negative values at low solvent volume fraction were attributed to the strong binding interaction of the water to the gelatin. Since the figure 6 data were derived from experiments between 6°C and 40°C, and the solvent volume fraction is known, the moisture content isoline data can be converted to solvent volume fraction coordinates and then used to estimate the range where the glass transitions for the gelatin-water system must have occurred. This range has been superimposed on the curve in figure 6. It is evident that the glass transition of the gelatin-water system correlates well with the steep change in the interaction parameter function reported by Yapel, et. al. The interaction parameter, χ, is seen to vary only slightly and perhaps in a statistically insignificant manner when the gelatin-water system is above T_g. Below T_g, the absorbed water plays a different functional role in the gelatin polymer matrix.

Much physical evidence exists to demonstrate the varying functional role of water in a gelatin-water system. The swelling isotherm behavior of a photographic grade gelatin is shown in figure 7. The data were measured for a moisture desorption cycle beginning at 90% RH so the strain values are negative. Both formalin hardened and unhardened gelatin were measured. No significant difference can be seen in the x-y coating plane of the gelatin layer for which the measurements were made.
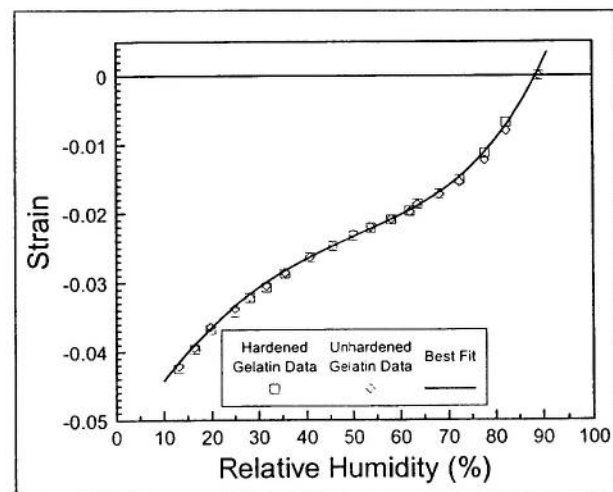

Figur 7. *Swelling Isotherm data measured at 22°C for photographic gelatin.*

The equation of "best fit" shown in figure 7 is:
Eq. 1). $\varepsilon = -0.055 + 0.0004 \times RH^{0.5} + .00106 \times RH - 1.14xE^{-5} \times RH^2 + 6.5xE^{-10} \times RH^4 + 1.4xE^{-14} \times RH^6$

Where ε is engineering strain (percent dimensional change divided by 100) and RH is relative humidity.

The moisture coefficient of expansion, α, can be found by taking the derivative of equation 1:
Eq 2). $\alpha = d\varepsilon/dRH = 0.0002 \times RH^{-0.5} + .00106 - 2.28xE^{-5} \times RH + 2.6xE^{-9} \times RH^3 + 1.4xE^{-13} \cdot RH^5$

Figur 6. Flory-Huggins Interaction Parameter for gelatin-water polymer system.

The moisture coefficient of expansion with respect to relative humidity is plotted in figure 8. Referring to figure 9, an effective modulus has previously been reported for gelatin with respect to relative humidity at room temperature (8). The effective modulus was measured under quasi-equilibrium conditions after restrained gelatin samples developed stress in response to small reductions in relative humidity. The desiccation intervals were small in order to avoid yielding by plastic deformation. Due to the diffusion limited process of water desorption, the loading rate is significantly lower than rapid loading rates typically used in mechanical stress-strain analyses. The effective modulus as a function of relative humidity at room temperature is therefore lower than values reported for rapid loading tests of gelatin (9). Additionally, rapid loading tests show an increasing modulus at decreasing RH levels, and water is commonly regarded as a plasticizing agent for gelatin in the "dry state". This behavior is not reproduced when the effective modulus, (i.e., the stiffness of the gelatin under moisture equilibrium conditions at room temperature) is measured. Under natural loading conditions the effective modulus actually reaches a peak value at approximately 40 to 50% RH over the tested range (approximately 15 to 73% RH). Collectively, figures 8 and 9 show that the gelatin-water system reaches maximum stiffness and maximum dimensional stability (lowest value of α) in the 40 to 60% RH range at room temperature under environmental

conditions that occur naturally. Hence, water is not merely a simple solvent when the gelatin-water system is below T_g. It chemically interacts with the gelatin at various sites to change the structural properties of the polymer. Some water is clearly able to become a structural component in the polymer matrix. This finding is consistent with chemical descriptions of gelatin and collagen in which a distinction is drawn between "bound water" versus "free water" (10).

Conclusions

The use of moisture content isolines to determine the glass transition of a hygroscopic polymer is perhaps a novel method. Moisture absorption isotherm data are largely ineffective in evaluating the glass transition. It is well known that gelatin emulsions can be quickly and severely damaged by mold and fungus growth at high relative humidity levels, and that emulsion sticking (often called ferrotyping) is also related to high humidity. However, the relationship between image degradation and the glass transition of the gelatin has not been considered in the photographic literature. It is reasonable to expect that the gelatin loses much if not all of its ability to serve as a protective coating for the image bearing materials (e.g., embedded silver particles) when it is above T_g and that ferrotyping is also a direct consequence of gelatin at or above T_g. The fact that the T_g can be exceeded at or near typical room temperature values when relative humidity levels reach 70 to 75%RH helps to explain why photographic materials are especially vulnerable to environmental conditions commonly encountered in basements or in non-air conditioned buildings located in humid geographic regions.

Implications for cold storage environments

Current recommendations for sealed package cold storage call for preconditioning photographic materials to low relative humidity (20 to 30%) (11,12). Humidity controlled cold vaults are also typically operated at 25 to 35% RH (13). The research presented in this paper has shown that photographic materials sealed in a closed system with little free air space naturally move towards the desired lower relative humidity conditions when the temperature is reduced. The results further imply that for humidity controlled vaults which operate at -18°C, a 30 to 35% RH environment does not actually extract any more moisture from photo materials previously conditioned to 45 to 50% RH at room temperature. Thus, the microclimate of a package sealed under moderate humidity conditions at room temperature and then stored at sub-zero temperature is essentially equal to the macroclimate found in a traditional humidity controlled cold vault operating at -18°C and 30% RH. Lower RH levels (20-30%) are required in the sub-zero temperature cold vault before further moisture extraction from the photographic material occurs. However, the net chemical benefit of a 20 to 30% RH versus 30 to 40% RH level at sub-zero temperatures may not be worth the extra effort or expense. Excellent chemical stability is achieved in either case.

Environmental conditions for the use and display of photographic materials which do not cause excursions above the glass transition temperature of the gelatin allow materials to be placed and sealed directly into moisture proof bags. Under these circumstances, additional RH conditioning procedures prior to packaging are unnecessary. The
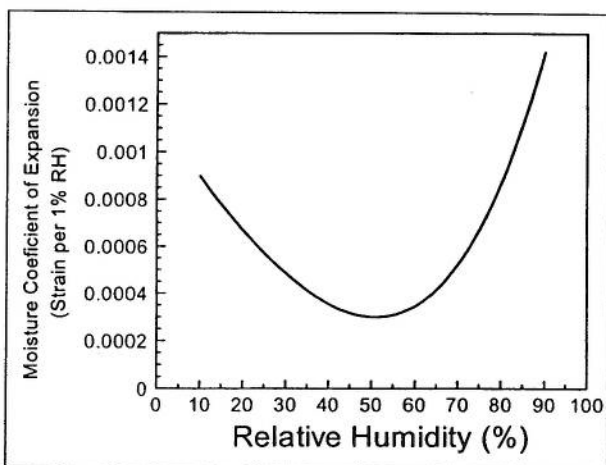

Figur 8. Moisture coefficient of expansion versus relative humidity for photographic gelatin (data measured at 22°C).
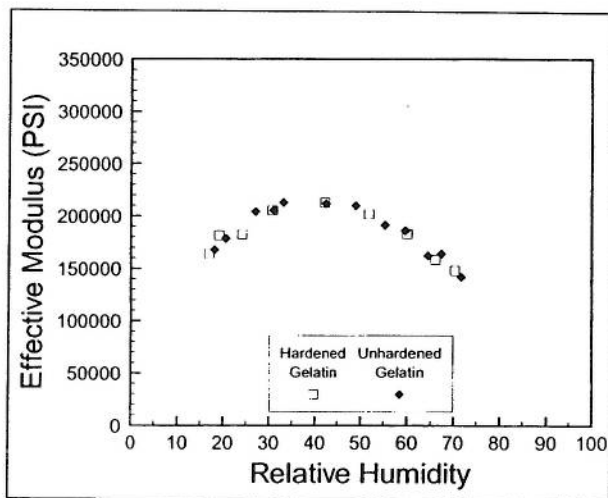

Figur 9. Effective modulus of photographic grade gelatin with respect to relative humidity (data measured at 22°C).

photographic emulsion layers will remain well below T_g during freezer storage and safely below T_g upon return to room temperature as long as the integrity of the moisture proof packaging is intact.

Implications for accelerated aging

The low value of T_g at moderate moisture content levels must be considered when accelerated aging studies are conducted. Such tests are often used to determine the role of both temperature and relative humidity on the reaction kinetics of various photographic material degradation processes. For example, deleterious agents such as ozone, peroxides, nitrogen dioxide, hydrogen sulfide, etc., will reach silver sites in the gelatin emulsion more easily, and their reaction with the silver will occur more readily as diffusion rates through the gelatin increase. Although increasing the temperature increases diffusion rates and reaction kinetics in general, crossing the glass transition may disturb the actual rate of increase with respect to temperature. Data collected above T_g may not provide a useful extrapolation to data taken below T_g because the glass transition represents a fundamental phase change in material properties. It is also likely that the effect of relative humidity on the reaction rate may no longer function proportionally once the glass transition has been crossed even though additional swelling of the gelatin-water matrix and a corresponding increase in the water weight fraction occurs. This situation is postulated because, in effect, the free water available for the reaction may become infinite for all practical purposes. For a given temperature above T_g, the statistical probability of nearby water molecules entering into the reaction may then approximate that of an aqueous solution, the volumetric increase caused by the addition of more water having little or no consequence.

Two experimental methods are commonly used to perform accelerated aging studies of photographic materials. One method uses a humidity and temperature controlled chamber in which the samples are freely hung and allowed to equilibrate to the temperature and relative humidity in the chamber. Some fresh air usually enters the chamber, so it is not a sealed system. The temperature and relative humidity levels maintained by the test chamber are the reported accelerated test parameters. The other method relies on sealed sample incubations. Samples are preconditioned to a given moisture content by equilibrating them to a specified relative humidity at room temperature, sealed inside a moisture proof container or bag, and then aged in a standard oven at specified temperature. Temperature of the oven and the relative humidity used at room temperature to moisture condition the samples are usually reported as the accelerated test parameters. The results presented in this paper clearly show that the two experimental methods as presently practiced cannot be directly compared. Relative humidity does not stay constant in a sealed package of photo materials "over buffered" by hygroscopic materials as the temperature changes.

In comparison to sealed test conditions, the "free hanging" sample test method maintains a constant value for the relative humidity, but the moisture content of the samples change as different temperatures are selected. In other words, Arrhenius type data will project aging rates along lines of constant moisture content for sealed package samples and along lines of constant relative humidity for free hanging samples. The extrapolations from both tests may coincide at room temperature if the sealed packages were conditioned at room temperature, but at other temperature values there will be a systematic error due to the environmental differences between the two test methods. More importantly and as previously noted, serious anomalies can result from the inadvertent mixing of data above the T_g of gelatin with data below the T_g. By following moisture preconditioning methods at room temperature, the sealed package tests tend to cross glass transition temperatures at a lower test temperature simply because they retain higher moisture levels at the elevated temperatures. The test results will therefore appear worse when compared to free hanging tests, and this poor behavior may be unfairly attributed to a hypothesis of trapped decomposition products promoting higher aging rates. At moderate to high moisture content levels, the glass transition is so low for photographic gelatin that testing by means of accelerated aging is inherently more difficult than for other types of materials such as high quality paper products. This is because of the inability to stay below the T_g and still use a practical incubation temperature.

It is recommended that Arrhenius tests be designed so that the gelatin emulsion remains below T_g unless the testing objective is to determine how the photographic material will behave when stored under adverse conditions (i.e., conditions that allow the gelatin to cross the T_g threshold).

As noted previously, the predictable moisture content, relative humidity, and temperature relationships shown in figures 1 and 2 for gelatin may be altered by the presence of more than one type of hygroscopic material in a sealed system. Mixed material situations are inevitable for manufactured films and papers, and are likely to produce an averaged resultant humidity response inside the package that depends on the constituent materials and their proportionate quantities. Hence, the actual measurement of relative humidity and temperature under equilibrium test conditions is probably the most practical way to ensure that the accelerated aging test parameters are correctly reported.

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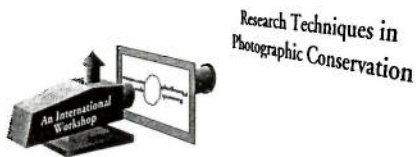
Research Techniques in Photographic Conservation
Proceedings of the Copenhagen Conference
14 - 19 May 1995.

Edited by Mogens S. Koch, Tim Padfield,
Jesper Stub Johnsen and Ulla Bøgvad Kejser.

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The factory owners house, from 1797 in Brede, now part of
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negative from the 1950's has shrunk from 9 to 8.3 cm due to
the "vinegar syndrome".