PRACTICAL GUIDE

TEMPERATURE AND RELATIVE HUMIDITY EFFECTS ON THE MECHANICAL AND CHEMICAL STABILITY OF COLLECTIONS

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and

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The environmental factors affecting the chemical stability of objects in the collections of museums and historic sites include temperature, moisture, reactive chemicals in the air, and biological attack. The concentrations of deleterious airborne chemicals such as nitrogen oxides and sulfur oxides are usually a function of a museum's proximity to cities, industrial sites and airports or to materials used in the building's construction. These chemicals can be filtered and avoided. Pest and biological issues such as insect and rodent infestations and mold growth are also important issues but will not be discussed here. The mechanical instability of museum objects may be seen in cracking, delamination, flaking of paint, powdering, etc., and may be the result of chemical changes in the materials and/or environmental action. However, this paper discusses only the principal effects of moisture and temperature on mechanical and chemical stability of collections.

Relative Humidity Effects On Mechanical Properties

The physical, or more accurately mechanical, properties of cultural materials have been largely responsible for the current "standard museum environment" of around 22°C and 50% ±5% relative humidity (RH). Fluctuations of RH greater than ±5% RH were considered responsible for the cracking of wood furniture and the flaking of panel and canvas supported paintings. While it is certainly true that materials such as some varieties of wood, ivory, and hide glues (including photographic gelatin) are quite responsive dimensionally to changes in ambient moisture vapor, many artifacts constructed of such materials, including paper, have lasted centuries in remarkably good condition in spite of having never been in the "optimum" museum environment. If one can understand the response of materials to the environment, then one will have a better insight into its effects on the longevity of objects.

The mechanical properties of cultural materials can be measured in much the same way as traditional structural materials such as steel and concrete, particularly noting significant time dependent behavior. This aspect of testing is accommodated by conducting tests at extremely slow strain rates.[1] Many cultural materials, such as wood, exhibit similar mechanical properties to steel in that they have both elastic and plastic regions. In the elastic region, the material returns to its original dimensions after the applied stress is removed.

In the plastic region, the material takes a permanent set after the applied stress is removed.

Like steel, these materials exhibit fairly well defined yield points at strains of 0.004 mm/mm and above. They also often show significant strain hardening. However, unlike the mechanical properties of steel, organic cultural materials are affected by moisture. In general, low RH levels tend to stiffen these materials and high RH makes them more flexible.

Figure 1 shows the results of an unload compliance tensile test of a cottonwood specimen cut in the tangential direction. In this test, stress is alternately applied and released. The dimensional changes with each cycle of applied stress are noted. The initial yield point occurred at a strain of about 0.0045 mm/mm, but further loading in the plastic region hardened the yield strain to about 0.0078 mm/mm. The ultimate strength of this wood is the stress at failure, in this case about 5 MPa (725 psi). Typically woods tested in the radial and tangential directions tend to fail at an ultimate strain between 0.015 mm/mm and 0.04 mm/mm.[2] Additional testing has shown that cultural materials can withstand thousands of repeated loading cycles if the loading remains in the elastic region.[3]

Most cultural materials swell with increased moisture and shrink with moisture loss. Two of the most responsive materials, wood and ivory, will be discussed here. Both of these materials are highly anisotropic, having considerably different mechanical and dimensional properties in each of their three primary directions.

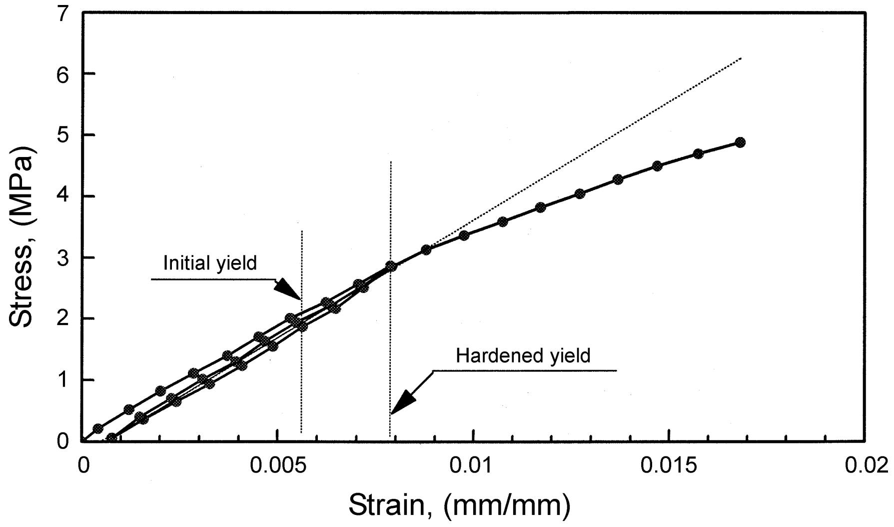

Figure 1: The results of an unload compliance test of a specimen of cottonwood cut in the tangential direction. The higher yield point was a result of straining the material beyond the initial yield point and into the plastic region. Unloading the specimen determines the amount of permanent plastic deformation that occurs.

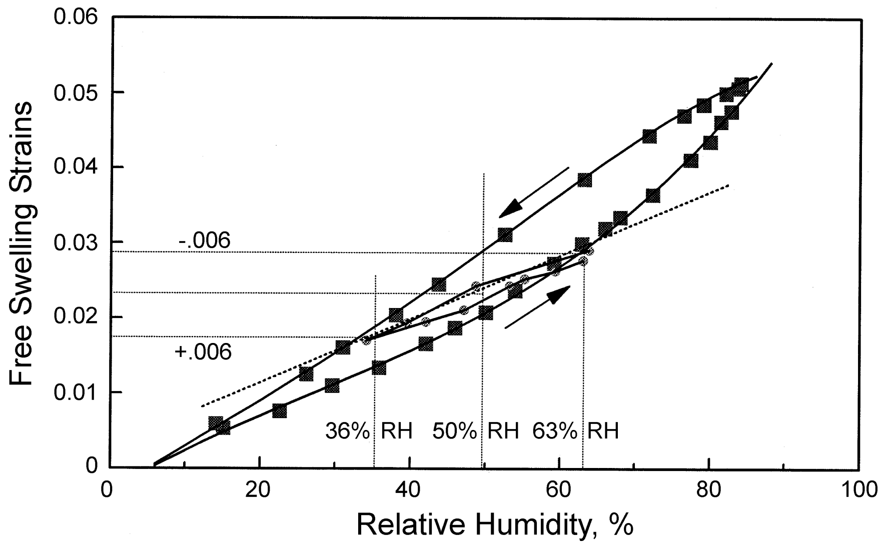

Figure 2: The free swelling strains versus the relative humidity (RH) for a sample of 350-year-old Scotch pine. This sample was cut in the tangential direction and subjected to both large and moderate RH cycles. The tangential direction is the most dimensionally responsive to moisture in woods. The rate of swelling for the smaller RH cycles is considerably less than the large cycles.

Figure 2 shows the dimensional response of a sample of 350-year-old Scotch pine in the tangential direction, which is the most responsive direction for woods. These tests were conducted at 22°C (72°F). Samples were allowed seven to 10 days at each relative humidity to come to equilibrium. *Figure 3* shows the dimensional response for a sample of ivory in the radial direction, which is its most responsive direction. These tests were also conducted at 22°C (72°F).

The squares show the individual test data. The dots show the slope of the curves or the rate of change at each relative humidity. Note that the rate of dimensional change is nearly constant between 35% and 65% RH, indicating comparative dimensional stability within that range.

Both wood and ivory demonstrate a considerable hysteresis with large changes in RH, as is typical of dimensionally responsive materials. Further, the slopes of the upward and downward plots are quite steep, and there are significant dimensional changes with changes in RH. Conversely, when the RH changes are moderate, both the wood and ivory exhibit a much less responsive behavior as shown between 35% and 65% RH. Both materials would have remained well within their respective elastic regions. If either the cottonwood or ivory samples had been restrained from movement and the ambient RH changed significantly, both materials would have developed considerable mechanical stresses and strains. Calculating moisture-related stress and strain development is directly analogous to the development of thermal stresses and strains.[4]

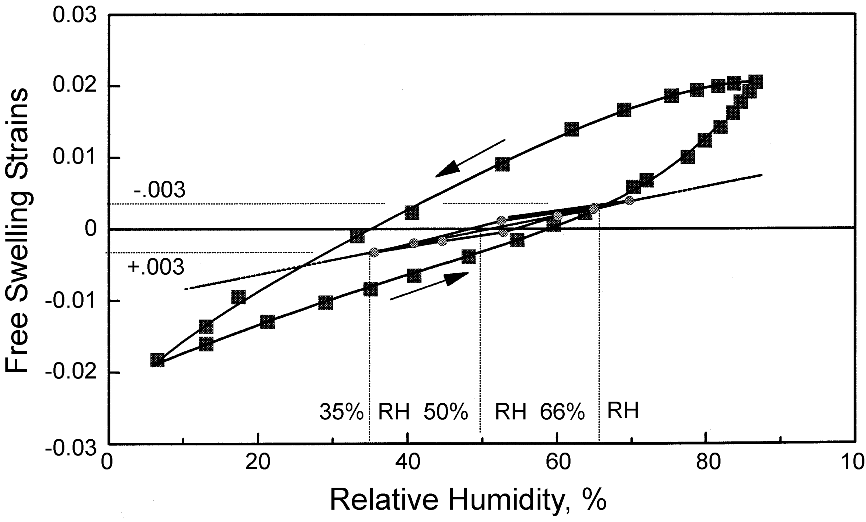

Figure 3: The free swelling strains versus the RH for a sample of ivory. This sample was cut in the radial direction and subjected to both large and moderate RH cycles. The radial direction is the most dimensionally responsive to moisture in ivory. The rate of swelling for the smaller cycles is considerably less than the large cycles.

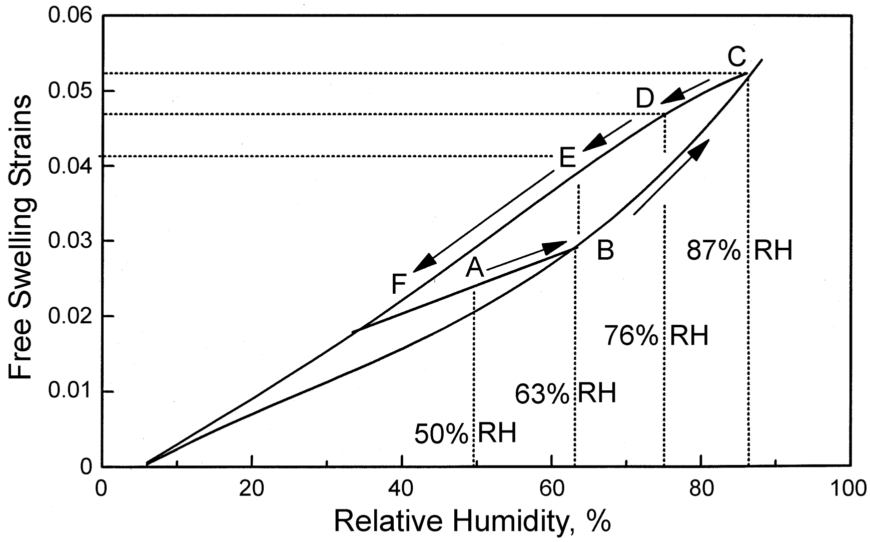

Figure 4: A simplified free swelling diagram for the strains versus the RH for the sample of 350-year-old Scotch pine. This diagram is used to illustrate the history of mechanical strains developed when a restrained wood sample is subjected to large RH changes.

For example, the mechanical stresses and strains of a restrained material can be calculated by assuming that the material is initially unrestrained and allowed to shrink freely as a result of either a drop in temperature or a decrease in RH. At the new environment, the material is then stretched to its original restrained length. Even though it has no apparent movement (no external dimensional change), a restrained material experiences mechanical stresses and resulting strains as a result of temperature or RH changes. These stresses and strains are the same as observed in a tensile test and can be directly calculated by the following equations:

$$\varepsilon_t = \alpha_t \, \Delta T$$
$$\sigma_t = E \, \alpha_t \, \Delta T$$
$$\varepsilon_{RH} = \alpha_{RH} \, \Delta RH$$
$$\sigma_{RH} = E \, \alpha_{RH} \, \Delta RH$$

where:

ε_t and ε_{RH} are thermal and moisture related strains, respectively,

α_t and α_{RH} are the thermal and moisture coefficients,

σ_t and σ_{RH} are the thermal and moisture stresses.^{5}

E is the equilibrium modulus of elasticity for the material at the given temperature or RH.

Using these equations allows one to utilize diagrams such as *Figures* 2 and 3 and directly calculate the mechanical strains developed when a specimen is restrained and the environment changed. Such an exercise gives insight into the effects of large changes in RH. For example, consider a typical average yearly environmental change in RH. If a restrained specimen of the Scotch pine were stress free at 50% RH, and the RH were allowed to rise gradually so that the specimen was fully equilibrated to the environment, the mechanical strains developed in the wood can be determined using a chart such as *Figure 4*. *Figure 4* is a simplified version of *Figure 2*. The related stresses could have been determined from relevant values of E, the modulus of the material, or from stress-strain plots of the material tested at a variety of environments. But here the strains alone serve the purpose.

As the RH rises from 50% (Point A) to 63% (Point B), the wood increases in compressive strain to approximately 0.006. It begins to make the transition from elastic to plastic behavior. As the RH continues to rise from 63% (Point B) to 87% (Point C), the wood, if it does not buckle, experiences full plastic strain (permanent deformation), and the stresses are fairly constant. At Point C, the RH starts to drop until the specimen reaches 76% RH (Point D) where the specimen unloads all elastic compressive strain so is again stress free. At this point the specimen has experienced "compression set" and has completely reinitialized its equilibrium position (i.e., stress is zero).

If the RH continues to decrease, tensile stress builds and at Point E (63% RH), the specimen yields in tension. From this point on, further desiccation causes plastic deformation in tension until Point F (40% RH) where the specimen cracks. If the specimen had not been subjected to the large RH excursion, it could have been equilibrated to very low RH levels without failing.

If a sample of restrained ivory were subjected to the same high RH cycling as shown for the 350-year-old Scotch pine, it would surely have failed at somewhere between 30% and 40% RH. If the ivory had remained within the 35% to 65% RH range, it would have stayed within its elastic region in spite of thousands of such cycles.

The two previous examples are not unusual conditions. Cradled panel paintings often lock up and inhibit free expansion and contraction. Wood veneers and ivory inlays bonded cross-grained to a wood substrate are also effectively restrained from motion. Furniture is nearly always constructed such that some assembled components restrain another.

Between 0% and about 75% RH, oil paints have considerably less dimensional response to moisture than woods.[1] So much so that oil paint applied to inert substrates such as copper can withstand very large RH changes without leaving their elastic region. Above 75% there is a marked increase in oil paint swelling, but still less than woods. Modern paints such as acrylic emulsions and alkyds have quite low dimensional responses to moisture.[6]

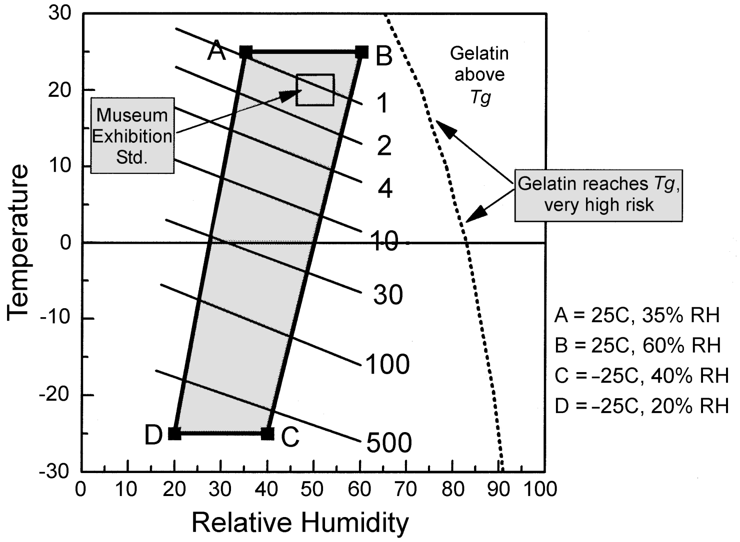

Figure 5: Diagram illustrating the safe allowable environmental ranges for 20th century gelatin binder photographic materials. The boundaries of the box enclosure were determined from both chemical and mechanical research. The diagonal lines marked with numbers indicate the relative chemical stability of the photographic materials.

Damage to painted wood objects comes from two primary sources. The first is from very large RH excursions of an unrestrained wood substrate, such as a panel painting; the second is from low temperatures.

The Effects of the Rate of Change of RH

Most materials absorb water vapor quite slowly. It takes about 24 hours for a 1 mm thick oil paint film to reach 90% equilibrium when subjected to a new environmental moisture level, and it takes about a week to achieve full equilibration. Woods are only slightly faster. Large objects can take months to come to a near equilibrium and often may never catch up to annual environmental changes. Smaller, thinner objects such a photographs and films, papers, and parchments can fully equilibrate within hours. However, even these objects do not experience instantaneous responses. The rate at which even these objects respond does not cause brittle stress development as might be encountered during a one hertz cycling test. The more important criterion for stability is that the materials not experience RH changes outside the limits between 35% and 60%.

Temperature Effects
On the Mechanical Properties

While RH related damage is clearly established, temperature changes (independent of RH) are a subtler source of considerable damage. In fact, much of the damage found in painted surfaces (panel and canvas paintings, and painted furniture) that was attributed to RH was probably caused by exposure to low temperature. In general, thermal changes act in a manner similar to the dimensional changes caused by moisture changes. Mismatches of the thermal coefficients of joined materials are often not significant but on occasion can cause serious enough strain to induce cracking. The real problem is that low temperature severely embrittles materials such as paints.

Traditional oil paints have a glass transition temperature, T_g, around –15°C (5°F). This is the temperature where the material changes from ductile to brittle behavior. Below this temperature, the material becomes extremely fracture sensitive. Artists' alkyd paints have a T_g about –5°C (23°F), and acrylic emulsion paints have a T_g of about 5°C (41°F). A good example of temperature induced cracking of a painted surface on a wood substrate is observed when cracks occur perpendicular to the grain of the wood. Other materials, such as woods, hide glues, and photographic emulsions, can sustain very low temperatures without severe embrittlement and can be safely stored below freezing.

Effect of Age

While many artists' materials such as oil paints tend to strengthen and stiffen with age (several centuries), only serious chemical degradation will ultimately cause a loss of strength. So far our research has shown that time alone has no or little effect on the dimensional response of the materials to moisture or on the yield point. This means that the safe reversible RH range is not necessarily affected by an object's age. It is the current condition or state of degradation of the objects and their materials, not age, that ultimately govern their response to the changes in the environment.

Chemical Considerations

The chemical effects of temperature and relative humidity (RH) on collection stability can be approached systematically. As a product of his research, Mark McCormick-Goodhart,[7] developed a way to present an overview of the relative chemical stability of 20th century photographic materials. His illustration, presented here as *Figure 5*, shows the large safe environmental range, i.e., the area containing ABCD, for photographic materials.

More importantly, this figure shows the chemical advantages of lowering the temperature and/or relative humidity while storing photographic materials. These effects are shown as the contour lines of relative chemical stability. For example, if a photograph "lasts" 80 years in the "museum environment" indicated in the illustration, it will last 8,000 years at –10°C (14°F) and 40% RH. It should be noted that in the case of the photographs, there is some modest benefit to lowering the ambient RH at any given temperature. However, lowering the temperature is a considerably more effective preservation strategy.

The boundaries established in *Figure 5* reflect a combination of chemical and mechanical considerations. For example the left boundary, line A-D, limits mechanical tensile stresses developed in the emulsion due to desiccation. The lower boundary, line D-C, limits thermally induced stresses. The right boundary, line B-C, limits mechanical compressive stresses caused by excessive moisture. The upper boundary, line A-B, limits chemical degradation caused by excessive heat.

In many ways *Figure 5* illustrates a general approach in helping to determine the museum environment. The issues raised in this specific analysis of photographs are the same for nearly all other museum objects.

The rates of chemical reaction have been described quite effectively by the work of Svante Arrhenius. His famous equation is:

$$k = A \exp(-E_a/RT)$$

The equation may be rewritten as:

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

where:

k is the reaction rate

A is a constant, often called the frequency factor

E_a is the activation energy. In general, as this value gets larger the rate of degradation decreases.

R is the gas constant

T is the absolute temperature

This equation states that the chemical reaction rate increases with increasing temperature, and conversely, decreases with decreasing temperature. Another important aspect of this effect is related to the different chemical activation energies of cultural materials. If the activation energy for a process is lower in Material A than in Material B, then Material A will degrade faster than Material B in the same environment. Higher temperatures will markedly accelerate chemical degradation of both materials but at different rates.

It is important to note that the ambient environment has many mechanisms for degradation besides temperature and moisture. For example, protein fibers such as wool and silk are also prone to light degradation, more so than cellulose. Therefore, in similar environments a wool tapestry may degrade faster than a cot-ton textile.

Organic materials change their moisture content with changes in ambient humidity. This behavior is best illustrated using a moisture isotherm. A typical moisture isotherm for cotton[8] is shown in *Figure 6*.

Typical of this isotherm is the S-shaped form, steep sections at the lower and higher RHs and a less steep curve connecting the two RH extremes. This curve is actually the sum of two absorption curves. One is for the bound water and the other is for the free water. The practical impact of this behavior is that in intermediate RH regions (30% to 60%) there is not a great change in available moisture content (water) for hydrolysis reactions to utilize.

David Erhardt, in a study examining the chemical degradation of cellulose, showed the effects of different temperatures and different levels of RH.[9] Cellulose is found throughout museum collections in the form of fibers, papers, woods and textiles. Erhardt found that humidity affects the type of reaction while temperature affects the rate of reaction.

In hydrolysis reactions, materials decompose by reacting with water. Hydrolysis reactions are directly associated with free water. Erhardt found that hydrolysis reactions dominated at RH levels above 35% over the full range of temperatures he studied. Hydrolysis reactions increased markedly with increasing RH. For cellulose, 35% RH was optimum to minimize hydrolysis.

In cross-linking reactions, materials form new bonds between molecular chains. These new bonds make the material less plastic. Erhardt found that cross-linking reactions dominated below 30% RH, also over the full range of temperatures studied. Cross-linking reactions are directly associated with bound water. Increasing the temperature accelerated the rate of these reactions.

Materials stored in cool, wet basements will deteriorate primarily by hydrolysis reactions. Because the temperature is low, the rate will be slow. Materials stored in hot, dry attics will deteriorate faster by cross-linking reactions. This is, of course, why hot summertime attics are poor storage environments.

Temperature controls the rates of the reactions. At room temperature and moderate RH, cellulose is relatively stable. This is evidenced by the longevity of watercolor rag papers, wood panel paintings, structural timber, and furniture. The average activation energies for major soluble products of cellulose are between 22.7 and 26.8 kcal/mol. For photographic gelatins it is about 22.4 kcal/mol. Early 20th century film bases are a greater problem than the image emulsions in terms of rates of chemical degradation.

All organic materials found in museums are governed by very similar processes, so the rates of deterioration are going to be governed by the various chemical process activation energies. For organic materials, a relative humidity range of 35% to 45% would be better chemically for collections in a museum environment. Metal corrosion though, is considerably reduced at even lower RH levels. Lower temperatures, however, would reduce chemical deterioration of all materials, regardless of reaction mechanism. However, there are mechanical limitations on lower temperatures.

For exhibition areas, the human comfort zone is typically about 20°C to 22°C (68°F to 72°F). So a significant compromise to long term preservation of the collections has been already decided. For objects in storage other factors may apply. Cold storage can discourage convenient access to collections by scholars, although this is a management issue. More importantly, however, is that some cultural materials cannot physically withstand cold temperatures.

The research results suggest that (for the exhibition spaces) an RH range from 35% to 60% is not out of consideration for most museums.[10] For example, a summer environment of 55% RH ±5% at 23°C (73°F) and for the winter time, 40% RH ±5% at 20°C (68°F). The research also reveals that the rate of change of the environmental conditions is not a factor if the object is maintained within the allowable range. Tighter controls that maintain high RH in the wintertime are almost guaranteed to damage buildings, especially old historic sites. Other factors might require tightening this environmental range a bit.

However, except when the ultimate strength of a material has degraded close to its yield strength, there is little evidence to suggest there is a situation where nearly flat-line environmental control is necessary or even recommended. Materials degraded to the point where their strength is near the yield point are almost impossible to handle. These research results are based on a multi-year effort to study the effects of the environment on materials and objects in the collections.

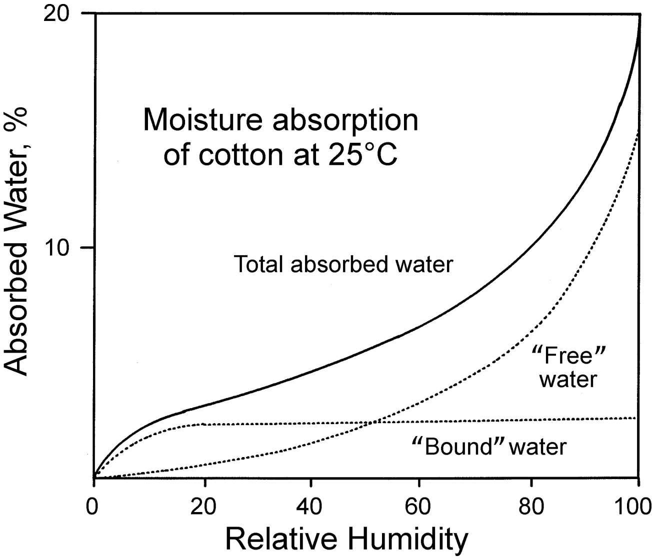

Figure 6: The moisture isotherm for cotton, showing the absorbed water versus the RH. (adapted from [8]) The dashed lines indicate the different types of absorbed water contributing to the total amount.

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