## **SMITHSONIAN INSTITUTION**

## CONSERVATION ANALYTICAL LABORATORY

#### **MUSEUM SUPPORT CENTER**

Washington, D.C. 20560

Mechanics Research on NASM Materials and Environmental Effects on their Properties Interim Report #1

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Mechanics Research on NASM Materials and Environmental Effects on their Properties Interim Report #1 October 27, 1994

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# Mechanics Research on NASM Materials and Environmental Effects on their Properties Interim Report #1

#### Introduction

The research for determining the effect of the environment on the mechanical and physical (dimensional) properties of materials typically found in the National Air and Space Museum has gotten to the point where preliminary data is available. The materials that are unique to NASM are certain woods, fabrics, glues, and aircraft paints and coatings. The museum has a considerable amount of exposed and uncoated metal found in many of the aircraft, space craft and engines. These materials will be addressed later in the research.

NASM collections contain materials which were traditionally used in objects typically found in other museums. Information on these materials will be included in Appendix A of this and other reports as it is developed. Appendix A is important in that it lays the foundation for determining allowable RH fluctuations in restrained materials. It also develops the rational for determining the effect of composite construction on determining allowable RH fluctuations. Keep in mind that when reading Appendix A, the section discussing the effects of wood as a stiff substrate can be easily modified to include metal as an alternate substrate.

In this first report, the background information on the testing of some aircraft paints and woods is presented. Preliminary results on the testing of these and other materials is included.

# **Mechanical Testing**

# Determining the Drying Time of Typical Aircraft Paints and Coatings

Clear nitrate dope, clear and pigmented butyrate dopes, and pigmented nitrocellulose lacquers were obtained from the Garber Facility for testing. These are paints typically found in antique aircraft and are used in the restoration of aircraft. The dopes are applied to fabrics stretched over aircraft frames and in effect have little firm structural support. Since they are supported by fabrics, these paint systems have many structural similarities to traditional canvas paintings. This means that in many ways the coatings must provide much of the structural support themselves. Fabrics in general will not endure significant tensile forces over a substantial period of time. This is particularly true in environments with seriously fluctuating relative humidity (RH). (See Appendix A, page 16)

In traditional canvas paintings hide glue (which acts as a tightening size), not the canvas, provides the large proportion of the paint support. In the aircraft fabric-paint systems, the clear nitrate dope performs a similar function. This coating shrinks and tightens upon drying and

effectively tightens the stretched aircraft fabric. Unlike hide glue in traditional paintings, nitrate dope minimizes the effects of RH fluctuations on the structural performance of the aircraft skin. If a sound understanding of the structural relationship of the different materials in the coated fabric is to be developed, the mechanical properties of the individual materials must be determined.

Before any systematic analysis of the mechanical and physical properties of the paints could begin, the cast films had to be dry and relatively free of solvents. All of the paints supplied by NASM were coated onto mylar sheets. After drying for several days, the films were easily removed from the mylar and could be cut into free, unsupported test specimens. The mechanical tests used to assess drying were relatively slow tensile tests. The paint specimen was allowed to stress relax 30 seconds after each loading increment, then subsequently loaded to the next step. This testing technique removes nearly all of the time dependent effects on the mechanical properties of these materials. The specimens were typically 5 to 6 inches long, .25 inches wide, and between .005 to .014 inches thick. The initial test environment was approximately 50% RH at around 23° C.

The presence of solvents in the paints tend to make them flexible with the ability to elongate. As the solvents evaporate, the paint specimens get stiffer, stronger, and stretch less. When there is no effective difference in the results between subsequent tensile tests, the specimen can be said to be sufficiently dry for further analysis. Figures 1-5 show the tensile tests results for a variety of clear and pigmented nitrate and butyrate dopes. In Figure 1, the tests results show that clear butyrate dope has completed drying after about 16 days. The 33 day test shows no significant difference from the 16 day test. The tangent line drawn from the origin of the tests indicates the modulus of elasticity (E) for the dried paint. In this case, the modulus is 120,000 pounds per square inch (psi) The addition of some types of pigmentation to butyrate dope can slow the drying process down considerably. The addition of aluminum paste seems to have little effect on drying time (Fig. 2) since the paint appears to be dry in about 16 days. However, it takes about twice that long with the addition of colored pigments as shown in Figures 3 and 4. Figure 4 shows a dark green butyrate paint that was stored in the can since 1985. This paint did deteriorate while in the can but seemed to lose little strength as a cast paint. Deterioration was detected by the presence of butyric acid.

Figure 5 shows the test results of cast films of clear nitrate dope. This material took about 33 days to dry. It is extremely strong when dry and is the "sizing" coat for fabric stretched over aircraft frames.

Both the butyrate and nitrate dope paints can sustain considerable extension (strain) when dry, at least 2% elongation. Early failure of a test specimens was always associated with the presence of a crack formed during the cutting of the test specimen. This crack initiated slow tearing across the specimen and resulting in a loss of strength during the late part of the test. Many of the tests over 7% extension (strain = .07) did not fail but were simply discontinued.

Three different pigmented nitrocellulose lacquers were tested and the results are shown in

Figures 7-8. These paints take an extremely long time to dry and the lacquer containing aluminum pigment shows some embrittlement.

In all cases, the yield point for all of the paints tested is at least .004. This information is important when determining the allowable RH fluctuations for these materials.

## The Effect of RH on the Mechanical Tests.

Testing for the effects of ambient RH on the mechanical properties has just begun. The effect of RH on the paints is typical of several types of paints tested. (see appendix A to this report) Figure 9 shows the results of clear butyrate dope tested at three different environments, 5%, 50% and 80% RH. The test temperature was 23° C. There is some stiffening and loss of ductility with desiccation. Testing at 80% RH shows an increase in flexibility (lower modulus) with a loss of strength and strain to failure. The paint still maintains a minimum of .02 strain at failure even at 5% RH. The spacing at the start of the tests reflects the length increase of the material due to changes in the moisture content. This spacing is small indicating that moisture is not swelling this material much. This is borne out from the tests measuring the swelling isotherms which in presented in the next section.

# The Dimensional Response of the Paints to RH

The restrained desiccation of any hygroscopic material will result in the development of tensile stresses and strains. The magnitude of these stresses is a direct function of the capacity of a materials to swell or shrink with moisture change and the modulus of the material. This relationship is detailed in Appendix B, where environmentally (RH) induced stresses are related to the mechanical properties of materials as measured by externally loaded testing techniques. In effect, this research demonstrates that the way a material reaches a state of stress, strain, temperature and RH can be independent of the path taken. It also implies that the failure mechanisms of materials determined through externally loaded testing are the same as failure mechanisms resulting from environmentally induced stresses and strains. Therefore, determining the moisture (or thermal) coefficient of expansion is critically important.

Figures 10-14 show the dimensional response versus RH for some of the paints used on fabric coated aircraft. These paints include clear butyrate dope, three pigmented butyrate dopes, and a clear nitrate dope. At the time of testing of these materials, the nitrocellulose lacquers were not sufficiently dry to test. These paints show some of the least dimensional response to moisture of all of the materials examined. Only flake (white) lead oil paint comes close to these magnitudes (see Appendix A, Figs. 41 and 49). For comparison purposes, sheet mylar was also tested as an example of a polymer with exceptionally low moisture absorption (Fig. 15). The moisture coefficients of expansion were calculated for the dopes and mylar by taking the derivative of polynomial fits passing through the dimensional data. These coefficients are illustrated in Figure 16. Comparing these coefficients with any of those shown in Figures 11, 21, 24, 32, 41, 46, 47, and 49, in Appendix A, demonstrates how little moisture affects these paints.

# Calculating the Allowable RH Fluctuations for Aircraft Paints Subjected to Full Restraint

If a yield strain of .004 is used for the paints and using equation 3 of Appendix A, allowable RH fluctuations for these paints when under full restraint can be determined. The results of these calculations are presented in Figure 17. Here the calculated RH fluctuations needed to reach a yield strain of .004 for fully restrained paints are presented. For example, if the clear nitrate dope was restrained at 45% RH, the change in RH needed to reach yield in tension is down to 6% RH. If the nitrate dope had been applied to metal or any hydrophobic solid material, it would attain a compressive yield strain if the RH increased to 77%. This would also be the result if it had been applied to wood and the strains are calculated for the parallel to grain direction. All of the butyrate dopes can take even more severe RH changes than the nitrate dope. If the paints has been applied to fabric, the increase in RH only tends to relax any pre-existing strains.

### **Existing Pre-tension**

Nitrate dope is actually under some tension at midrange RH levels. Otherwise it would not be useful as a component of fabric aircraft covering. This could be represented as a pre-existing strain of .002, which is a significant stress (200-300 psi depending on the environment) considering the modulus of the material is fairly high. Even with this pre-tension condition, the RH has to drop to at least 25% to reach yield in the nitrate dope. The dashed line in Figure 17 show the effect of a .002 pre-strain on the allowable fluctuation of the nitrate dope.

A more complete battery of mechanical testing has to be completed to verify that the yield point is not substantially modified by RH. It has not been in any of the other materials tested so it is not expected to vary much with RH in these materials. It is also important to determine the strengths and final breaking strains of the materials at other RH values.

### Preliminary Results of Temperature Effects

The effect of temperature on the dimensional response of NASM materials has just begun. The thermal coefficient of expansion for clear butyrate dope was determined by measuring the dimensional response of the material with respect to temperature and determining the slope of the strain versus temperature plot (Fig. 18). Moisture does not seem to affect the thermally induced dimensional changes as the same tests were conducted at 50% RH and 4% RH and there is no measurable difference in the test results. The thermal coefficient of expansion for clear butyrate dope (Fig. 19) was calculated as a constant, .000072 strains per degree C, irrespective of the moisture content of the material and over a test temperature range from - 23° C to + 40° C. The significance of this is that if the clear butyrate dope were to be restrained at 20° C, it would take changes of  $\pm$  50° C to reach a yield strains of .004 in tension or compression. This is a substantial change. What needs to be determined is the glass transition temperature,  $T_g$ . Also the mechanical properties testing needs to be completed in order to determine the actual low temperature yield points, strengths, and the brittle-ductile transition zones.

# A Preliminary Look at Rubber

Samples of sheet rubber were mechanically tested at two levels of RH (Fig 20). There was no dimensional change detected with the different RH levels and the tensile test are nearly identical. Rubber is known to be hydrophobic so changes in the mechanical properties were expected. Rubber can be stretched up to 400%, (a strain of 4.0). The tests were carried to an extension of 120% which is 300 times greater than the extension to reach a yield of .004 which is found in other materials. The decay of stress at the end of these tests is stress relaxation with time after the test was discontinued. The yield point of this rubber has not yet been determined but it is expected to be substantial. There should be no stresses or strains induced by changes in RH. The thermal and chemical effects on the properties of rubber is to be considered of greater significance than the moisture induced behavior.

#### Woods

Several woods including yellow pine, sugar pine, spruce, white oak, mahogany, and cottonwood were obtained from the Garber facility. Cottonwood, mahogany, and white oak were also used as supports for traditional panel paintings. The research information for these woods and spruce are presented in detail in Appendix A. The tangential direction test results for sugar pine and yellow pine are included in this report. The tangential direction is chosen since it represents the worst case dimensional response for woods. As such, allowable RH fluctuations from a structural point of view will always be significantly greater in the radial and longitudinal (parallel to grain) directions. Mechanical testing of the sugar pine reveals (Fig. 21) that this material actually gets stronger with desiccation. Many other woods, such as yellow pine (Fig. 25), tend to get brittle at low RH and fracture at lower stresses than those measured around 50% RH. Sugar pine wood has a moderately low dimensional response to moisture. Over the entire RH region, it swells about 3.5% (Fig 22) and can be compared to yellow pine data showing about 6% (Fig. 26). As with most hygroscopic materials, the moisture coefficients of expansion (Figs. 23 and 27) for both sugar pine and yellow pine are minimum in the middle of the RH range. This is the region of least dimensional response. The allowable RH fluctuations for both woods were calculated using a yield strain of .004 as the limiting criteria. These calculations are graphically presented in Figures 24 and 27. As seen from these graphs, both woods are able to sustain significant RH fluctuations with out yielding.

# Fabrics See Appendix A

#### Summary

From the preliminary results obtained from mechanical and physical testing of the materials examined, all are able to sustain significant RH fluctuations from a structural consideration. The criterion for calculating the RH fluctuations were yield points, which mark the transition from elastic (reversible) to plastic (permanent) deformations and total restraint from movement. The actual RH fluctuations required for failure are even greater and are calculated for many materials where the failure data is available (see Appendix A). Chemical and thermal considerations for

the long term stability of rubber are probably going to be a greater issues than those related to RH. For fabrics found in aircraft, lower RH, 35% to 55% would be preferable from a chemical stand point. More detailed structural analysis may be needed for complex constructions.

As this project proceeds, more of the chemical behavior of materials will be included as it is made available.

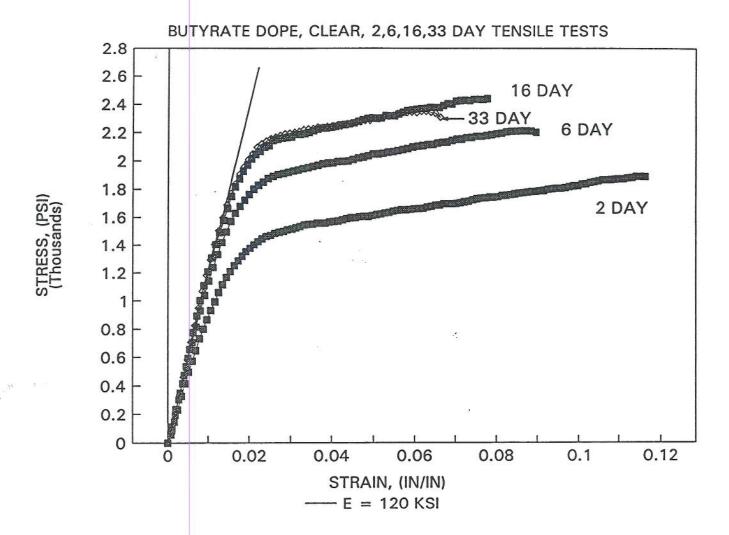


Figure 1. The mechanical tests conducted for determining the drying time for clear butyrate dope. This information also provides the yield point, strength, and strain to failure at 50% RH and 22° C.

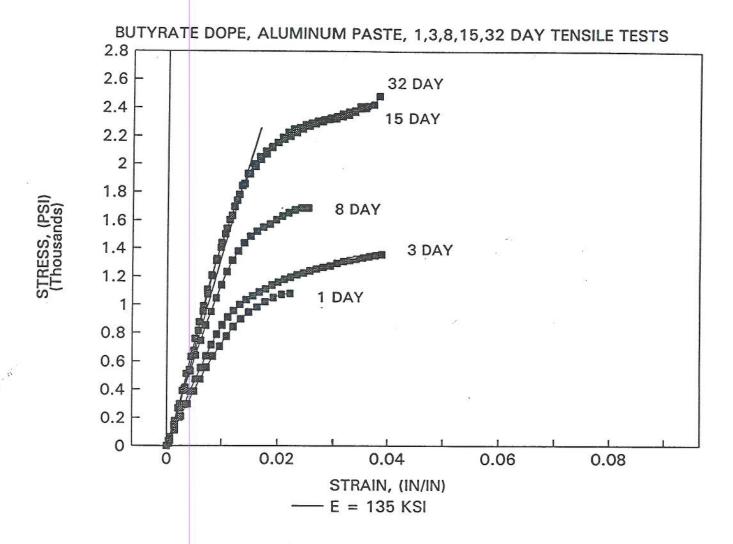


Figure 2. The mechanical tests conducted for determining the drying time for butyrate dope containing aluminum paste. This information also provides the yield point, strength, and strain to failure at 50% RH and 22° C.

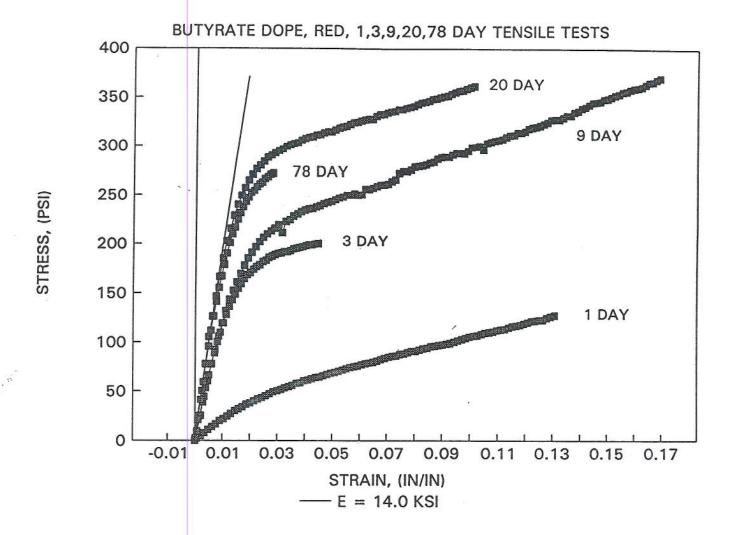


Figure 3. The mechanical tests conducted for determining the drying time for butyrate dope containing red pigment. This information also provides the yield point, strength, and strain to failure at 50% RH and 22° C.

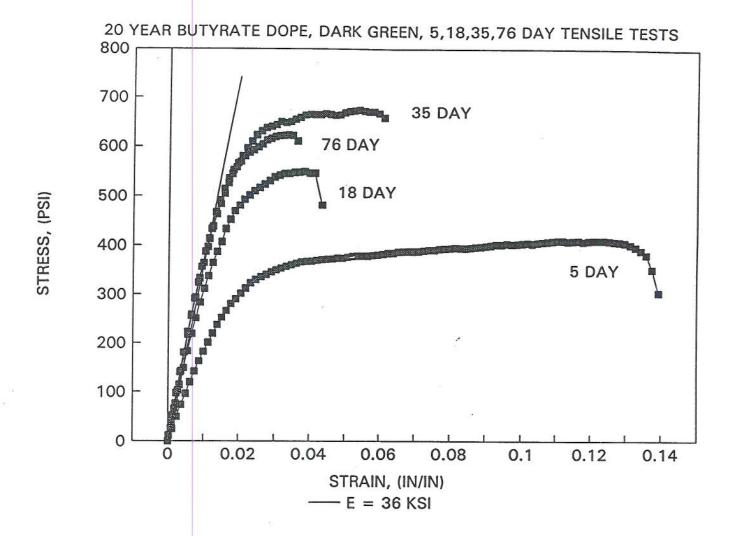


Figure 4. The mechanical tests conducted for determining the drying time for butyrate dope containing dark green pigment. This information also provides the yield point, strength, and strain to failure at 50% RH and 22° C.

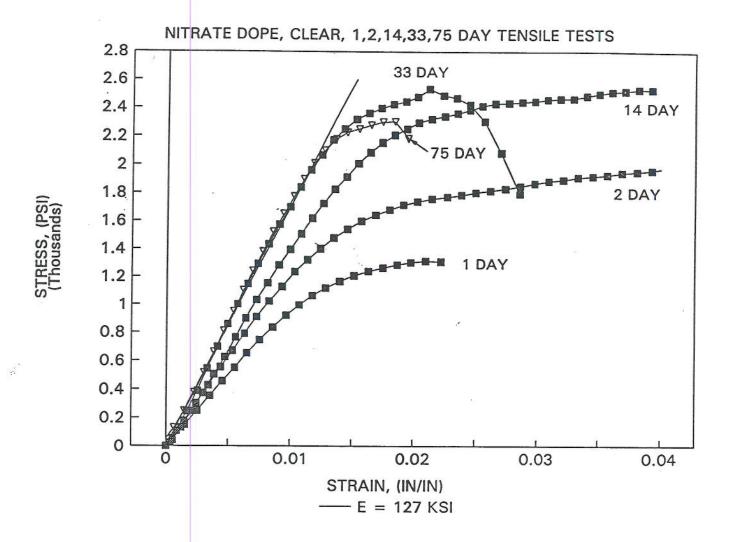


Figure 5. The mechanical tests conducted for determining the drying time for clear nitrate dope. This information also provides the yield point, strength, and strain to failure at 50% RH and 22° C.

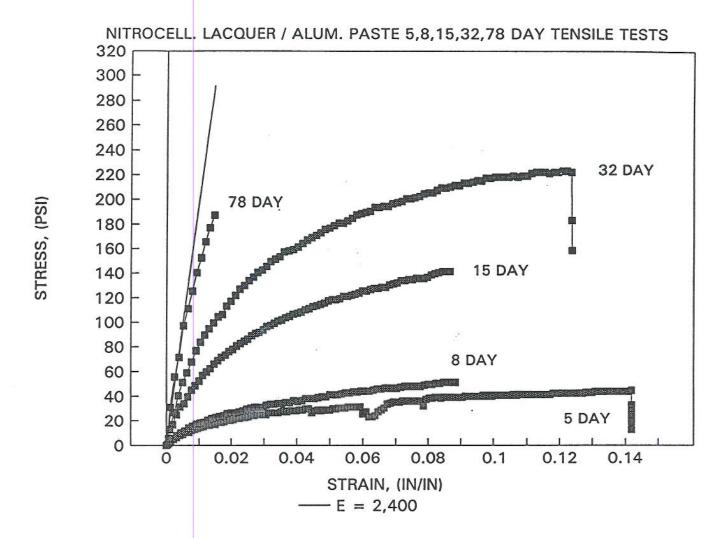


Figure 6. The mechanical tests conducted for determining the drying time for nitrocellulose lacquer containing aluminum paste. This information also provides the yield point, strength, and strain to failure at 50% RH and 22° C.

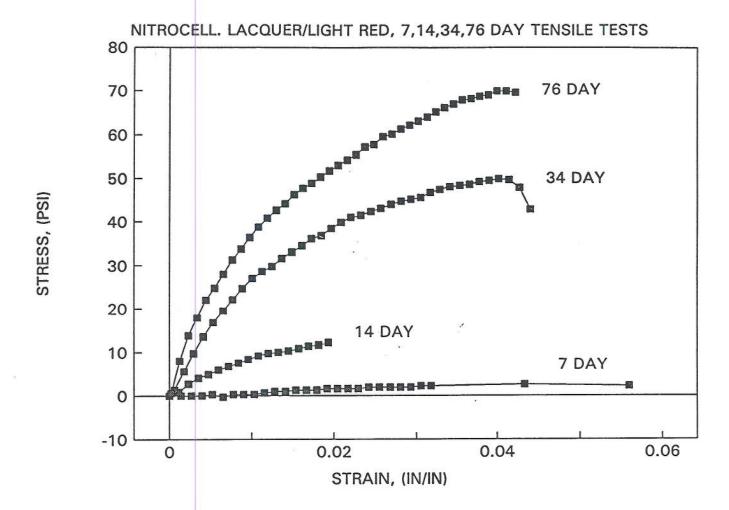


Figure 7. The mechanical tests conducted for determining the drying time for nitrocellulose lacquer containing red pigment. This material still has not dried sufficiently for complete analysis. Tests were conducted at 50% RH and 22° C.

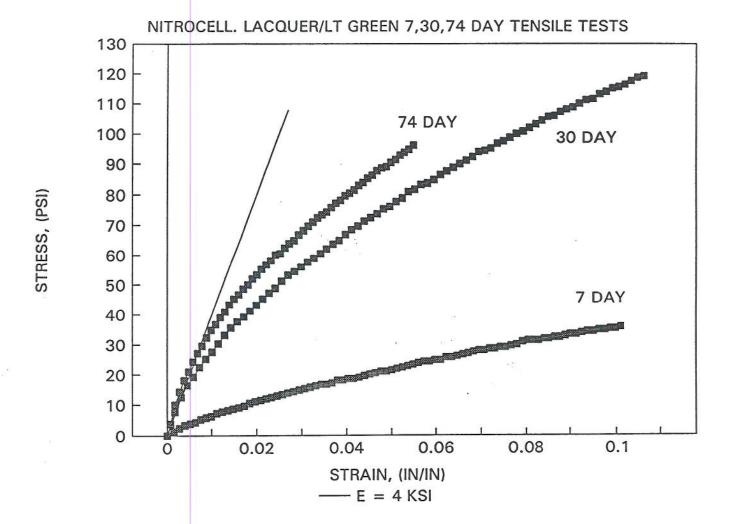


Figure 8. The mechanical tests conducted for determining the drying time for nitrocellulose lacquer containing light green pigment. This material still has not dried sufficiently for complete analysis. Tests were conducted at 50% RH and 22° C.

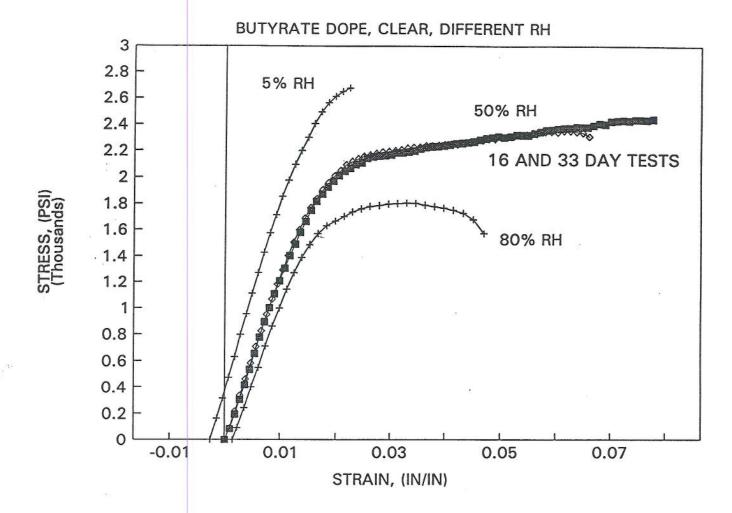


Figure 9. The mechanical tests conducted for determining the effects of RH on the mechanical properties of clear butyrate dope. Tests were conducted at 5%, 50%, and 80% RH at 22° C. The stress free strains separating the origins of the tests represent the dimensional change caused by the change in moisture content.

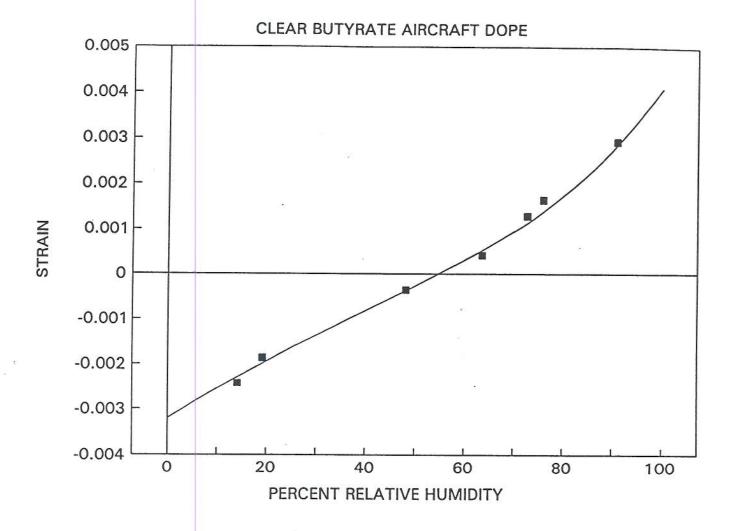


Figure 10. The swelling isotherm for clear butyrate dope. The maximum swelling over the entire RH range is only about .7%

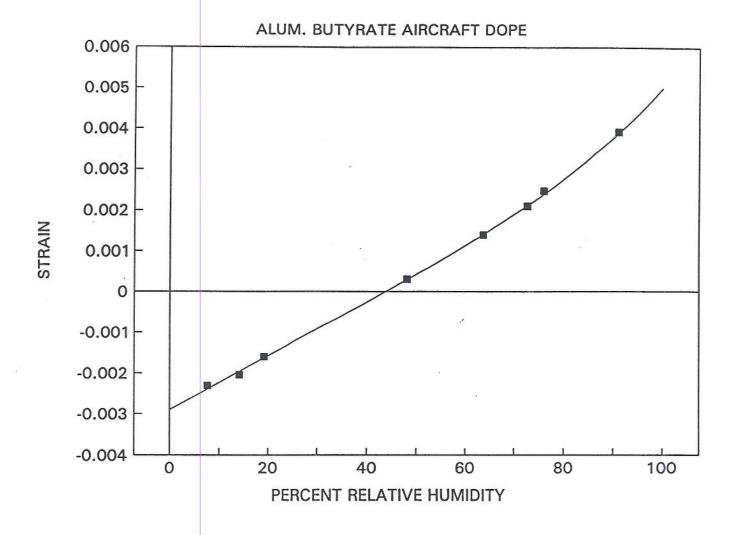


Figure 11. The swelling isotherm for butyrate dope containing aluminum paste. The maximum swelling over the entire RH range is only about .8%

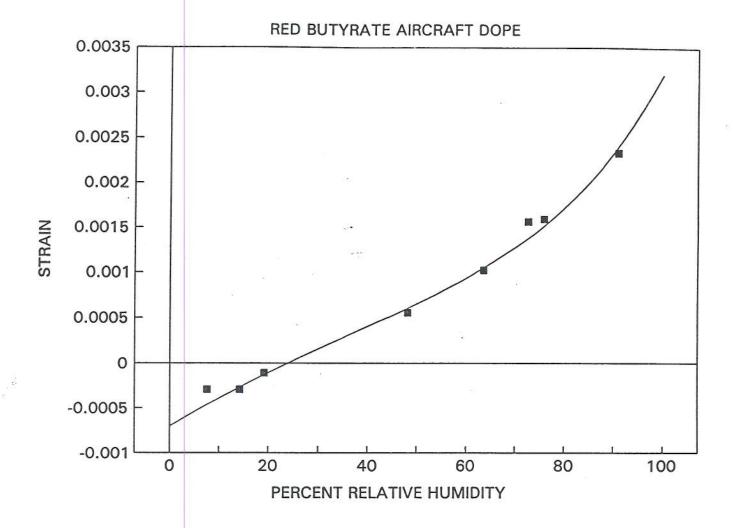


Figure 12. The swelling isotherm for butyrate dope containing red pigment. The maximum swelling over the entire RH range is only about .4%

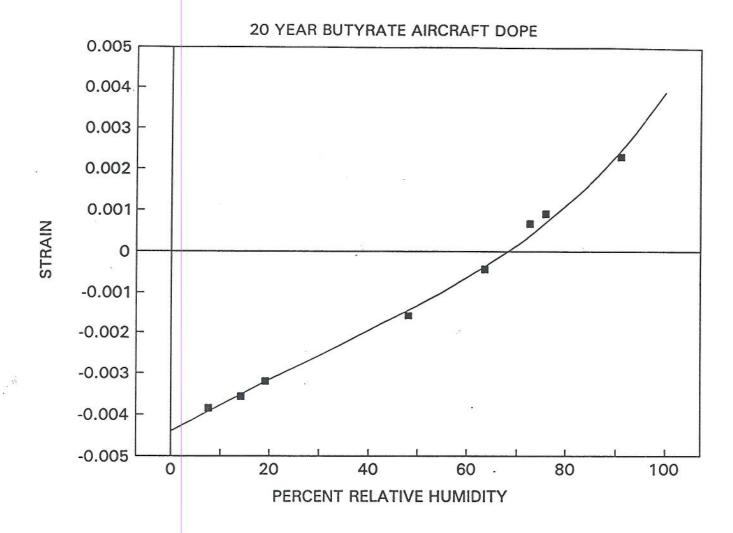


Figure 13. The swelling isotherm for 20 year old butyrate dope containing green pigment. The maximum swelling over the entire RH range is only about .8%

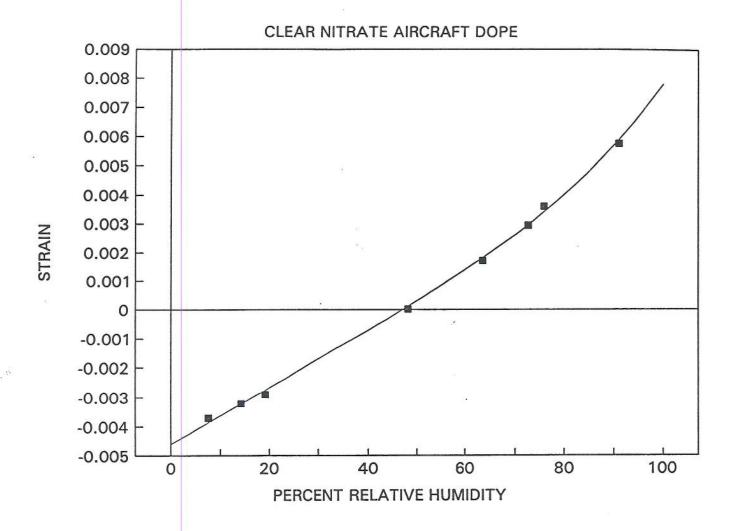


Figure 14. The swelling isotherm for clear nitrate dope. The maximum swelling over the entire RH range is about 1.3%. This is somewhat greater than any of the butyrate dopes tested.

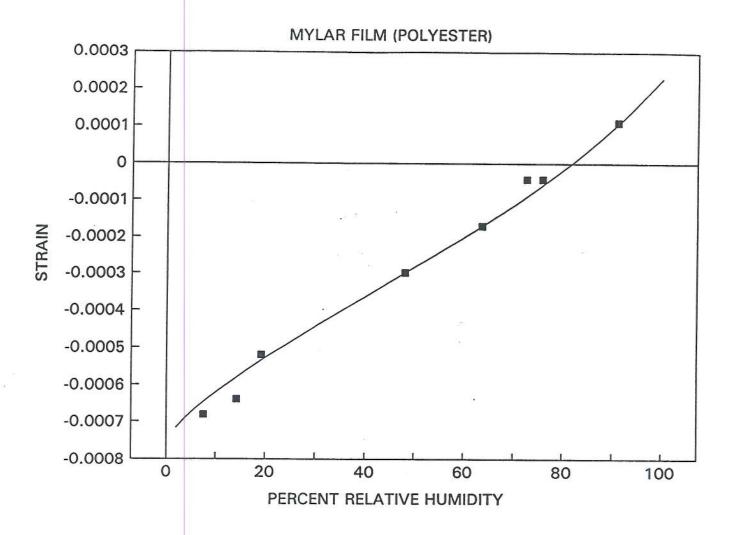


Figure 15. The swelling isotherm for mylar sheet film. The maximum swelling over the entire RH range is less than .1%. This is one of the least dimensionally responsive polymeric materials.

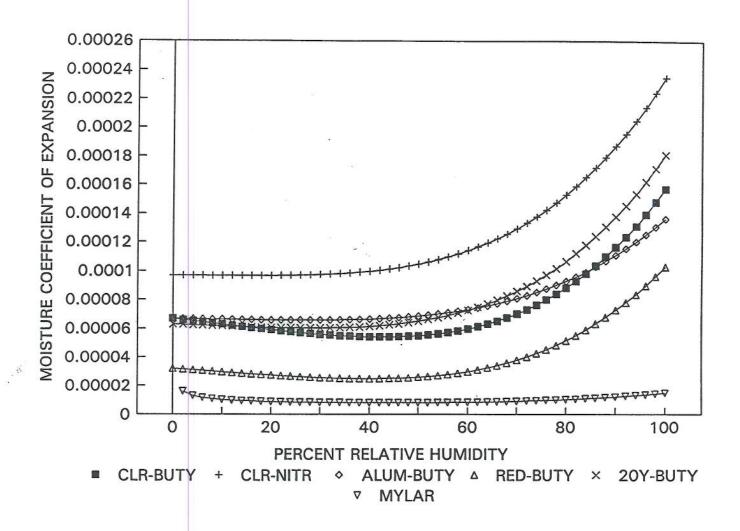


Figure 16. The moisture coefficients of expansion for clear nitrate dope, different butyrate dopes, and mylar sheet.

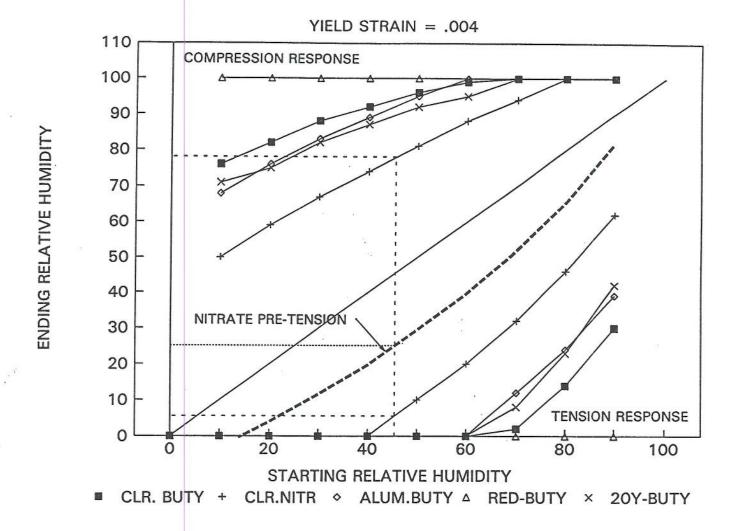


Figure 17. The RH fluctuations required to induce both tension and compression yielding in fully restrained aircraft paints. These paints include clear nitrate dope and different examples of butyrate dope. The bold dashed line illustrates the effect of a .002 prestrain in the nitrate dope.

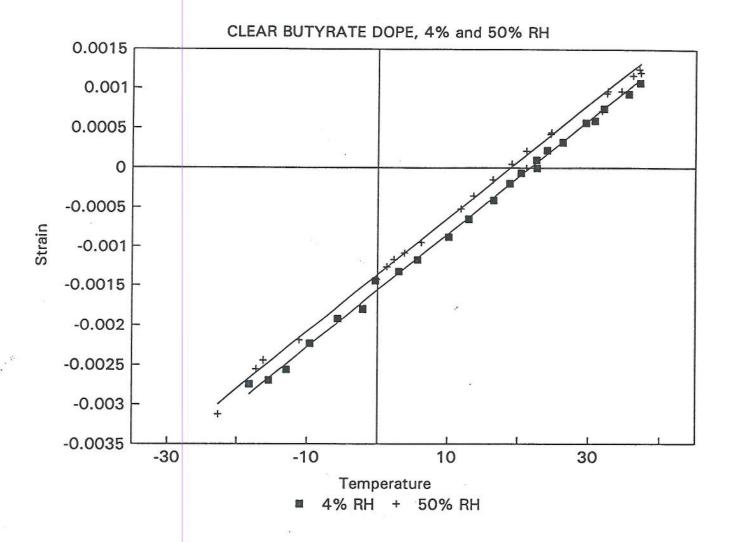


Figure 18. Free swelling strains versus temperature at two relative humidities for clear butyrate dope. The data shows that there is a linear response to dimensional change for the temperature values examined.

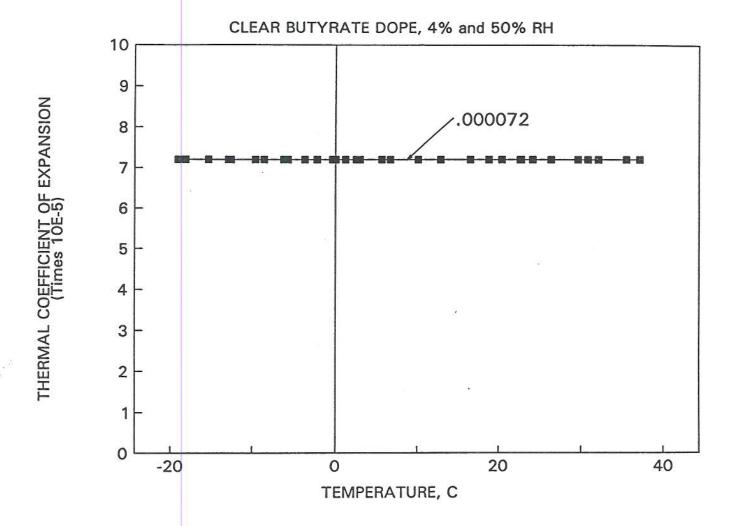


Figure 19. The thermal coefficient of expansion for clear butyrate dope.

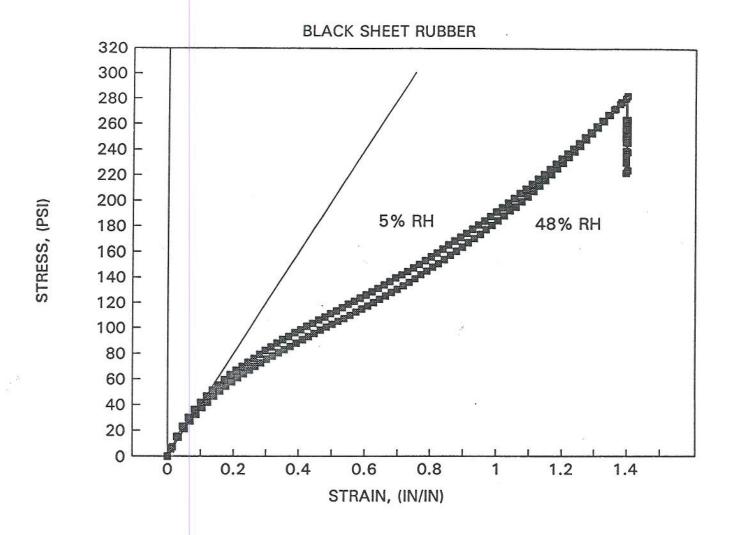


Figure 20. The stress-strain tests of samples of sheet rubber conducted at 5% and 50% RH. There is no significant difference even at an elongation of 140%

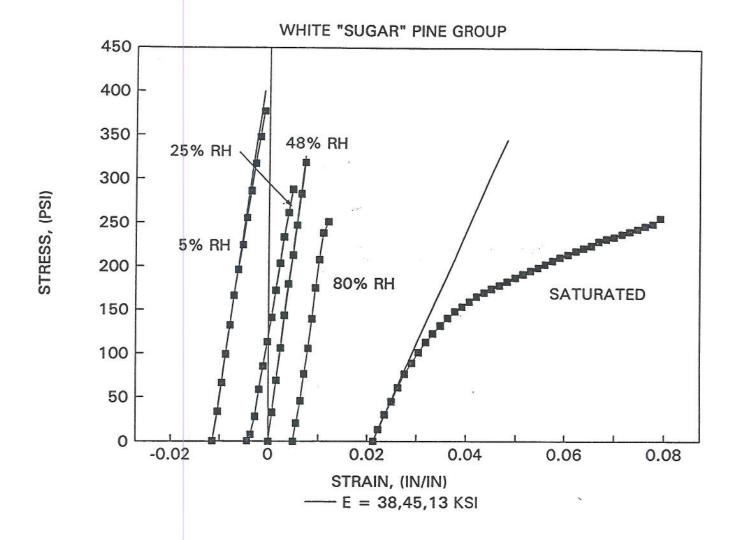


Figure 21. Stress-strain tests of sugar pine conducted at different levels of relative humidity. The stress free strains reflect the dimensional response of the wood to different moisture contents.

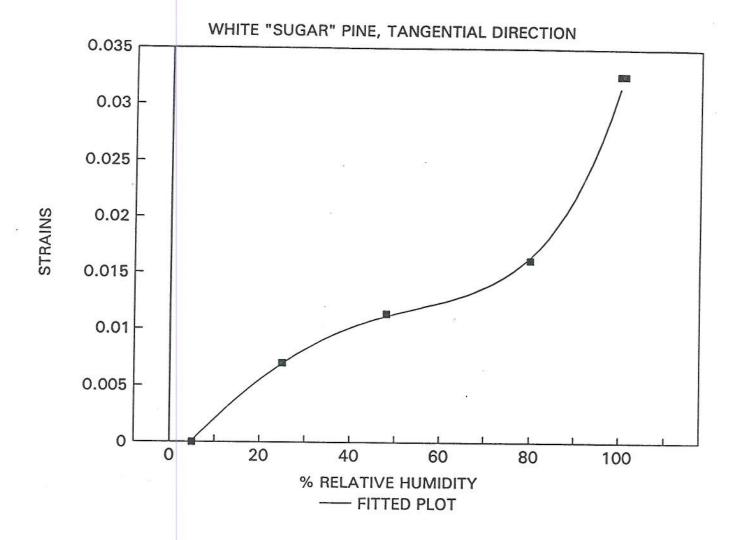


Figure 22. The moisture swelling isotherm for sugar pine. The total dimensional response of this wood to moisture is about 3.5%. This is actually a low response when compared to most woods.

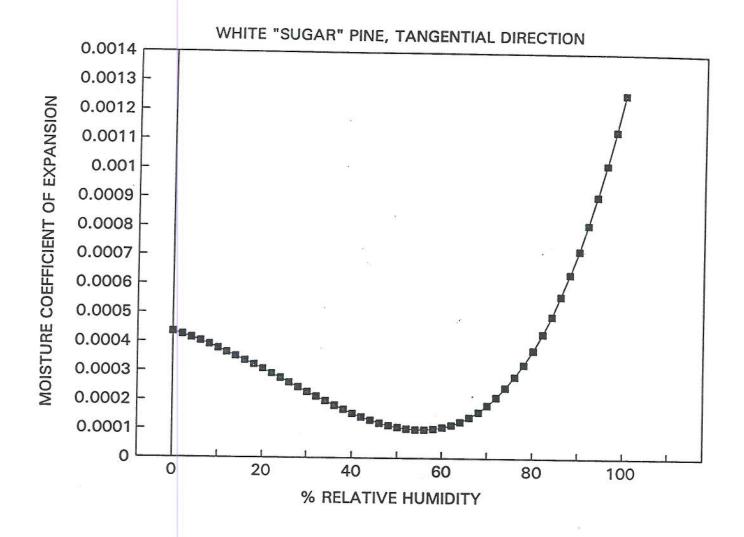


Figure 23. The moisture coefficient of expansion for sugar pine.

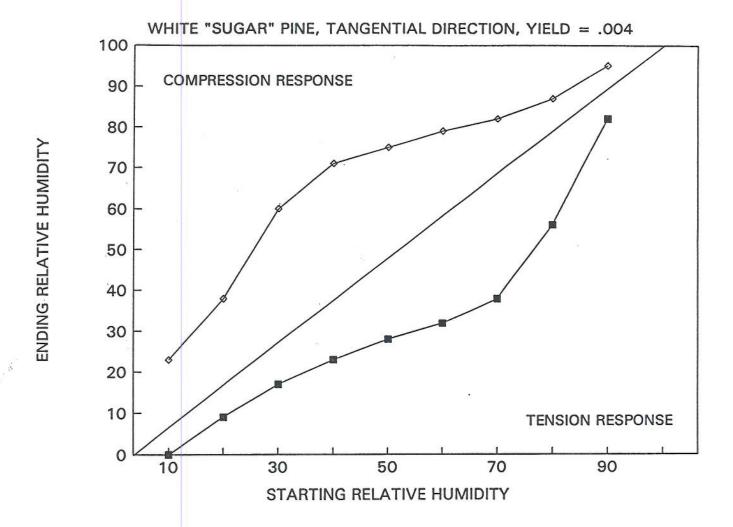


Figure 24. The RH fluctuations required to induce both tension and compression yielding in fully restrained sugar pine in the tangential direction. If 50% RH is the initial starting RH this wood can fluctuate plus 25% RH and minus 21% RH before yielding occurs.

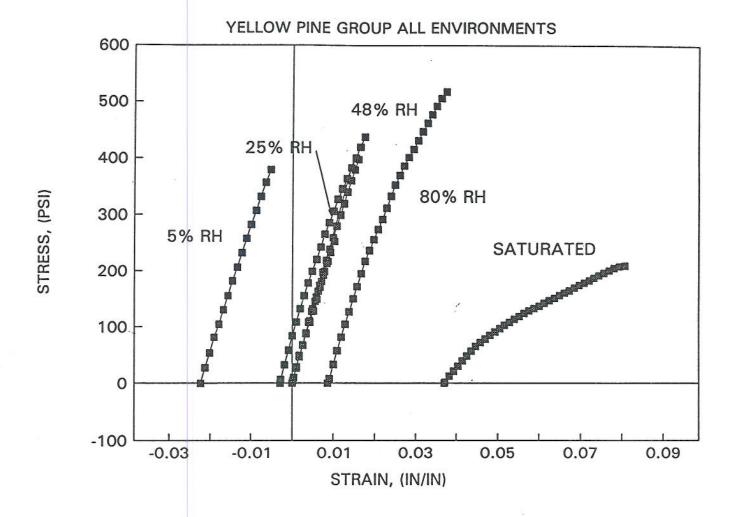


Figure 25. Stress-strain tests of yellow pine conducted at different levels of relative humidity. The stress free strains reflect the dimensional response of the wood to different moisture contents.

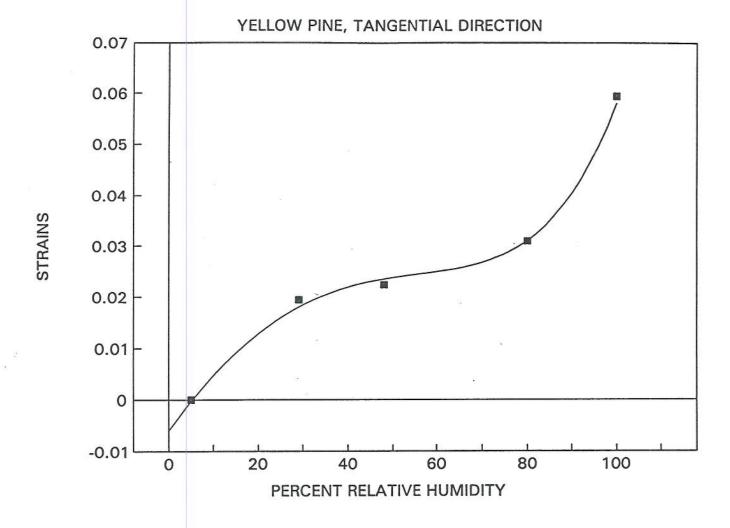


Figure 26. The moisture swelling isotherm for yellow pine. The total dimensional response of this wood to moisture is about 6.5%. This is an average response when compared to most woods.

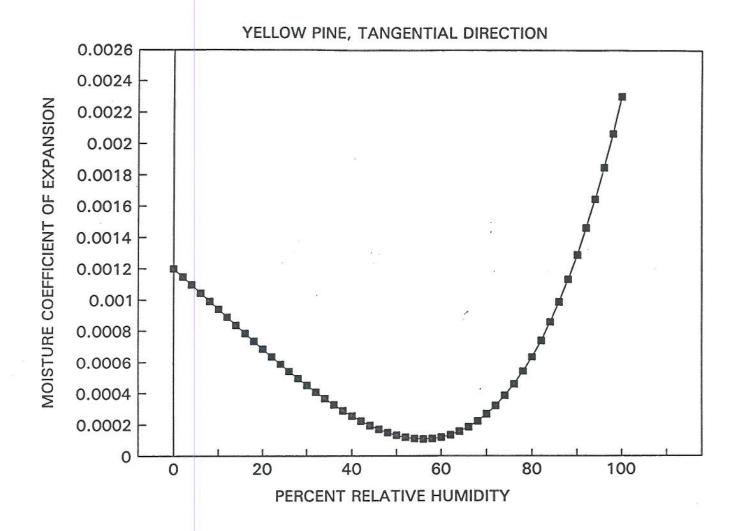


Figure 27. The moisture coefficient of expansion for yellow pine.

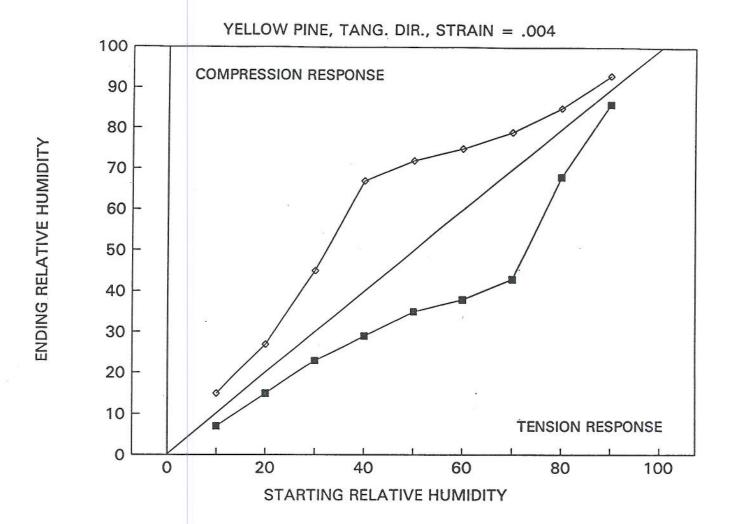


Figure 28. The RH fluctuations required to induce both tension and compression yielding in fully restrained yellow pine in the tangential direction. If 50% RH is the initial starting RH this wood can fluctuate plus 22% RH and minus 15% RH before yielding occurs.

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# Appendix A

# STRUCTURAL RESPONSE OF WOOD PANEL PAINTINGS TO CHANGES IN AMBIENT RELATIVE HUMIDITY

# Structural Response of Wood Panel Paintings to Changes in Ambient Relative Humidity

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#### Abstract

The effects of ambient relative humidity (RH) on the structural response of wood supported easel paintings are examined. Individual materials such as wood, glue, gesso, and oil paints are tested to determine their mechanical properties and their dimensional response to RH. This information is then used to examine the possibility of determining the RH fluctuations that do not harm, cause irreversible deformation, or induce actual failure in the painted design layer of a panel painting. Examining the mismatch of material moisture coefficients of expansion is shown to be useful in determining the allowable fluctuation a painting might endure without damage. In the directions parallel to the grain of the wood support, the applied sizing, gesso and paint layers are considered to be nearly fully restrained. In the cross-grained directions, where wood is the most responsive to changes in RH, the moving unrestrained wood panel often completely overrides the dimensional response of the applied layers. In this situation, stresses induced in the gesso and paint layers due to changes in RH are completely opposite those in the parallel to grain directions. Allowable RH fluctuations are determined for many materials found in typical panel paintings.

#### Introduction

Traditional painted wood panels are composite structures composed of a wide range of materials. These materials can include wood of different species, hide glues, gesso composed of glue and gypsum (calcium sulfate) or chalk (calcium carbonate), and different types of paints and resin varnishes. Paint media can include wax, egg tempera, oils, and combinations of these. These materials have different mechanical properties and seemingly respond to moisture changes differently. Panel paintings are found consisting of some or all of the materials listed. There are, however, some combinations of materials that appear more frequently than others. For example, early Italian panel paintings containing tempera as a painting medium will normally have gesso grounds as a painting surface preparation. Often there will be a layer of fabric attached to the wood prior to the application of the gesso. On the other hand, many Dutch panel paintings consist of oil paint applied directly to the prepared wood panel. For the last four centuries, oil paint, rather than tempera, applied to wood panels in some form or another seems to have been the technique of choice.

In this paper, the oil painted panel painting will be the focus of the discussion. Some concentration on gesso will be included since this material has special mechanical aspects that should be considered. It will be useful to discuss properties of the individual materials properties first, then explore some aspects of the painted panel as a composite structure. There are some basic conditions that are of concern. One is the case where the wood is held restrained in the cross-grained direction and subjected to fluctuations in relative humidity (RH). A variation of

this is where the wood is its own restraint. Moisture penetration partially into the wood induces strain into both the dry and wet regions of the wood. Another is the condition where the glue size, gesso and paints (the design layer) are restrained by the panel in the direction parallel to the grain of the wood support. A third and equally important consideration is the response of the size, gesso and paint layers in the direction perpendicular to the grain of the panel support when it is unrestrained. In this condition, potential mismatches in the swelling coefficients of the different materials are to be considered. These three conditions will be examined and the worst case conditions identified.

#### The Wood Support

Many types of wood have been used as painting supports dating back thousands of years. However, in each area of use some woods were more popular and available. According to Doerner (1), painters from Northern Germany and Holland preferred oak while in Southern Germany several other types of wood were used. These woods included pine, fir, larch, linden, ash and others. In Italy, Italian popular and cypress were used. Doerner also reports that American woods such as American cottonwood and mahogany were imported into Europe for use as supports.

Wood responds to moisture by swelling and shrinking with increases and decreases in ambient RH. But wood is anisotropic, in that moisture related dimensional changes are different in its three principal axes, longitudinal (parallel to the grain), radial, and tangential. The most severe moisture response is in the tangential direction and the least is in the longitudinal. The wood in the tangential direction can swell up to 80 times as much as in the longitudinal direction. The radial direction swells about one-half as much as the tangential direction. (2)

If restrained during changes in relative humidity, wood can develop high stresses and strains. If the change in environmental moisture is severe enough the wood can be plastically (permanently) deformed or even crack. Before cracking however, wood must be plastically deformed. This raises the question, what changes in relative humidity are required to cause plastic deformation and failure in wood when the wood is fully restrained?

#### Mechanical Testing of Woods

Recent research in the mechanical response of wood samples to changing RH examined the behavior of wood samples in the tangential (worst case) direction (3). The mechanical properties of several species of wood were measured in the crossed-grain direction. Using this testing program, the yield points and strengths of the wood samples could be established. Figures 1-3 show the stress-strain plots of different samples of cottonwood, white oak, and American mahogany conducted at different relative humidities. The samples are all loaded in the largely tangential direction and these tests were conducted allowing 30 seconds of stress relaxation at each loading point. In this way, time dependent variations in behavior are greatly reduced. The strain values between the starting points of the tests reflect the length change due solely to the change in moisture content of the wood at different values of RH. The test temperature was

approximately 22° C in all cases. The strengths of the woods are the stresses noted at failure, the end of the test. Cottonwood, white oak and American mahogany are strongest at around 50% RH. White oak has the highest strength at around 1340 pounds per square inch (psi).

Tests conducted with American mahogany (Fig. 3) were periodically interrupted, unloaded, then reloaded for the duration of the tests. These unload compliance tests show that there is no significant change in the elastic stiffness or modulus of the material, and that the wood strain hardens with increased straining as well. The amount of strain required to go beyond the elastic (reversible) region to the plastic (non-reversible) region increases. The unload-reload paths are the same but if allowed to continue to a complete unloading, there would be a permanent strain. In other words, wood can be stretched irreversibly if stretched too far but there are domains of strain that are reversible.

#### Strains and the Yield Point

If a new sample of wood is tested within a restricted strain domain the unload path will return to the original starting point. When this occurs the material is said to be elastic and reversible. It is not necessary that the unload path be the same as the loading path. In fact many polymeric materials demonstrate different loading and unloading paths. This is commonly called non-linear elasticity. This is shown in samples of cottonwood tested at different environments. Figures 4-7 show cottonwood samples loaded to strain levels of about .004 and then unloaded. The specimens return to practically their original length without permanent elongation. If a material, such as cottonwood, is stretched to a point that upon unloading the material it is permanently longer than before the test, the material can be said to yield. The point on a tensile or compression test that defines the separation between elastic (reversible) and plastic (permanent deformation) is said to be the yield point. The best way to determine the yield point is by periodic unloading of the specimen to determine if permanent deformation has occurred. Testing wood samples at different environments can be conducted as illustrated below.

After loading and unloading at 38% RH (Fig. 4), a cottonwood specimen returned to the origin after a maximum strain of .004 was induced. This represents a strain near or below the yield point. At 45% RH (Fig. 5) two specimens return to zero after being strained to .0037. At 53% RH (Fig. 6) .004 is a still reversible strain but at around 71% RH, Fig. 7 shows that a strain of .004 causes the two specimens to be permanently deformed just slightly. This plastic "set" is .0002 and thus the actual yield point of new cottonwood is .0038 at this environment. If a sample of wood is subjected to a strain greater than its original new wood yield point, then there is plastic deformation as shown in Figures 8 and 9. In addition the yield point strain is now greater than before. In Figure 8 the old (.0045) and new (.0058) yield point strains are indicated. In Figure 9 unloading the specimen at a greater strain shows a permanent set of .0014 with an increase in the yield strain from approximately .0045 to .0071. These increases in the yield points are the results of strain hardening and show that pre-straining actually increases the elastic or reversible strains domain. Nearly all woods of any age have experienced some event that has caused some strain hardening. The conclusion here is that older woods can experience larger reversible strains than newer ones. Thus results derived from testing new wood samples will,

if anything, result in calculated allowable fluctuations that are more restrictive than necessary.

#### **Environmentally Induced Strains**

One can easily recognize that if a hygroscopic material is restrained and desiccated it will experience an increase in stress. What is not so evident is that there is an increase in strain. Too often strain is associated with external deformation when in fact no external movement is necessary for strain to occur. Consider a hygroscopic specimen that is allowed to shrink freely from an initial length, Li, to a final length of, Li, when desiccated from a high relative humidity, RH<sub>h</sub>, to a low relative humidity, RH<sub>l</sub>. If, under equilibrium conditions, the specimen is now stretched back to its original length L, it will clearly undergo an increase in stress and strain. It is, however, at the lower relative humidity RH<sub>f</sub>. This new state of stress, strain, and relative humidity is no different from a specimen that is restrained at Li, RHh and desiccated to RH, with out being allow to shrink (4). Both specimens have reached the same state following two different experiments ending up with the same length and the same relative humidity. The restrained test specimen has not experienced a length change. Nevertheless, this specimen has experienced an increase in strain. Now it is necessary to determine the amount of change in RH that will cause strains that approach the yield point when a material is fully restrained. If the yield point is not exceeded, then a fully restrained specimen may be subjected to variations in strain induced by variations in RH without damage.

### The Swelling Isotherm and the Moisture Coefficient of Expansion

The amount a material swells or shrinks can be measured in percent length change, or strain, versus RH. This simply entails holding the temperature constant, measuring the length,  $L_{RH}$ , of a specimen at different RH levels, then establishing an initialized length  $L_0$ , usually the dry length. The strain,  $\epsilon$ , is calculated as:

$$\epsilon = (L_{RH} - L_0)/L_0$$
 Eq. 1

This form of displaying the dimensional response of a material to changes in moisture is useful in relating dimensional properties to mechanical properties of materials. Figure 10 shows the swelling isotherm of cottonwood in the tangential direction. This plot shows that there is significant dimensional response to moisture at the extremes of the RH scale and there is relatively little response to moisture in the region bounded by 30% and 70% RH. The implications here are that moisture changes will have the most structural effects at the extreme low and high RH levels and the least in the central RH regions. It is necessary to establish what RH changes will cause strains no greater than yield for any ambient RH environment. One way to do this is to use the swelling isotherm and simply measure the change in RH needed to establish a strain of about .004. Another way is to determine the moisture coefficient of expansion,  $\alpha$ , from a polynomial fit of the swelling data. Then,  $\alpha$  is calculated as

$$\alpha = d\epsilon/dRH$$
. Eq. 2

The swelling coefficient of expansion for cottonwood is plotted in figure 11. Most texts on the swelling of wood report the swelling coefficient as a constant, and as can be seen in figure 11, this is not the case. This figure also points out that the lowest values of the coefficient of expansion correspond to the flattest portion of the swelling isotherm, namely from 30% to 70%

RH.

Using equation 2, the strain change,  $\Delta\epsilon$ , for any RH change can be calculated as:

 $\Delta \epsilon = \int \alpha \, dRH$ 

Eq. 3

where:  $\alpha = d\epsilon/dRH$ .

when integrating from one RH point to another. The yield point for new cottonwood is about .004 at all RH levels and the breaking strains increase with increasing RH. These strain values are shown on Figure 12.

Integrating equation 3 allows one to determine the change in RH for a related change in strain. One assumes a starting RH, say 50%, and integrates to another RH level associated with the strain change in question. In the case of cottonwood in the tangential direction, at 50% RH, the yielding strain is .004 and the breaking strain is .017 (Fig 12). The associated RH changes required to induce these strains for a restrained sample of cottonwood in the tangential direction are from 50% RH to 30% for yielding in tension, 50% to 67% for yielding in compression, and 50% to 14% for complete failure in tension. This is illustrated in Figure 13. No line for complete compression failure is shown as compression failures take different forms, from the crushing of the cell walls to buckling of the panel itself. Buckling of a panel is influenced by the geometry (thickness) and restraint (boundary conditions) of the painting.

#### Allowable RH fluctuations

Figure 13 is significant in that it effectively establishes the allowable RH fluctuations cottonwood restrained in the tangential direction may sustain without damage. The tension and compression yield lines set the RH limits (ending RH) from which the ambient RH (starting or equilibrium RH) can deviate. The zone between these lines can be viewed as the allowable RH zone. This also represents the "worst case" condition for cottonwood. If the wood is tested in the radial direction the allowable RH fluctuations would be greater. This is because the yield point is still at least .004, but the moisture response of cotton wood in the radial direction is about one-half of that in the tangential. If the wood is not restrained at all this diagram has no meaning. But conditions exist that force one to assume there is restraint. Battens and locked cradles on the backs of panel paintings do restrain the supports from freely expanding and contracting. Basic construction techniques where wood components are attached with the grains mutually perpendicular cause restraint. Bulk wood experiences internal restraint when exposed to an RH change and the exterior responds more quickly than the interior. The basic message here is that even under the worst structural circumstances this material can endure significant RH fluctuations if the ambient RH is centered between 35% and 60%. Outside this range the allowable fluctuations reduce dramatically. Cottonwood forced outside this central zone will experience yielding. If the excursion is severe enough it is possible that the material cannot return to the central zone without breaking.

If the wood has been strain hardened, which is probably the case for all old woods, the RH change required to reach the yield point increases. Figure 14 shows the plots for tension and compression when the yield points have increased from .004 (solid lines) to .0055 (dashed lines).

In effect the allowable elastic or reversible RH fluctuations have been increased. It is important to point out however, that the breaking strength of the material has not changed and the associated RH change needed to cause cracking is still the same.

If a cottonwood sample is restrained at 50% RH and the humidity is increased to say 85% RH, the wood will experience plastic deformation in compression or "compression set." The wood now has been effectively shortened and upon desiccation from 85% it begins to experience tension. The wood has been in effect re-initialized to a restrained condition at 85% RH. Figure 15 shows that, upon desiccation, by the time the wood has reached about 81% RH, the sample has attained yield in tension. Of equal interest is the fact that the sample upon returning to 50% RH will most likely crack. This illustration explains why restrained wooden objects, subjected to very high humidities, or stored outside in equally humid environments, often suffer damage when brought into a fairly well controlled museum environment. The degree of control of the museum environment is thus not the issue. The substantial change from the high humidity to a moderate environment is the cause of failure.

Since the tangential direction of wood is the most dimensionally responsive, when restrained, this direction is the most vulnerable to strain development with changes in RH. If one has to then set a criterion for the allowable RH fluctuations a restrained panel may undergo, the tangential direction strain development is the one to examine.

Figures 16 and 17 show the fluctuation plots for American mahogany and white oak in the tangential directions. They are quite similar to the cottonwood plot (Fig. 13). The American mahogany has a smaller swelling coefficient of expansion than the cottonwood and the RH changes required to induce yield strains are greater than the cottonwood. The RH changes to cause complete failure in tension are greater in part because of the lower swelling coefficient and in part due to this material's increased capacity to elongate before failure.

#### The Effects of Wood Variability in the Same Species.

Wood samples of the same species can vary considerably in their mechanical properties. It is of interest to know how this variability affects the material's response to fluctuations in the environment. Samples of spruce obtained from two different sources were tested mechanically and with respect to their dimensional response to moisture. The difference in their mechanical behavior was substantial. In Figure 18, results from tensile tests are plotted as stress-strain curves conducted at 50% RH and 22° C. The aircraft spruce was four and one-half times as stiff and twice as strong as the CAL sample of spruce. This difference was more or less consistent over the whole RH range. The yield points for new samples of both woods were .004, but the breaking strains were substantially different as shown in Figure 19. Even though the aircraft spruce was stronger, it demonstrated about one third the strains necessary to cause breaking over the entire RH range. When measuring the swelling behavior, the two materials showed little difference (Fig. 20) and the moisture coefficients of expansion are quite similar (Fig. 21). Computing the RH fluctuations required to induce yield strains (Fig. 22) in either compression or tension showed insignificant differences. In addition these RH changes were greater than the

other woods discussed previously in this paper. Differences occurred in the RH change required to cause failure in tension. The CAL spruce acted quit similarly to the three previous woods, while aircraft spruce is difficult to break with any RH change. The interesting aspect of this comparison of the two samples of spruce is that mechanical properties such as stiffness and strength don't necessarily influence the RH fluctuations required to reach yielding in restrained specimens. The strain to failure, on the other hand, is influenced by the stiffness and strength of the material and affects RH fluctuations required to break restrained specimens.

#### Hide Glue

Hide glue, or in this case, rabbit skin glue is a material often used to size wood panels prior to applying any other layer and it has been used to join component parts of furniture. It is also the material used to make gesso for preparing smooth painting surfaces. This material is without question one of the most dimensionally responsive to moisture. The swelling isotherm, shown in Figure 23, was developed from two separate samples of the same material. The newly cast material will freely shrink upon being subjected to initial high RH levels. (4) The total shrinkage of hide glue can be as much as 6% when desiccating from 90% to 10% RH. The swelling coefficient of expansion for this glue is shown in Figure 24. This is a highly non-linear plot and approximating this as a constant can lead to considerable error.

Hide glue has no covalent crosslinks and as such is prone to stress relaxation over long periods of time. These periods can be from six to twelve months depending on the RH level (5). In more rapid time frames, days to weeks, one can measure a yield point of about .004 to .005. The breaking strains of hide glue can reach 3% to 4% (strains of .03 to .04) in extremely slow tests. For changes in RH that occur within these shorter time spans, it is possible to determine the allowable RH fluctuation required to induce yield strains in restrained hide glue. Figure 25 plots the necessary change in RH required to develop yield strains for restrained hide glue in the short time frame. In effect, at 50% RH, the allowable short term RH fluctuation is ± 11%. Over time the glue stress relaxes. If subjected to excessive RH, over 85%, the glue reactivates and extremely high stresses can develop as this reactivated glue desiccates with decreases in RH. Extreme short term changes in RH can cause significant damage to paintings on canvas due to these high stresses. As a sizing on a wood panel, the mass of wood present provides substantial resistance to the stresses in a relatively thin layer of glue. Since wood in the parallel to grain direction has a very small dimensional response to moisture, it can, for all intents and purposes, be assumed to be a full restraint for all materials attached to it. In that direction, the glues, fabrics, gessos, and paint layers are restrained from movement due to moisture changes.

# Hide Glue Response When attached to an Unrestrained Wood Support

In the perpendicular to the grain direction, unrestrained wood will change dimensionally with RH changes. If the swelling coefficients of expansion of all of the materials attached to the wood panel are the same as the wood, then RH changes induce no stresses in the attached layers. By comparing the expansion coefficients of the different materials, it is possible to explore the results of RH changes in the cross-grained directions of an unrestrained panel. Figure 26

compares the expansion coefficients of cottonwood and hide glue. At approximately 70% the plots intersect which means that at this point both the wood and the glue are swelling or shrinking at the same rate. In the RH range from 35% to 60% there is some difference where the glue attempts to swell or shrink at a higher rate than the wood substrate. In this region, the glue develops stresses but only a fraction of those caused by full restraint since the wood tends to shrink or swell at approximately the same rate. The wood's movement is in effect providing greater RH tolerances for the hide glue. This is an example of partial rather than full restraint. The strains in the glue can be calculated using Equation 4 below. This equation can be used for any material applied to any substrate in any direction. For example, assume that the coefficient of expansion for the substrate is zero. In that case equation 4 simplifies to Equation 3.

$$\Delta \epsilon_{\rm G} = [(1 - \int \alpha_{\rm S} dRH) - (1 - \int \alpha_{\rm G} dRH)]/(1 - \int \alpha_{\rm S} dRH)$$
 Eq. 4

Where:  $\alpha_s$  is the swelling coefficient of the substrate which is quite thick relative to any attached layers. In the examples to follow cottonwood will be the substrate since it is one of the most dimensionally responsive woods.

and,  $\alpha_G$  is the swelling coefficient of the hide glue.

This calculated increase in RH tolerance for the hide glue coating can be illustrated in Figure 27. In this figure, the hide glue is applied to an unrestrained cottonwood support and the glue strains are plotted versus RH in both the tangential and longitudinal directions. The longitudinal direction, which for all intents and purposes is full restraint, is plotted by integrating equation 4 from 50% RH going in both increasing and decreasing directions. The coefficient of expansion for the wood in that direction is assumed to be zero. The strains are high in tension (positive values) with desiccation and high in compression (negative values) with increases in humidity and this is what would be expected when the glue is fully restrained. In the tangential direction the same integration was performed as before but the with wood coefficient shown in Fig. 26. The wood substrate is responding to the moisture changes and significantly affecting the strains in the glue layer. With desiccation, the glue strains are reduced to less than one-half those in the longitudinal direction and are still in tension. This is because the glue coefficient is greater than the wood coefficient from 50% to 0% RH. Increasing the humidity from the 50% RH starting point produces different kinds of results. At about 68% RH the wood coefficient becomes greater than the glue and the result is that the wood actually overrides the swelling of the glue. The wood ultimately starts pulling the glue layer in tension. From an allowable RH fluctuation point of view, the restrained (longitudinal) direction is still the worst case but it is of interest to see that severe desiccation could cause cracking in the glue in both wood directions. With severe humidification, the glue experiences tension in the tangential direction of the panel, and compression in the longitudinal direction. Theses kind of diagrams will be used in examining the response of gesso and paint layers when also attached to the panel.

#### **Fabric**

If a panel painting has a fabric applied to the wood surface, three directions should be

considered. I'we are in the plane of the panel and the third is perpendicular to the panel. The lattic would typically be a linea woven from yams made of flax fibers. As a results then has mechanical properties that respond to moisture in a manner opposite from all other respectations. An effect, it becomes suffer and smoneer with increasing moisture which suggested from the effect of my properties become more flexible and weaker. Figures 28 and 29 illustrate the effect of moisture on the mechanical properties of the very and fill (welft) descripts of samples of samples of moisture on the mechanical properties out to failure, but just far knowly to illustrate the local flow of moisture, have fibers are average that largely as a result, of very politic of moisture, have fiber breakage unless the fibers are average that itself degraded. This political intensity medium weight fullstar #3800) what a 32 yams per notifive weaver, it is firstly expect of a machine woven intensity. Bytan though flows appears to be a consideration difference to maxife proparties between the waye and fill directions, the material's response to the environment under restmined conditions is quite similar. Figure 30 shows the stress versus EFF plots for both directions of the restmined datases, from 10% to 65% RF the exponse is quite constant with only a slight decrease in stress with increasing RH. Expend 65% RF, the starting stress levels indicated by the "S" on the diagratus and the fact that the correct by the starting stress levels indicated by the "S" on the diagratus and the fact that the corrections emisses for each to this high hamility are some to occur in lexities made by pre-industrial evolution manufacturing processes (C).

As a component layer of a panel painting, labric will have little supround effect in the plane of the panel in the RH range from 10% to 05%. At higher RH, the fabrid could be discussive to that there will be a tendency to shrink when all of the other layers of the panel painting want to other and expand.

In the direction perpendicular to the plane of the panel, severe fiber swelling at very high RH (above 80 %) can disrupt the layers above which include the gesso, panu and variety layers.

## 0820

Gesso is a mixing of a filide glue and gypsum used to prepare a smouth working surface on the panet pairting. Sometimes ground chalk or other inert materials such as zero whate and clay were substituted for the gypsum. The ratio of inert solids to hide glue has a demande unitaritie on the processor and dimensional properties of the gesso. This ratio can be expressed in the pigment volume concentration (PVC). The higher the concentration (of focut the smaller the relative amount of glue. As the concentration of the filler incorases the resso tents to become relative amount of glue. As the concentration of the filler incorases the gesso tents to become weaker, sinfer and lest dimensionally responsive to ambient motiture. It gives the timensional responsitionally responsive no ambient motiture. The times the same RH rate which is about use concentration has a maximum change of about 1.5% (strain = 015) over the same RH rate which is about use the tagher concentration changes only about .6% over the same RH rate which is about use that that of pure hide gresso's strains to yield and tailure decrease dramatic by A good stream materials (N). The gresso's strains to yield and tailure decrease dramatic by A good stream explaining the respons for this can be found in a peren by Michaelski (N). Hence 'I2 shows the

difference in the moisture coefficients of expansion for the two gessos. Their lowest values are approximately at 55% RH and this is where the gesso is the least dimensionally responsive to moisture change.

As with all the materials examined, RH affects the mechanical properties of gesso. Tensile testing of one of the gessos, PVC = 58.3, shows a dramatic loss of strength with increasing RH (Figure 33). The yield strains are about .0025 and the breaking strains again vary with RH, but are generally lower than the other materials. The low RH strains for the gesso tested are actually higher than the mid-range RH tests. The interesting aspect of gesso is that even with the low yield and breaking strains, the amount of RH change that can occur before reaching the yield points is higher than most of the other materials. This is illustrated in Figure 34, which shows the RH changes required to induce yield and cracking in a fully restrained gesso layer. For example, at an ambient RH of 50%, this restrained (as would occur in the longitudinal direction of a wood panel support) gesso can desiccate to 26% RH before attaining yield in tension. The RH can go as high as 76% before yield is reached in compression. This is a direct result of the low swelling coefficient of expansion.

It is worth comparing the swelling coefficients of gesso and cottonwood perpendicular to the grain, such as the tangential direction. In figure 35, the swelling coefficients of the cottonwood and the gesso are not only the lowest but also are practically the same in the 40% to 60% RH range. This means that an unrestrained cottonwood panel and the gesso are swelling and shrinking the least possible amount and at almost exactly the same rate in this RH region. There is effectively little structural interaction in this zone. Deviation from this zone has quite dramatic effects. Equation 4 was again used to explore the composite effect when the gesso is bonded to a cottonwood panel. The integration was again started at 50% RH. The results of this analysis are illustrated in Figure 36, where gesso strains versus RH are plotted for the tangential and longitudinal directions of the wood support. In the longitudinal direction, full restraint is again assumed and the RH fluctuations needed to induce yielding are quite large, from 50% to 26% RH in tension with desiccation. With the addition of moisture the compression strains attain yielding when going from 50% to 76% RH. In the tangential direction, as the extremes of the RH range are approached, the swelling coefficient mismatch increases dramatically. As a result, desiccation induces severe compressive strains (which can cause cleavage and buckling) in the gesso layer and increases in humidity from 50% can actually cause the gesso layer to crack. The allowable RH fluctuation is reduced. In the tangential direction, the allowable RH fluctuation is from 50% to 66% and from 50% to 28%. The tangential direction is the one direction that represents the worst case but there is still a significant allowable fluctuation.

#### The Paint Layers

The mechanical testing of 15 year-old oil and alkyd paints under true equilibrium conditions shows the yield points for nearly all of the paints tested remain about .004. At 50% RH and 22° C, the breaking strains can vary from one paint to another. For example, flake white ground in safflower oil attains a breaking strain of .02, titanium dioxide in safflower oil breaks at .01 and cadmium yellow in safflower oil break at strains of .014 to .028. Increasing the RH decreases

the strength but increases the breaking strains. Lowering the RH increases the strength but lowers the strain to failure. A cadmium yellow alkyd paint also yields at .004, but has a breaking strain as high as .04. Figures 37, 38, and 39 show the tensile test results of three oil paints tested at different relative humidities. These paints were tested under true equilibrium conditions in that several weeks of stress relaxation occurred prior to the subsequent increment of loading. In these Figures, it can be seen that RH plays a considerable role in modifying the mechanical properties. Figure 37 shows that flake white is a fairly flexible paint and is not seriously affected by the change in RH from 50% to 5%. In Figure 38, the test results at 80% RH are given for titanium dioxide ground in safflower oil. This paint has practically no stiffness or strength at this environment. Figure 39 shows that titanium dioxide has been significantly altered by the change from 48% to 5% RH.

In general, the dimensional response of oil paints to moisture is considerably less than wood or hide glues. Figures 40 shows the dimensional response of the flake white oil paint to RH. The total change in length from 20% to 90% is only about one-half percent. Figure 41 gives the swelling coefficient of expansion for the same paint. This is one of the least dimensionally responsive materials considered in this discussion.

#### Effects of Solvents on Paint

Leaching out the soluble components of oil paints has a dramatic effect on the mechanical properties. Two 15 year-old paints, cadmium yellow ground in safflower oil and a cadmium yellow alkyd artist's paint were soaked in toluene for one week. Figures 42 and 43 show the before and after toluene treatment equilibrium tensile test results of the oil and alkyd paints respectively. Each paint experiences a five fold increase in stiffness and at least a three to four fold increase in strength after being exposed to the toluene and allowed to dry for eight weeks. Certainly the soluble components leached out by the toluene were acting as "plasticizers" to the paints. One of the possible "aging" processes of oil paints is the slow evaporation of free fatty acids as well as other low molecular weight components of oil paints (9,10). It is certainly conceivable that the increase in stiffness and strength of aged paints can be a result of the loss of volatile components. It is of considerable interest that the yield point of the toluene treated paints are unaltered from the untreated paints. In addition, there is no difference in the swelling characteristics of the treated and untreated paints. Figures 44 and 45 compare the dimensional response of the treated and untreated oil and alkyd paints respectively. All of the testing of these paints started at approximately 50% RH. Upon the first excursion into high RH, the untreated oil paint permanently swelled (Fig. 44) about 1% and maintained this permanent set throughout further cycles of humidity variation. The treated oil continued to return to the starting length at 50% for several cycles. On the other hand both the treated and untreated alkyds experienced a permanent contraction of about .25% upon the first exposure to high RH (Figure 45). The swelling coefficients of expansion for the treated and untreated materials are the same in each case. Figures 46 and 47 show these swelling coefficients.

Using the strain to yield values and integrating the expansion coefficients for several paints tested, it is possible to establish the RH fluctuations necessary to obtain yield for different

restrained paints. Figure 48 shows the RH changes required to reach yielding for flake white oil, cadmium yellow oil (toluene treated and untreated), titanium dioxide oil and cadmium yellow alkyd (treated and untreated) paints. It must be noted that since the toluene treatment did not alter either the yield points or the expansion coefficients of the paints tested, there is no difference in the RH change required to cause yielding. The difference, if there is any, will be reflected in any changes in strain to break caused by the solvent.

The swelling coefficients of expansion for oil and alkyd paints are small, around the range of the gesso examined in this paper. For comparison purposes, the coefficients of cottonwood, hide glue, gesso, and flake white oil paint are plotted in Figure 49. The paint and gesso are almost identical with the exception of the range from 70% to 100% RH. In this region the gesso rises a bit while the paint stays relatively flat. As with the gesso, the paint when applied to an unrestrained wood panel will experience a serious swelling mismatch outside of the mid-range RH. This mismatch in the coefficients can be shown by calculating the strains using equation 4 for the cottonwood and flake white oil paint. Figure 50 shows the flake white strains initialized at 50% RH. In the longitudinal direction the allowable fluctuations for the paint before reaching yielding are quite large. With desiccation from 50% RH the change can be down to about 10%. With humidification from 50%, the rise in RH can be up to about 95% RH. In the tangential direction, desiccation to 26% RH will cause compression yielding, and beyond that buckling and cleavage can occur. Increasing the RH to 70 % will cause yielding in tension with cracking possible at extremely high RH levels.

#### Conclusions

Yield points in organic materials separate reversible deformation from permanent deformation. The reversible strain domain allows materials found in panel paintings to be subjected to some level of both externally and internally applied forces without damage. Internal stresses and strains result from restrained hygroscopic materials being subjected to changes in RH. The externally applied forces result from mismatches in the moisture swelling coefficients of bonded materials. Materials such as wood supports will displace applied gesso and paint layers since woods have a significantly higher moisture swelling coefficient than the design layer materials.

It can be shown that changes in the moisture in the environment can cause strains in the materials used in constructing a cultural object such as a panel painting. Quantifying the moisture response of the materials permits one to determine the allowable RH fluctuation the object can safely endure. In the example case used above, a panel painting constructed with cottonwood, hide glue, gesso and oil paint, several conditions were examined to assess the potential for RH related behavior. For RH fluctuations that are moderately fast, the hide glue size was the limiting factor based on a yield strain criteria of .004. In this case the panel can experience a RH environment of  $50\% \pm 11\%$ . In the long run this actually has little meaning since the glue stress relaxes. The long term (annual) worst case fluctuation condition is really determined by examining each of the cases discussed. Assuming that the RH is centered at 50% one can determine the maximum possible allowable RH deviation for the example painting as a total object. One example is where the wood support is fully restrained from movement in the cross

grain direction. In this situation the allowable environment is 50% RH, plus 17% and minus 18%. For gesso in the longitudinal direction, the allowable fluctuation is 50% plus 28%, minus 27%. Gesso in the tangential direction for an unrestrained wood panel can take considerably less, 50% plus 16%, minus 22%. The worst case for the paint layer is similar to the gesso in that the unrestrained tangential movement is the limiting factor. Here, the allowable fluctuation is 50% plus 20%, and minus 24%. As a structure, then, the panel can endure 50% plus 16%, from the restrained wood case, and minus 22% from the gesso case. This is still a considerable fluctuation in the environment.

Equally important is that the research shows the type and occasion when damage is most likely to occur. For example, cracking is most likely in the gesso and paint layers when the panel is expanding due to a severe increase in RH. These cracks will run parallel to the grain of the panel support. Cracking might occur in the gesso and paint layers under extreme desiccation. These cracks will run perpendicular to the grain of the panel support. Also during severe desiccation, the gesso and paint layers could suffer compression cleavage and ridging. The ridges under these circumstances will run parallel to the panel grain.

Finally, the research shows that in the extremes of the RH region, high or low humidity provide very little variational latitude without yielding or damage. It also shows that if the panel painting is subjected to one of these RH extremes after equilibrating to the middle RH region, it cannot be returned to the moderate regions without damage.

From a structural point of view, picking the middle RH region (45% to 55%) as the environmental baseline makes the most sense since this is the region in which nearly all materials are the least dimensionally responsive (i.e., their swelling coefficients are the lowest) to environmental moisture fluctuations.

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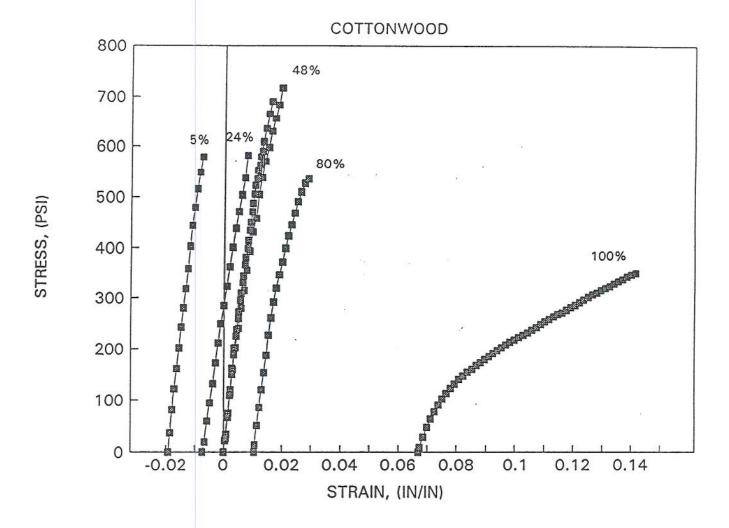


Figure 1. The stress-strain curves for cottonwood conducted at different relative humidities. The spacing between the plots is the stress-free swelling strains due to the change in ambient RH.

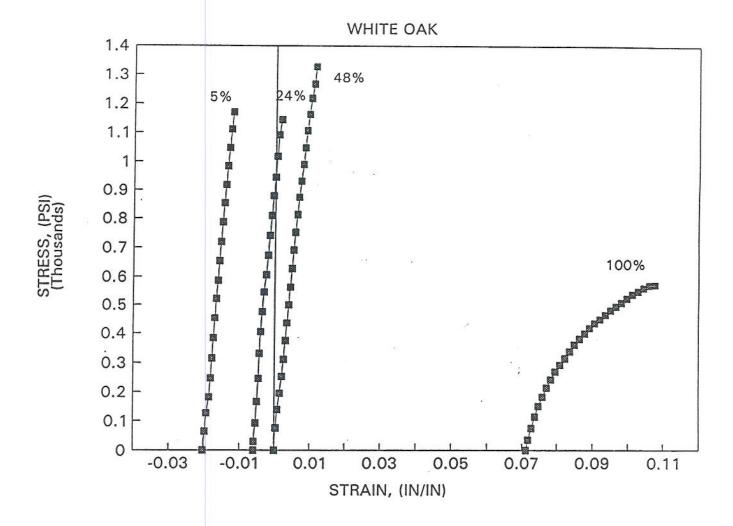


Figure 2. The stress-strain curves for white oak conducted at different relative humidities. The spacing between the plots is the stress-free swelling strains due to the change in ambient RH.

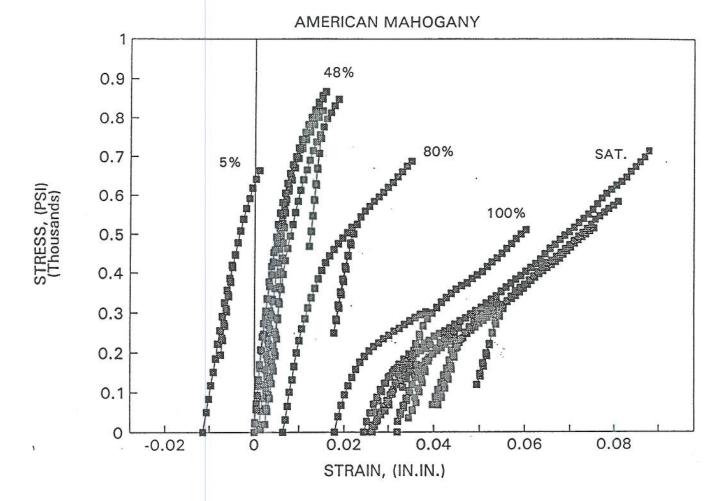


Figure 3. The stress-strain curves for American mahogany conducted at different relative humidities. The spacing between the plots is the stress-free swelling strains due to the change in ambient RH. The periodic unload slopes show that the modulus of the wood is unchanged from the initial slopes of the tests.

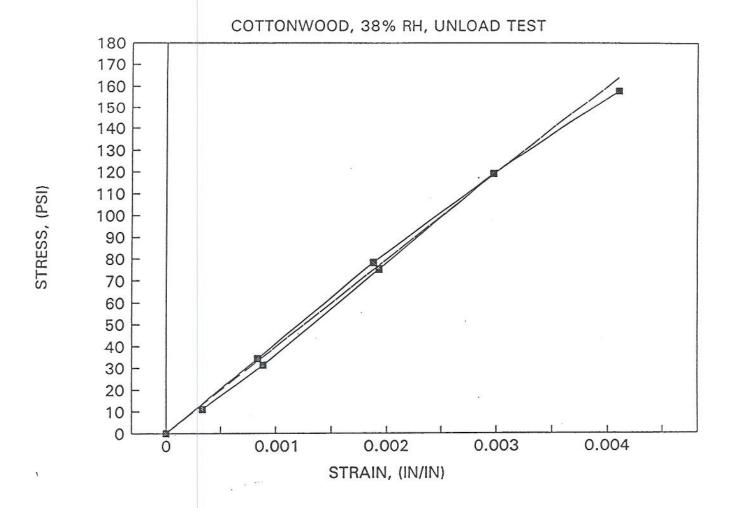


Figure 4. The stress-strain plot of cottonwood loaded only in the elastic strain domain at 38% RH. The specimen returns to the starting point after unloading.

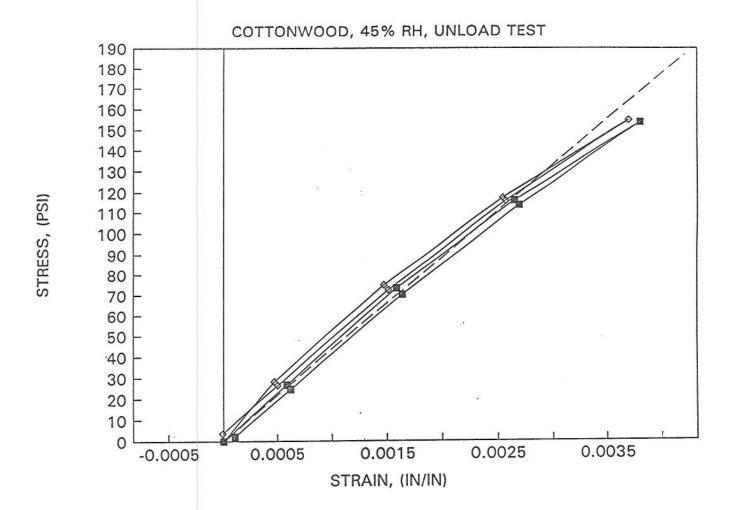


Figure 5. The stress-strain plots of cottonwood loaded only in the elastic strain domain at around 45% RH. The specimens return to the starting point after unloading.

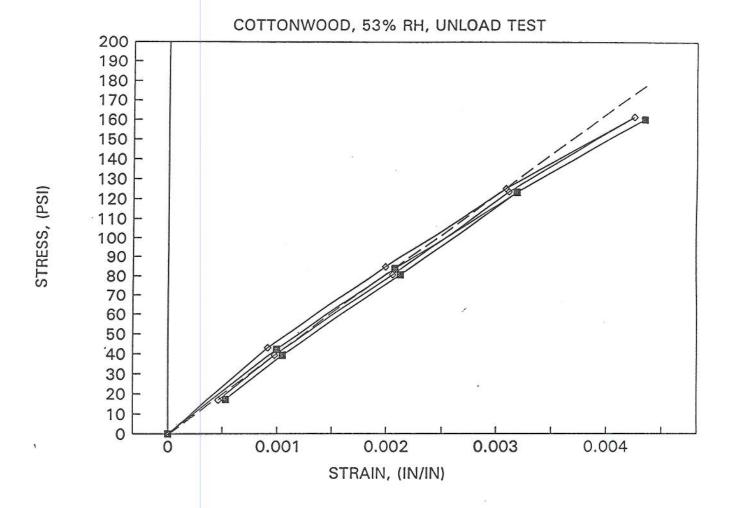


Figure 6. The stress-strain plots of cottonwood loaded only in the elastic strain domain at around 53% RH. The specimens return to the starting point after unloading.

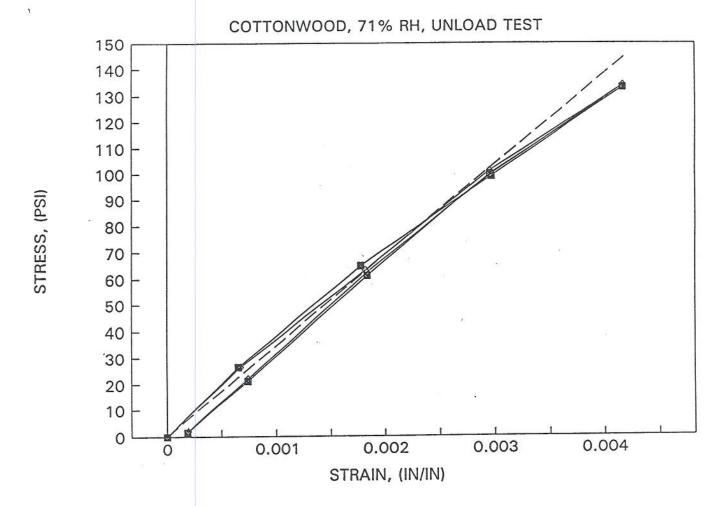


Figure 7. The stress-strain plots of cottonwood loaded slightly beyond the elastic strain domain at around 71% RH. The specimens do not return to the starting point after unloading but exhibit slight plastic deformation.

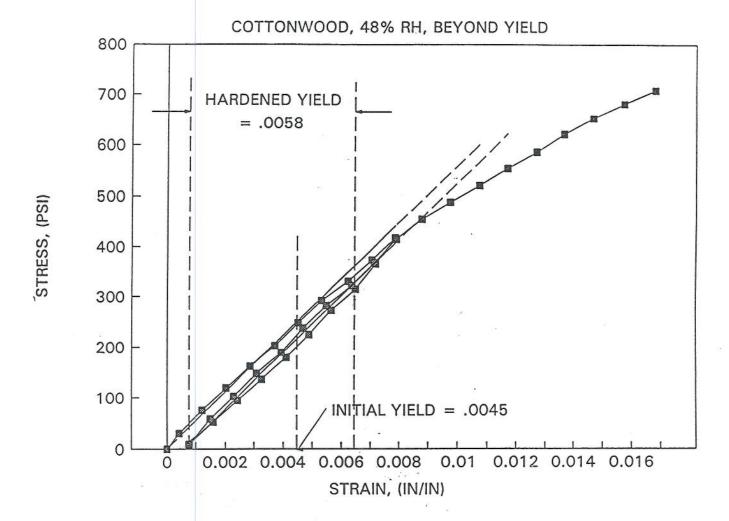


Figure 8. The stress-strain plot of cottonwood loaded beyond the yield point of .0045 at around 48% RH. The specimen does not return to the starting point after unloading but exhibits a plastic deformation strain of approximately .0007. The unloading and reloading of the specimen shows strain hardening and an increased yield point of .0058.

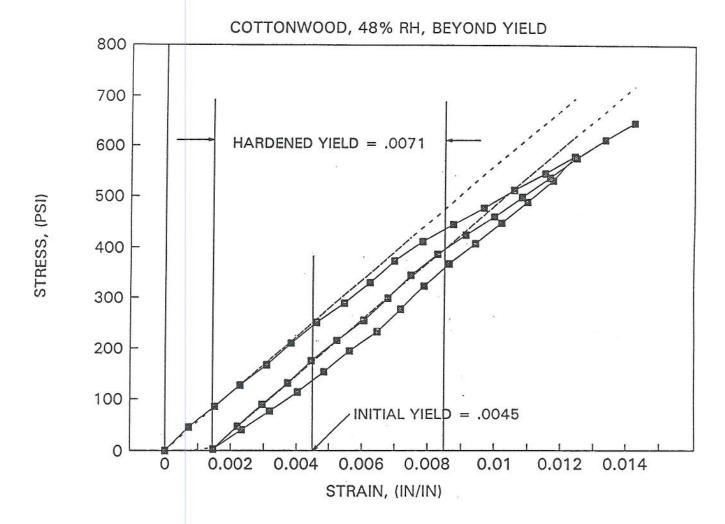


Figure 9. The stress-strain plot of cottonwood loaded beyond the yield point of .0045 at around 48% RH. The specimen does not return to the starting point after unloading but exhibits a plastic deformation strain of approximately .0014. The unloading and reloading of the specimen shows strain hardening and an increased yield point of .0071.

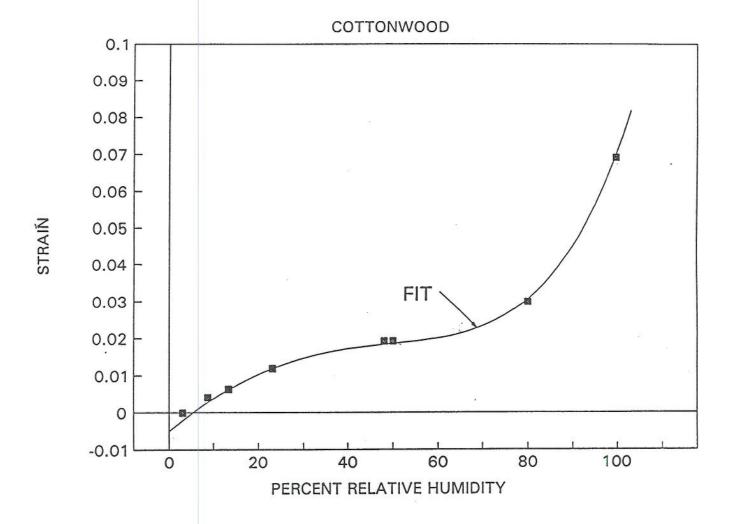


Figure 10. The swelling isotherm for cotton wood. The continuous line labeled "fit" is a polynomial fit used to derive the moisture coefficient of expansion. Cottonwood has one of the highest swelling capacities of all the woods tested.

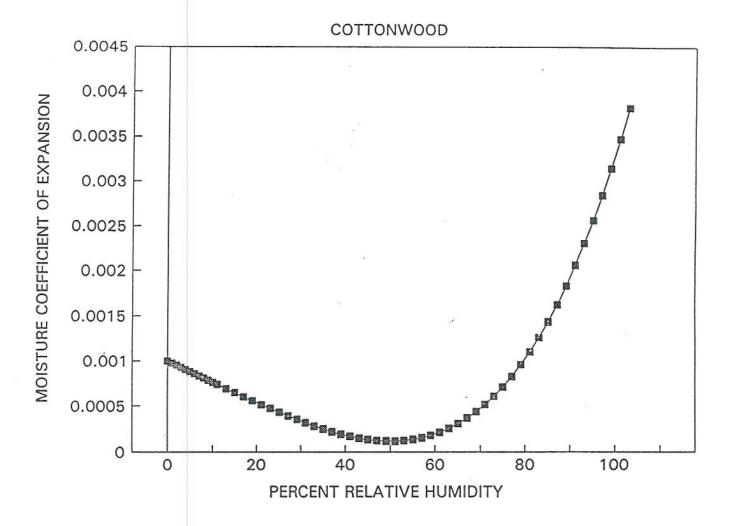


Figure 11. The moisture coefficient of expansion for cottonwood. This plot is the first derivative of the polynomial fit taken from figure 10. The lowest swelling response rate is in the central region of the total RH range between 40% and 60% RH.

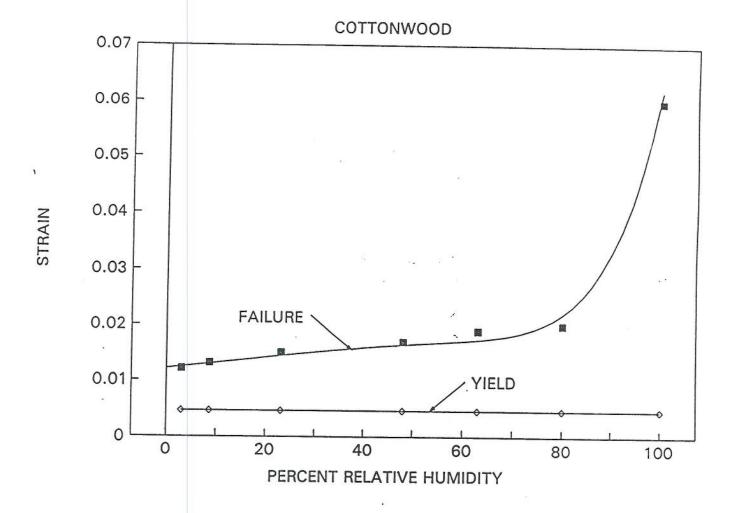


Figure 12. The measured yield and breaking strains for cottonwood at different RH levels. This data is used to determine the allowable RH fluctuations as well as the RH fluctuations needed to reach yield and breaking in cottonwood.

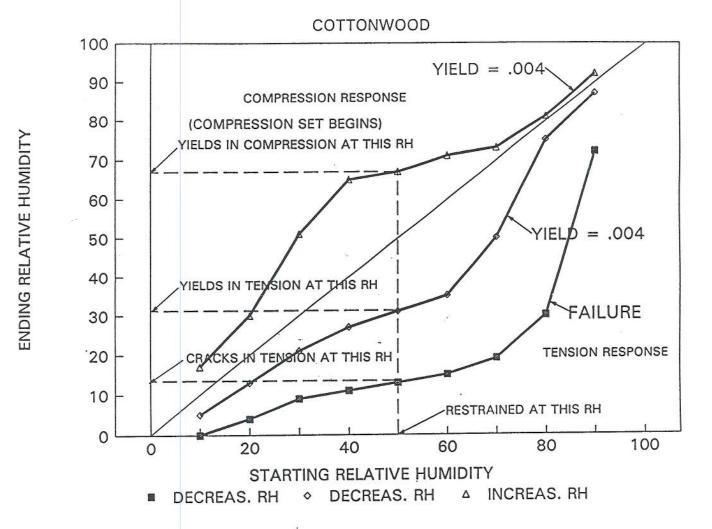


Figure 13. Yield and failure lines for fully restrained cottonwood in the tangential direction. This chart allows one to determine the RH changes needed to reach yielding and breaking in this wood. The area between the yield lines represent a zone of allowable RH fluctuations for any given ambient RH.

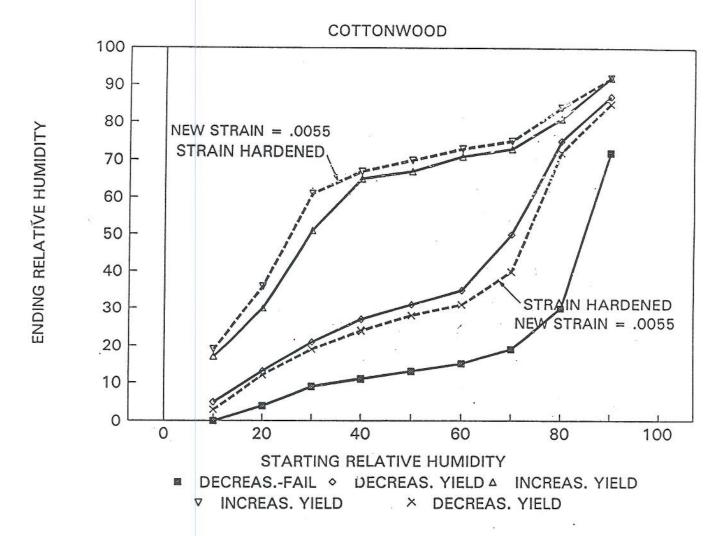


Figure 14. The effects of strain hardening on the allowable RH fluctuations for fully restrained cottonwood in the tangential direction. The dashed lines illustrate the increase in the allowable RH fluctuation from strain hardening from a yield point of .004 to .0055.

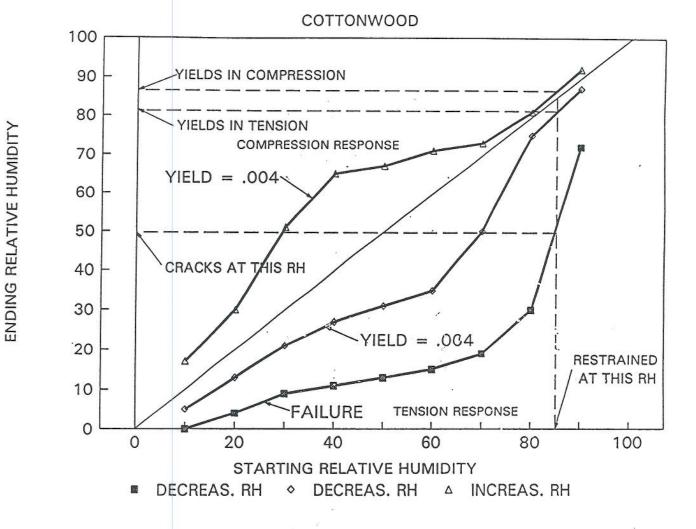


Figure 15. The effects of "compression set" on a fully restrained cottonwood in the tangential direction. Compression set re-initializes the wood to a high RH, which in this case is 85%. The woods now acts as if it is fully restrained at this high RH and the chart shows that it is impossible to desiccate below 82% with tensile yielding. It also shows that there is an extremely high probability of cracking the wood if it is desiccated to only 50% RH.

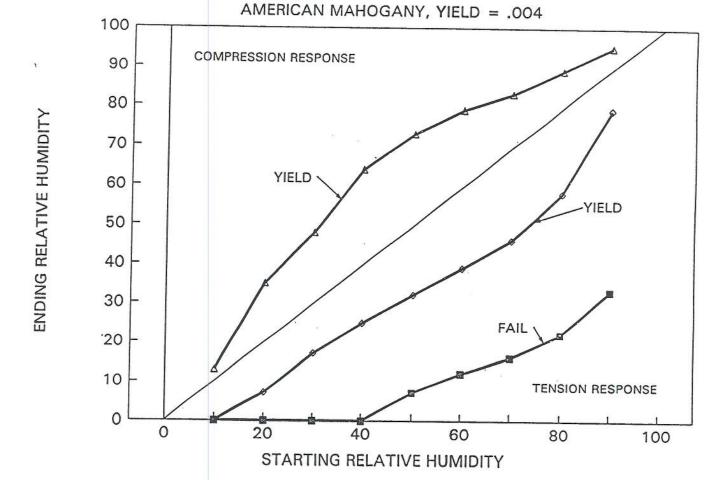


Figure 16. Yield and failure lines for fully restrained American mahogany in the tangential direction. This chart allows one to determine the RH changes needed to reach yielding and breaking in this wood. The area between the yield lines represent a zone of allowable RH fluctuations for any given ambient RH.

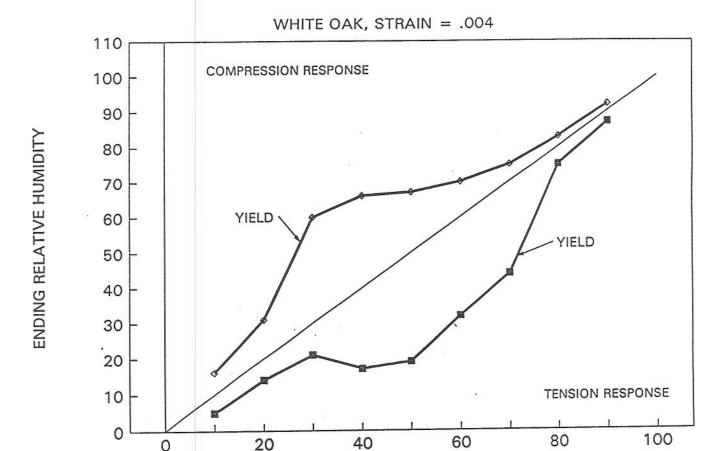


Figure 17. Yield lines for fully restrained white oak in the tangential direction. This chart allows one to determine the RH changes needed to reach yielding in this wood. The area between the yield lines represent a zone of allowable RH fluctuations for any given ambient RH.

STARTING RELATIVE HUMIDITY

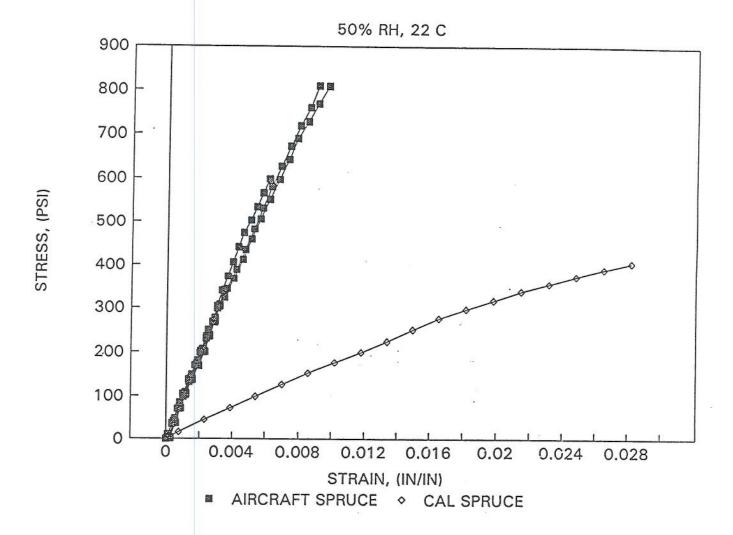


Figure 18. The stress-strain plots of samples of two different wood sources of the same species of wood. In this case the wood is spruce and the variability of the mechanical properties is substantial. The aircraft spruce attains a stiffness of nearly four and one-half time the CAL spruce.

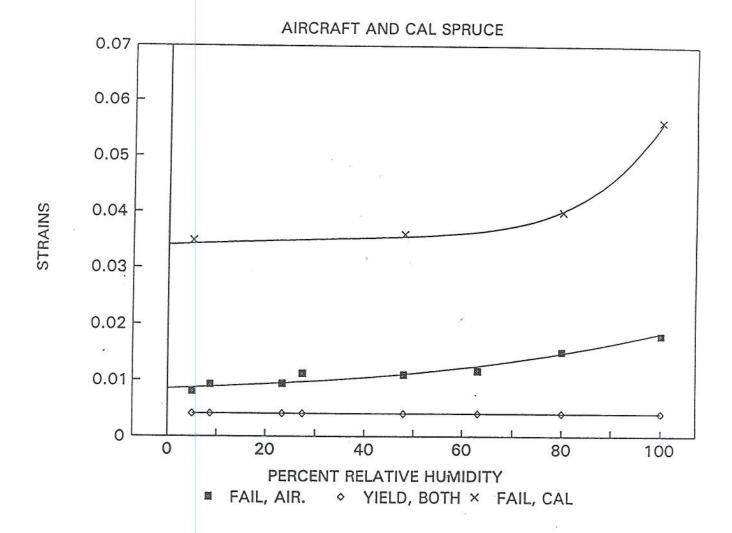


Figure 19. Measured breaking and yield strains for aircraft and CAL spruce as a function of RH. The breaking strains of the CAL spruce are three time higher than the aircraft spruce.

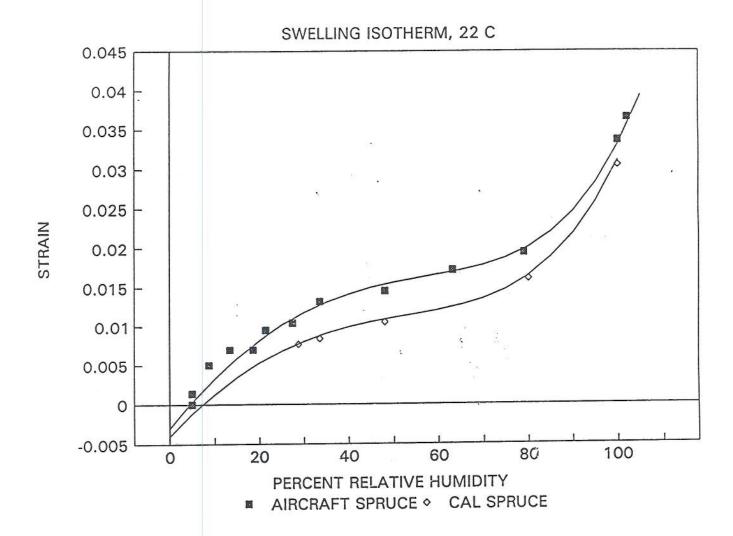


Figure 20. The swelling isotherms for CAL and aircraft spruce. There is little difference in these sets of data with the exception of the offset. The moisture coefficients of expansion are quite similar.

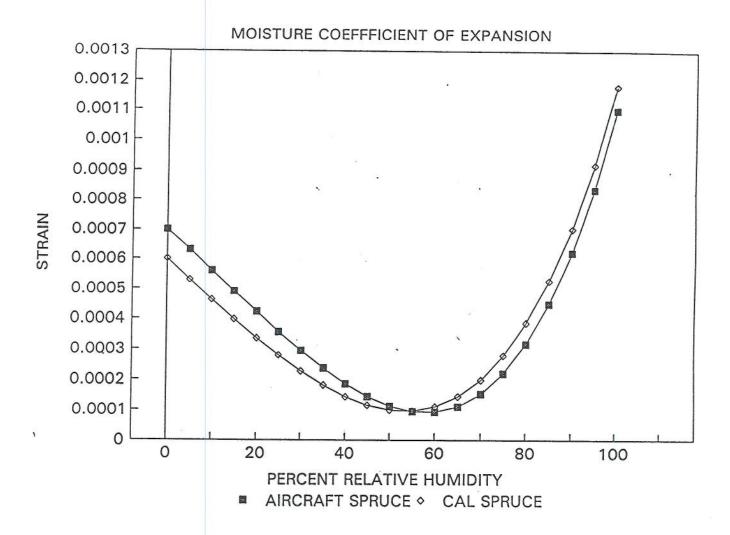


Figure 21. The moisture coefficients of expansion for the CAL and aircraft spruce. These coefficients are nearly identical.

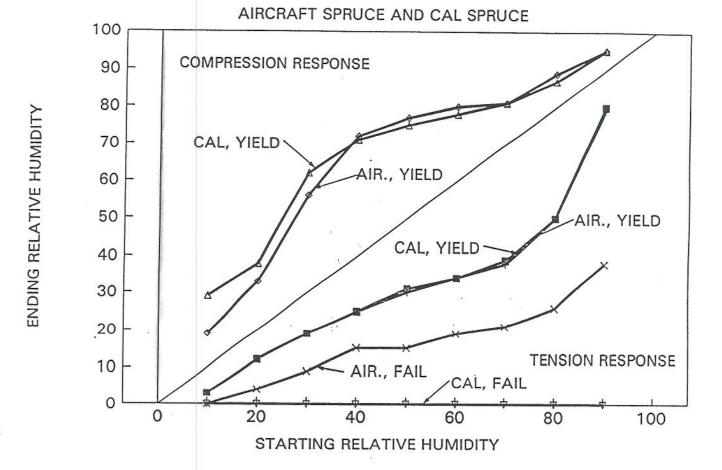


Figure 22. Yield and failure lines for fully restrained CAL and aircraft spruce in the tangential direction. This chart allows one to determine the RH changes needed to reach yielding and breaking in these woods. The area between the yield lines represent a zone of allowable RH fluctuations for any given ambient RH. There is effectively no difference in the allowable fluctuations of these woods even though they have significant differences in their mechanical properties.

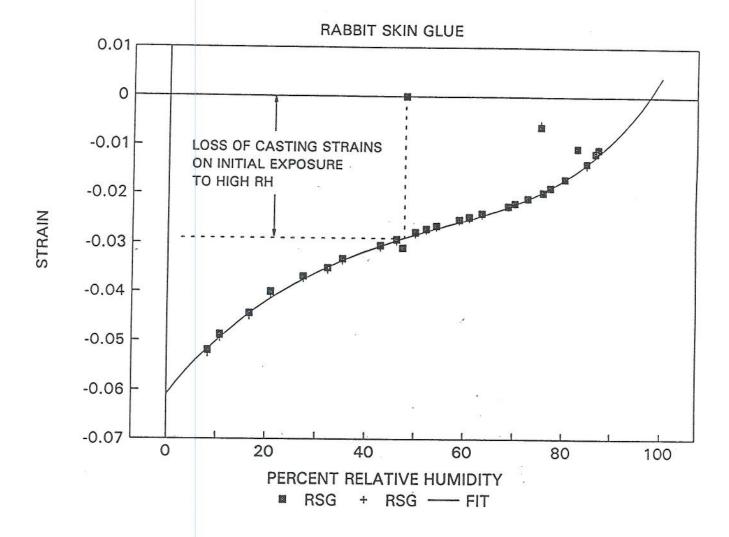


Figure 23. The swelling isotherm for hide glue. This figure is showing the results for two samples.

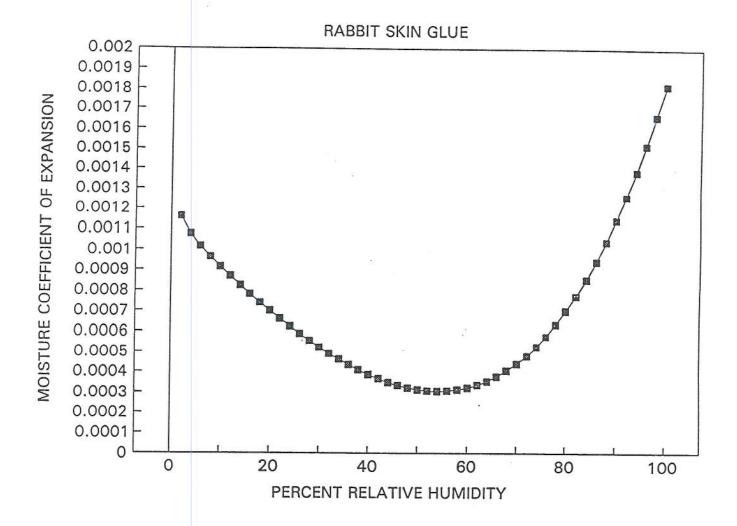


Figure 24. The swelling coefficient of hide glue. This material has the highest moisture coefficient expansion of the panel materials examined.

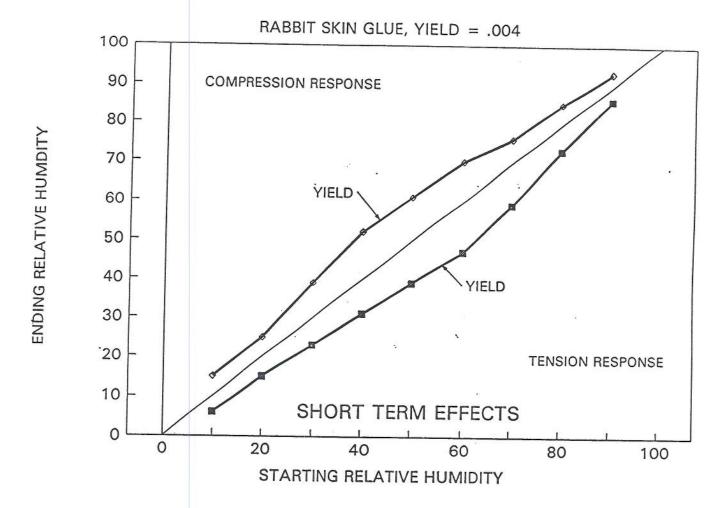


Figure 25. Yield lines for fully restrained rabbit skin glue in both directions of the plane of a panel painting. This chart allows one to determine the RH changes needed to reach yielding in this material for short term fluctuations of RH. The area between the yield lines represent a zone of allowable RH fluctuations for any given ambient RH.

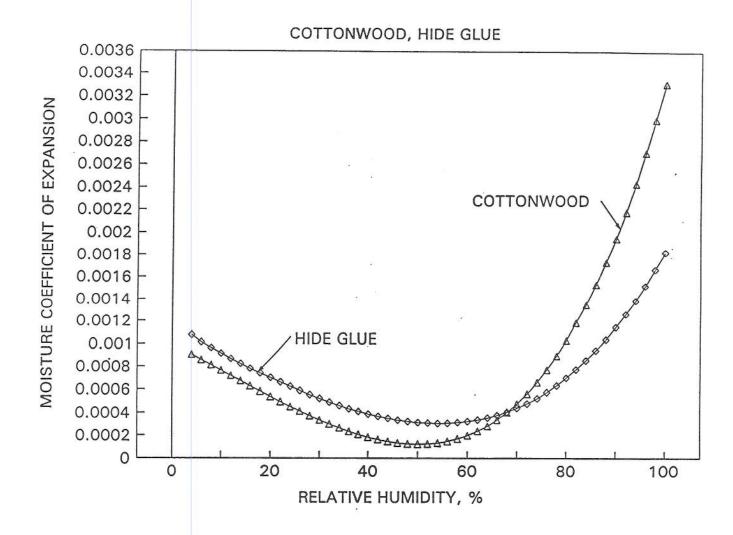


Figure 26. Comparison of the swelling coefficients of hide glue and cottonwood.

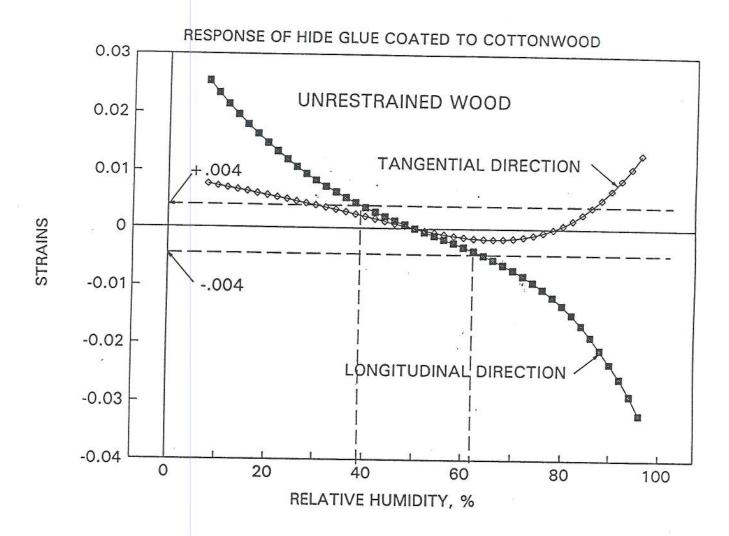


Figure 27. Environmentally induced strains in hide glue applied to an unrestrained cottonwood panel. This illustration shows the difference in response between the longitudinal and tangential directions. The hide glue is effectively restrained in the longitudinal direction while strains are considerably reduced in the tangential direction due to movement of the wood.

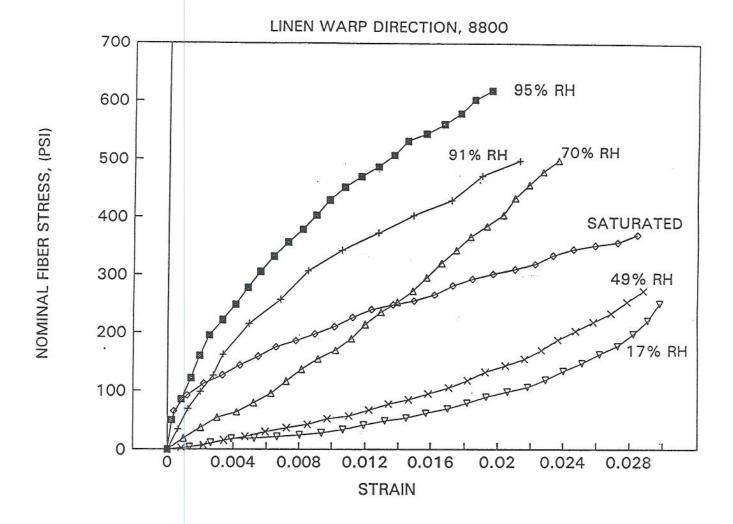


Figure 28. Stress-strain plots for linen fabric at different environments in the warp direction. Unlike other hygroscopic materials, linen stiffens with increases in humidity.

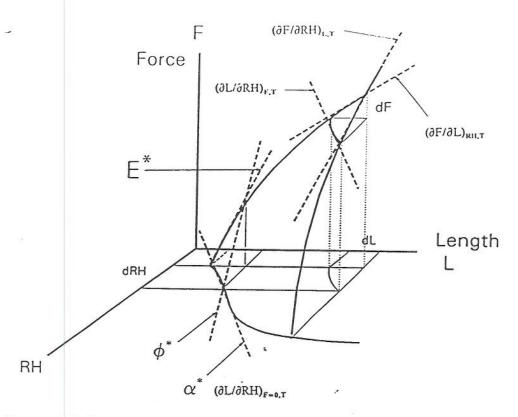


Figure 8. Theoretical force-length-relative humidity (F-L-RH) diagram illustrating the mathematical definitions and relationships.

## ENGINEERING APPLICATION OF THE CASE

It would be useful to apply these concepts to the engineering problems that confront the researcher. The immediate question that can be answered is, do environmental fluctuations induce plastic deformations? This can be approached by rewriting equation 5 into engineering terms. This conversion is accomplished by first dividing both sides of the equation by A, the cross-sectional area of the test sample:

$$(\partial F/\partial L)_{RH,T} (\partial L/\partial RH)_{F,T} (1/A) = -(\partial F/\partial RH)_{L,T} (1/A)$$
(7)

the equation then becomes:

$$(\partial \sigma/\partial L)_{RH,T} (\partial L/\partial RH)_{F,T} = -(\partial \sigma/\partial RH)_{L,T}$$
 (8)

and if  $L_o$  is the initial length of the specimen, and by multiplying the left side of the equation by  $(L_o/L_o)$ , i.e., identity (i.e. 1) the equation becomes:

$$(\partial \sigma/\partial \epsilon)_{RH,T} (\partial \epsilon/\partial RH)_{F,T} = -(\partial \sigma/\partial RH)_{L,T}$$
(9)

For linear elastic behavior of a material the term,  $(\partial \sigma/\partial \epsilon)_{RH,T}$ , is in fact the modulus of elasticity (E) or Hooke's Law. The term  $(\partial \epsilon/\partial RH)_{F,T}$  is  $\alpha$ , the moisture coefficient of expansion when  $\sigma=0$  and the term,  $-(\partial \sigma/\partial RH)_{L,T}$ , is  $\phi$ , the change in stress with the change in relative humidity when the length is fixed. This last term describes the restrained specimen stress development.

Looking at this specific relationship in symbolic form becomes:

$$(E)_{RH,T} (\alpha)_{\sigma=0,T} = -(\phi)_{L,T}$$
 (10)

This equation was found to be applicable to all classes of materials studied such as, hide glues, photographic gelatin, epoxy adhesives, oil and alkyd paints.

### CONCLUSIONS

A series of experiments were performed on several classes of museum materials. These described the dimensional response with respect to temperature and relative humidity, the stress-strain curve under rapid and equilibrium conditions, and stress development under restrained conditions with variation in temperature or relative humidity. From this data one unifying observation emerged.

From the changes in force with respect to length, the changes in length with respect to relative humidity, and the changes in force with respect to RH, a general equation for the behavior of materials under environmental changes was developed. A similar treatment relating temperature to force, dimensional change and temperature is being developed.

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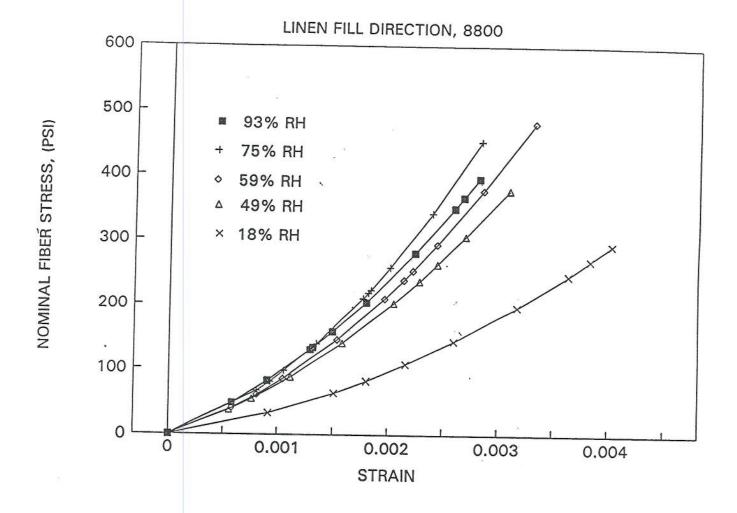


Figure 29. Stress-strain plots for linen fabric at different environments in the fill (weft) direction. Unlike other hygroscopic materials, linen stiffens with increases in humidity.

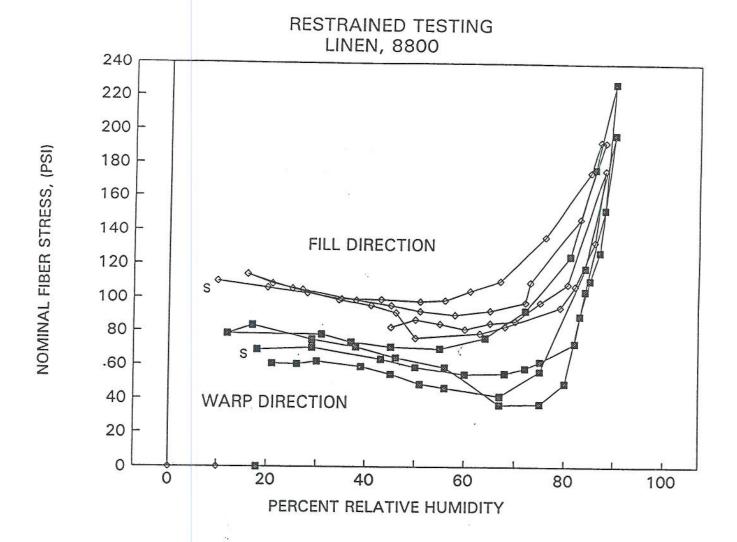


Figure 30. Stress versus RH for restrained linen in both the warp and fill directions. The difference in weave has little effect in the restrained response to RH.

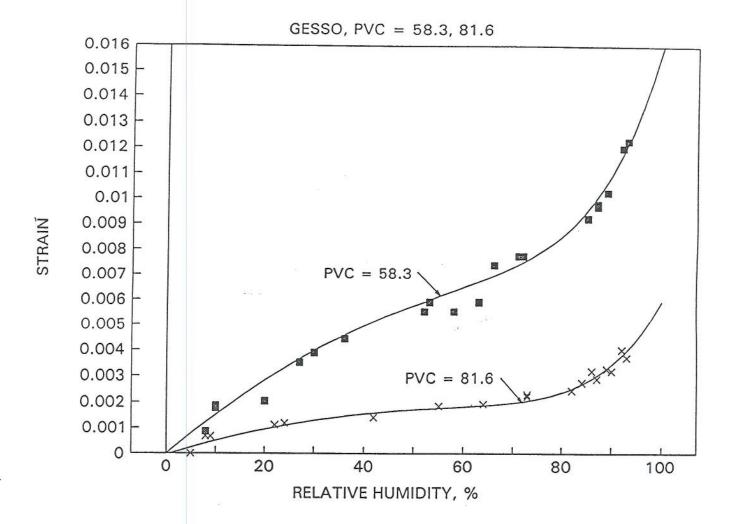


Figure 31. The swelling isotherms for two different mixtures of gesso. Increases in the filler concentration reduce the swelling behavior of the material as well as reducing the strength.

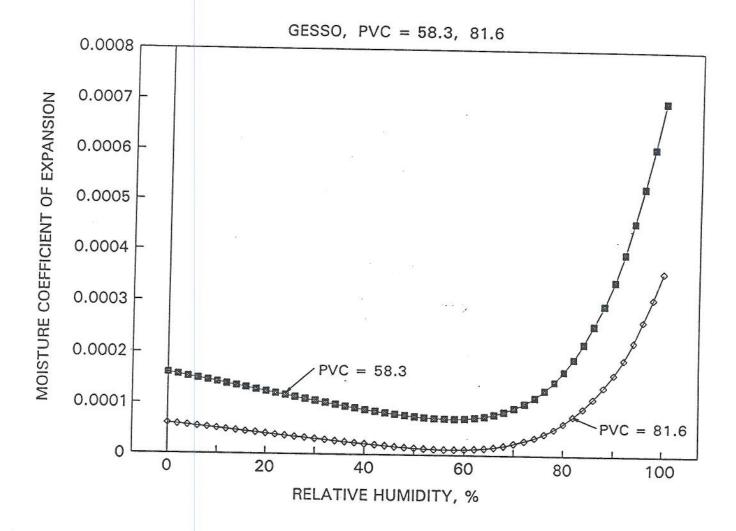


Figure 32. The swelling coefficients of expansion for two gesso mixtures.

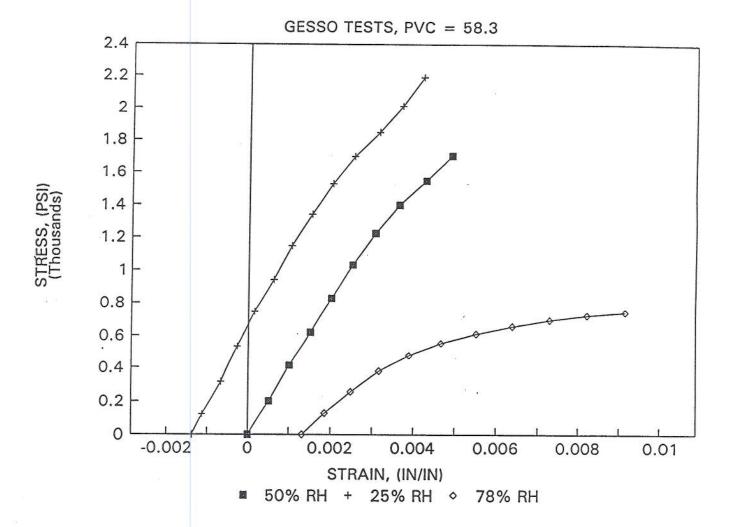


Figure 33. Stress-strain plots for gesso with a PVC of 58.3 at different environments. The spacings between the starting points of the plots reflect the stress free swelling when going from one environment to another.

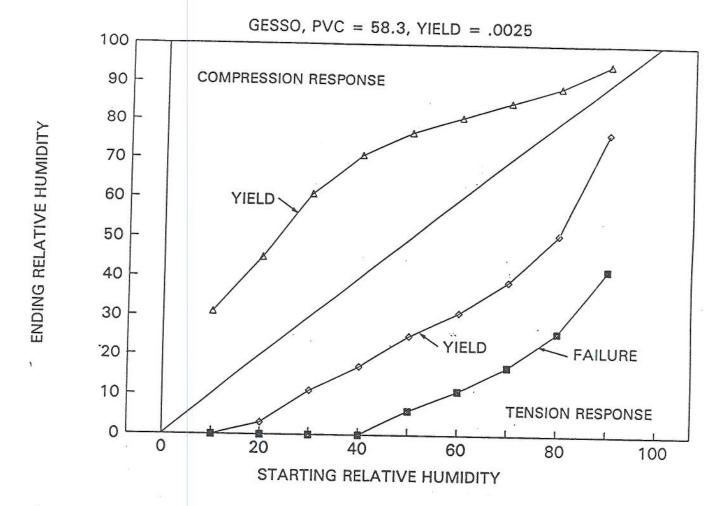


Figure 34. Yield and failure lines for fully restrained gesso samples. This chart allows one to determine the RH changes needed to reach yielding and breaking in this gesso. The area between the yield lines represent a zone of allowable RH fluctuations for any given ambient RH. The fail line designates the RH change required to cause cracking at the indicated starting environment.

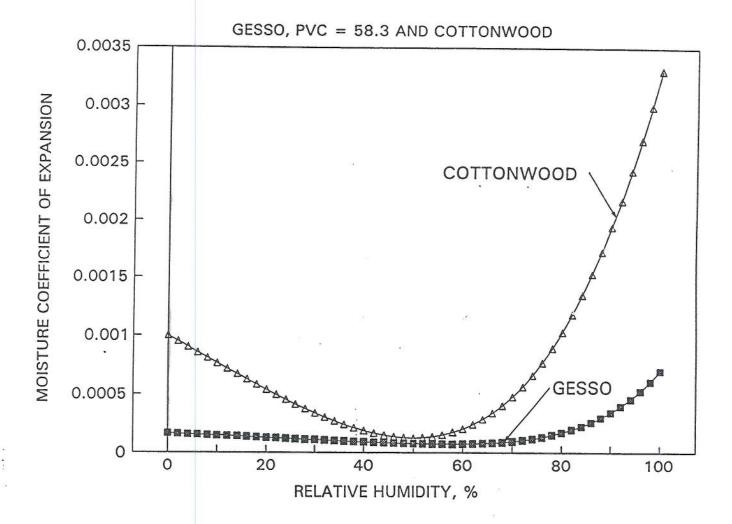


Figure 35. Comparison of the swelling coefficients of gesso and the tangential direction of cottonwood. These coefficient are nearly identical in the region between 40% and 50% RH. This means that the dimensional response of these materials in this region are closely matched. In the RH regions of 70% and above and 30% and below, there is a significant coefficient mismatch and excursions into these RH regions has the probability to cause damage.

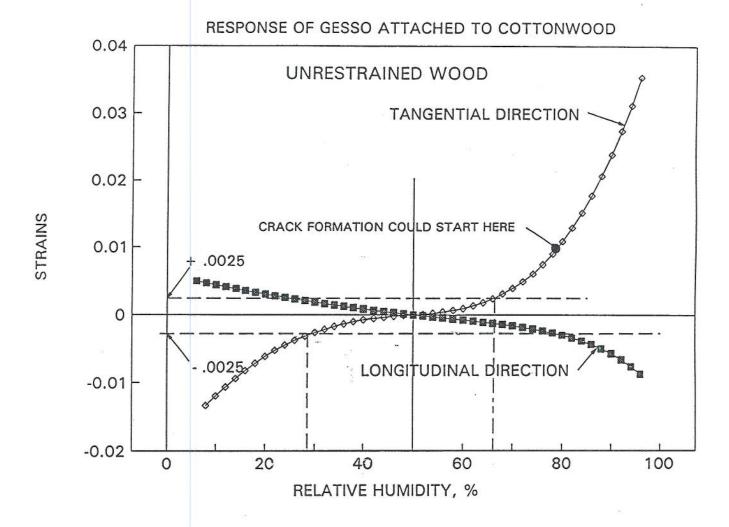


Figure 36. Environmentally induced strains in gesso applied to an unrestrained cottonwood panel. This illustration shows the difference in response between the longitudinal and tangential directions. The gesso is effectively restrained in the longitudinal direction. In the tangential direction the wood movement induces severe strains in the gesso in the extreme RH regions. The strain directions (compression and tension) are reversed in the two directions.

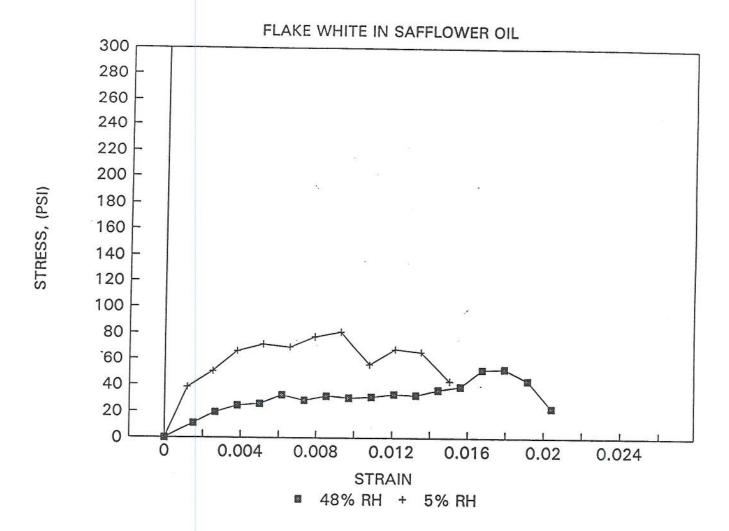


Figure 37. The equilibrium stress-strain plots at two different environments for flake white ground in safflower oil. Lead carbonate based paints are affected relatively little by RH when compared to other oil paints.

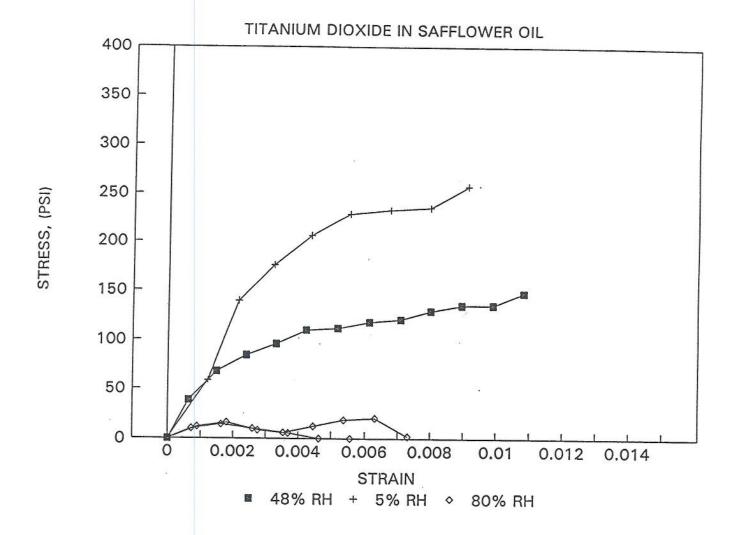


Figure 38. The equilibrium stress-strain plots at three different environments for titanium dioxide ground in safflower oil. RH has a significant influence on the mechanical properties of this paint. At 80% RH this paint has no load carrying capacity.

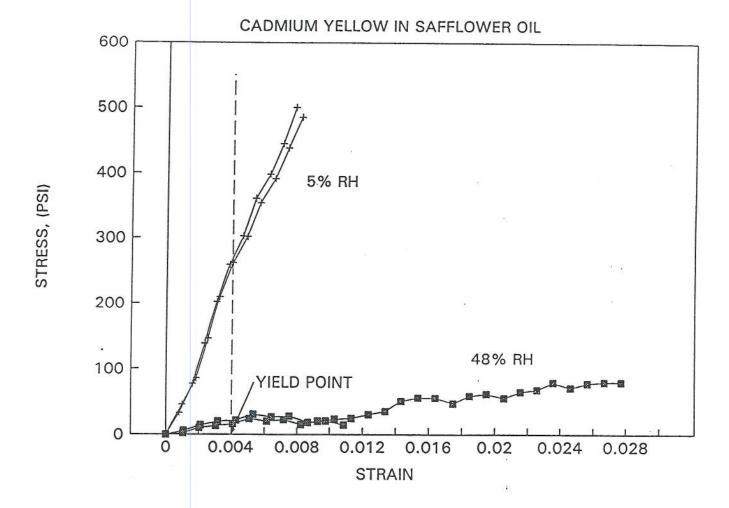


Figure 39. The equilibrium stress-strain plots at two different environments for cadmium yellow ground in safflower oil. RH has a significant influence on the mechanical properties of this paint.

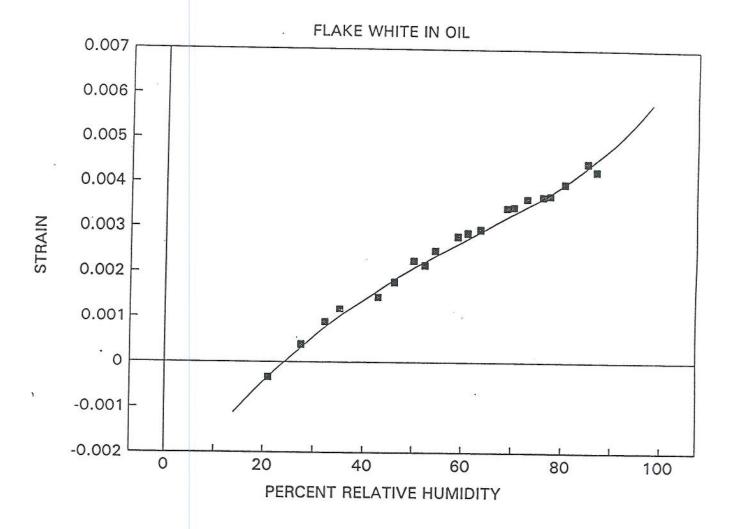


Figure 40. The moisture swelling isotherm of flake white in safflower oil. This paint swells only about .08% when subjected to a RH change from 10% to 90% RH. This is another indication of this paint's low moisture response.

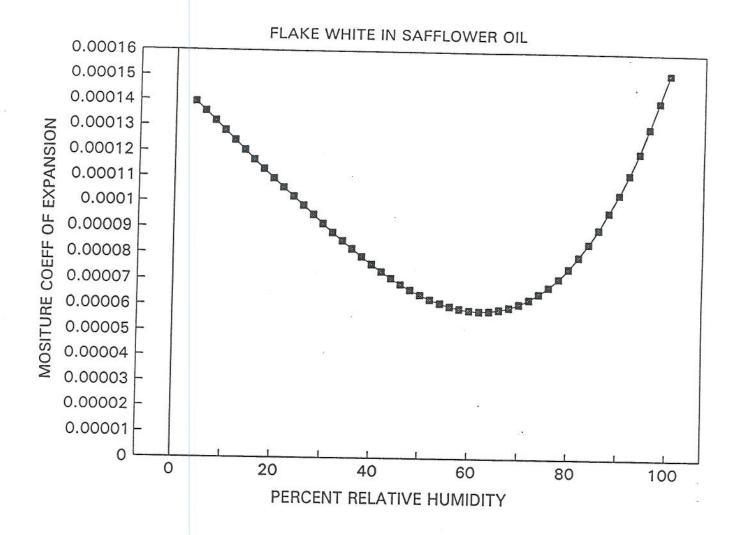


Figure 41. The moisture coefficient of expansion for flake white in safflower. This material has the lowest coefficient of expansion of all of the materials examined for this paper.

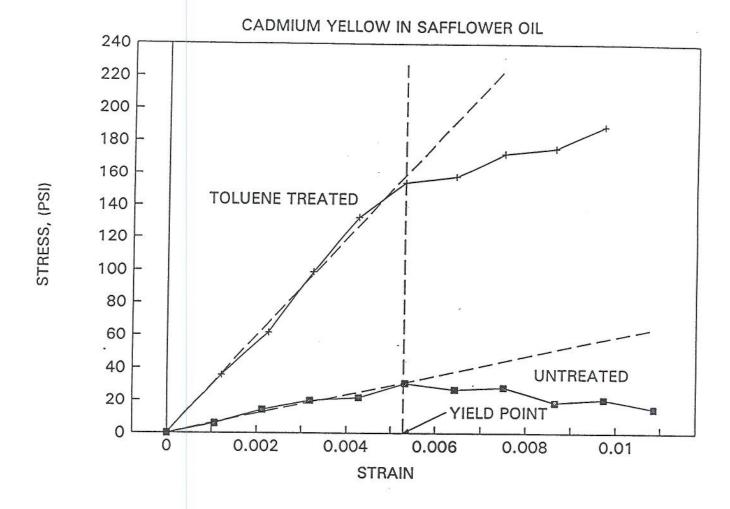


Figure 42. The equilibrium stress-strain curves for cadmium yellow ground in safflower oil with and without soaking in toluene for one week. In effect, the toluene has removed those oil components that act as plastizers and the paint increases its stiffness five times.

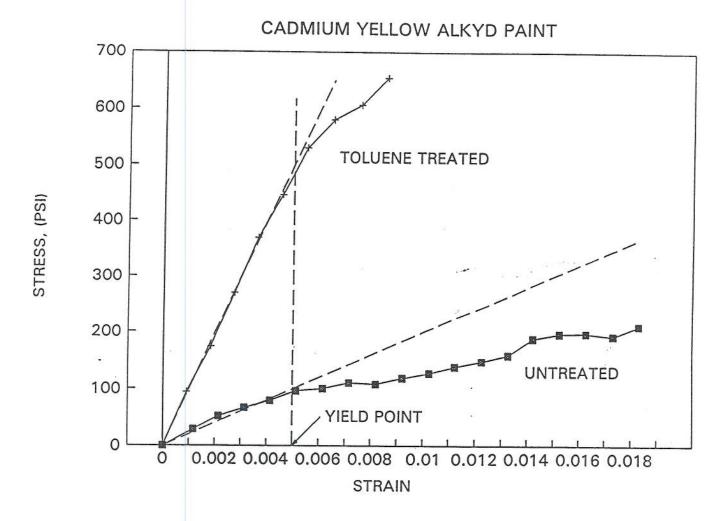


Figure 43. The equilibrium stress-strain curves for cadmium yellow alkyd paint with and without soaking in toluene for one week. As with the cadmium yellow in oil, the toluene has removed those components that act as plastizers and the paint again increased its stiffness five times.

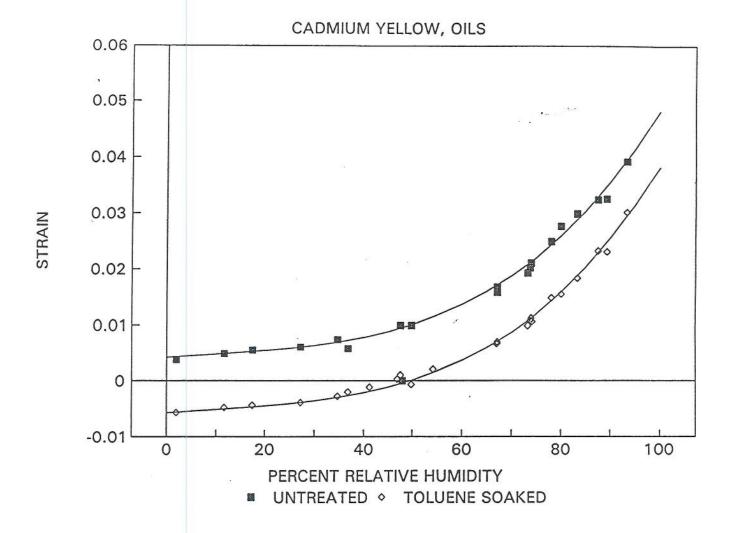


Figure 44. The moisture swelling isotherms of the cadmium yellow oil paint with and without soaking in toluene for one week. The fits to these sets of data are identical. This means that treatments such as solvents that affect the mechanical properties of a paint do not necessarily affect the dimensional response to moisture.

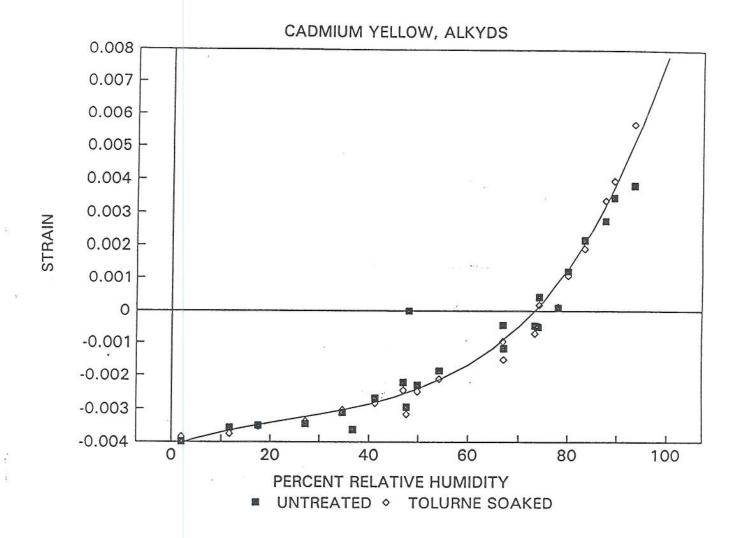


Figure 45. The moisture swelling isotherms of the cadmium yellow alkyd paint with and without soaking in toluene for one week. The fits to these sets of data are again identical as with the oil paint. Also as with the oil paint, the mechanical properties of this paint is affected but not the dimensional response to moisture.

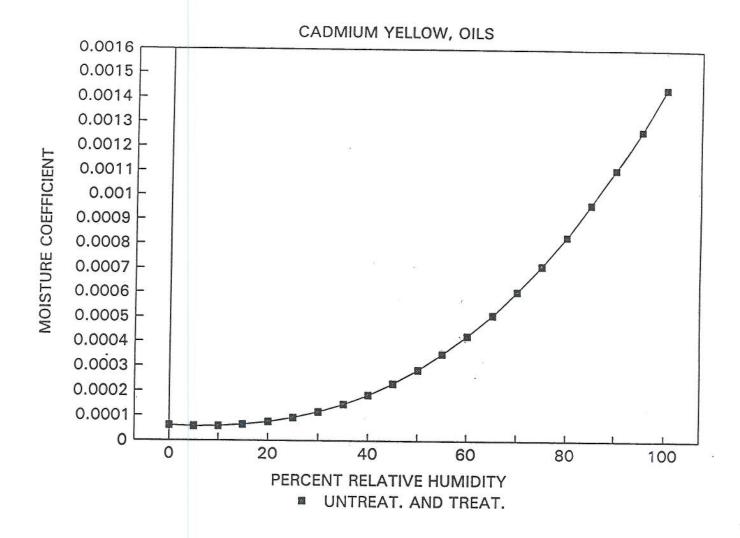


Figure 46. The moisture coefficient of expansion for both the untreated and toluene treated cadmium yellow oil paint. Unlike previous materials discussed, where the coefficient of expansion is the lowest at the central RH region, this paint has its lowest values at the extreme low RH region. This is typical of many paints.

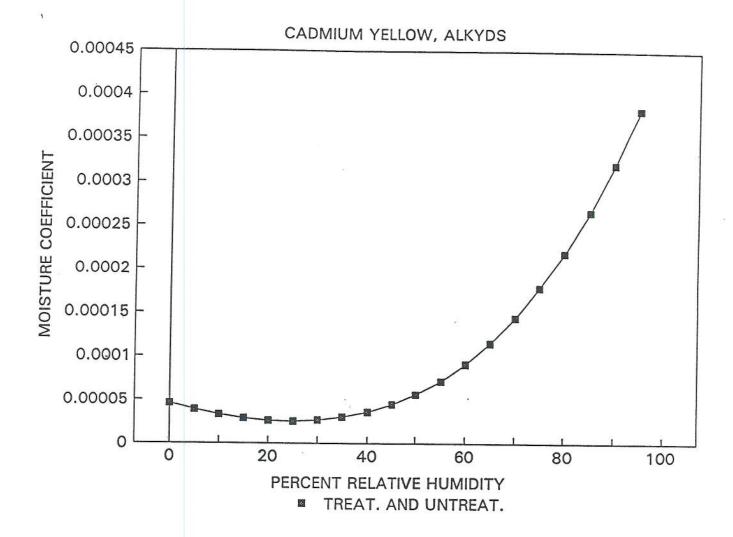


Figure 47. The moisture coefficient of expansion for both the untreated and toluene treated cadmium yellow alkyd paint. Like the cadmium yellow oil paint, this paint also has its lowest coefficients values at the extreme low RH region.

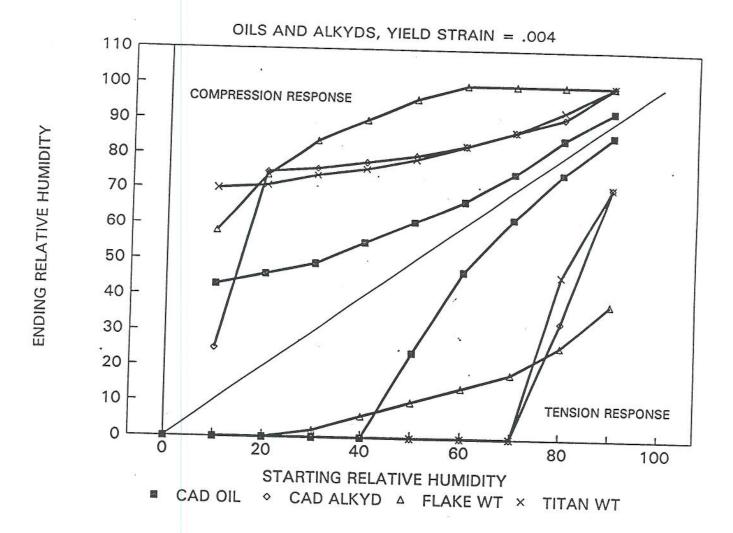


Figure 48. Yield lines for different fully restrained paints. This chart allows one to determine the RH changes needed to reach yielding of flake white in oil, titanium white in oil, and the toluene treated and untreated cadmium paints. The area between the yield lines represent a zone of allowable RH fluctuations for any given ambient RH. With the exception of the cadmium yellow oil paint, these paints can sustain extremely wide fluctuations in RH without yielding, wider than any of the other artists material examined.

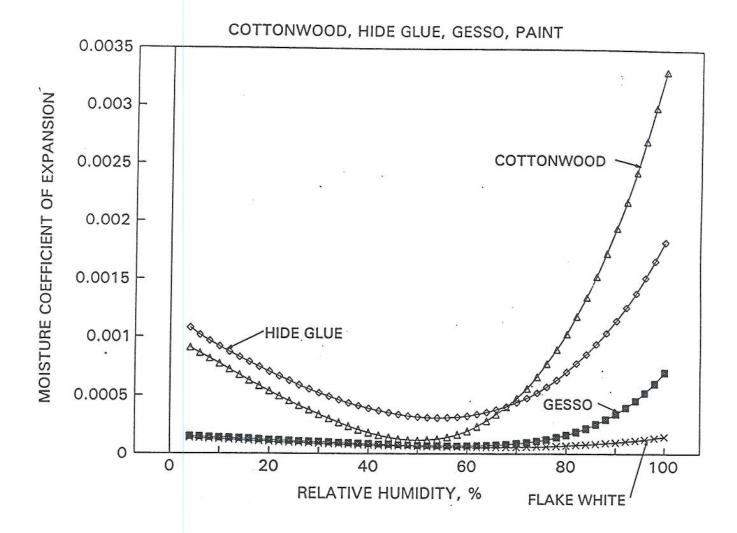


Figure 49. A comparison of the moisture coefficients of expansion of cottonwood, gesso, hide glue, and flake white oil paint. The flake white paint and the gesso are nearly identical except for the region above 75% RH. This figure illustrates the points of relative match and mismatch of the coefficients of all of the painting materials discussed.

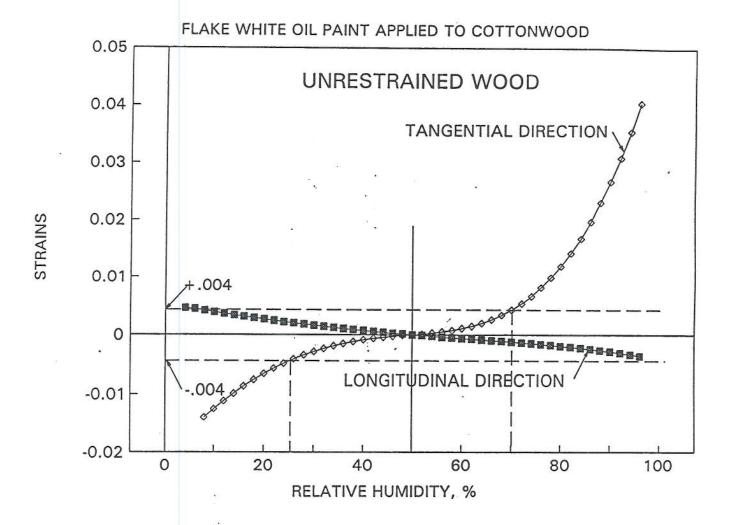


Figure 50. Environmentally induced strains in flake white oil paint applied to an unrestrained cottonwood panel. This illustration shows the difference in response between the longitudinal and tangential directions. The oil paint is effectively restrained in the longitudinal direction. As with the gesso, in the tangential direction, the wood movement induces severe strains in the paint in the extreme RH regions. The strain directions (compression and tension) are reversed in the two wood grain directions.

# Appendix B

A GENERAL MODEL RELATING EXTERNALLY APPLIED FORCES TO ENVIRONMENTALLY INDUCED STRESSES IN MATERIALS

# A GENERAL MODEL RELATING EXTERNALLY APPLIED FORCES TO ENVIRONMENTALLY INDUCED STRESSES IN MATERIALS

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### **ABSTRACT**

The structural degradation effects of temperature (T) and relative humidity (RH) are important considerations in the setting and maintaining of museum environments. An approach to determining the acceptable values for this environment would be useful if a general model could be developed from simple physical (mechanical) measurements. In this paper, a general model is developed in which the mechanical behavior of materials composing museum objects can be described using the easily determined parameters, stress development (force), environmental conditions and dimensional change.

### INTRODUCTION

Changes in relative humidity (RH) cause changes in the moisture content of hygroscopic materials. Since all organic materials are hygroscopic to some extent, most traditional cultural materials are subject to swelling and shrinking with these moisture changes. These dimensional changes are largely responsible for environmental structural damage to objects. Temperature variations also cause dimensional changes in all materials and these environmental fluctuations can also be a very real source of damage.

The mechanism for inducing stress in materials from changes in temperature or RH involves restraint of the object. If hygroscopic materials are restrained and desiccated then they will develop tensile stresses. Materials that are restrained and then cooled will similarly develop stresses. This is, in part, a result of the inability to contract which is the normal behavior if the materials were unrestrained. It would be quite useful to relate this behavior to the mechanical properties of materials as measured by externally applied loads. This requires the equilibrium stress-strain plot as described in reference 1.

### ALTERNATE PATHS TO STRESS DEVELOPMENT

Interesting observations were made during the materials testing program at a constant temperature. If any hygroscopic material specimen were allowed to swell from one RH to another; say RH<sub>o</sub> to RH<sub>1</sub>, restrained and then desiccated back to RH<sub>o</sub>, it will attain the same state of stress  $(\sigma)$ , length (L), and RH as a specimen subjected to an equilibrium tensile test at a constant RH, in this case RH<sub>o</sub>. This is illustrated in figure 1, where the separate paths from one state of stress  $(\sigma_o)$ , to another state of stress  $(\sigma_{10})$ , are described. In this diagram the coordinates are relative humidity (RH); length (L); and stress  $(\sigma)$ . It simplifies the analysis if length is used instead of strain as the elongation coordinate. The paths from  $\sigma_o$  to  $\sigma_1$ , are either the equilibrium stress-length test or two separate tests: first, free swelling, and second, the desiccation of the restrained specimen. Paths in planes parallel to the stress-length plane are equilibrium tensile tests at constant temperature and relative humidity. Paths in planes parallel to the stress-relative humidity plane are restrained desiccation tests. The paths in the length-relative humidity plane are swelling isotherm measurements which can be either stress free or under a constant stress.

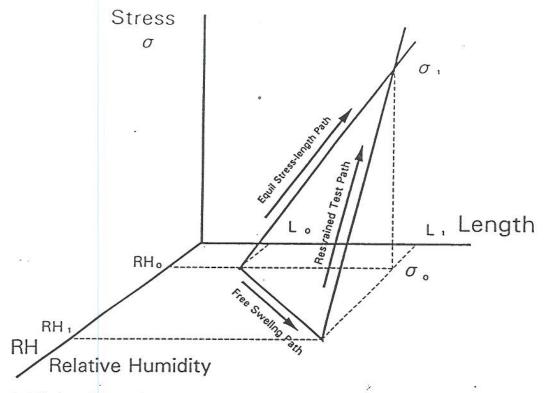


Figure 1. Diagram illustrating the different paths from one state of stress to another state of stress. One path is the equilibrium stress-length (strain) test and the other path consists of the free swelling test combined with the restrained desiccation test.

This, of course, implies that there is a link between the environmentally induced stress and the externally applied loads of a simple tensile test. It also implies that fundamental mechanical and dimensional properties of the materials govern the ultimate state of stress and strain whether the forces are externally applied or environmentally induced in the materials. In addition, this permits the modeling of environmentally induced structural behavior using traditional mechanical data.

Several different types of materials were tested at ambient temperature (23°C) to determine if this is a general concept. Some of the data of this test program are illustrated in figures 2-7. Figure 2 illustrates the different paths to two states of stress in a 13-year-old unsupported cadmium yellow alkyd paint film. The intersection points are indicated as I1 and I2. In figure 3, four intersection points, I1-I4 were established in a 13-year-old titanium dioxide pigment in safflower oil paint. Figures 4-6 are three different epoxy films. The first is a commercial product HYSOL™ EA 9394, which is modified with powdered aluminum and amorphous silica. This material has a very high moisture coefficient of expansion and has been stiffened with "inert" solids. As a result, it develops very high stresses with desiccation. Even with these modifications, it was a simple process to establish three intersection points as shown in figure 4. Figures 5 and 6 show Epoxy Adhesives 96 and Epoxy Adhesive 3H respectively, structural adhesives developed for a research program at the Martin Marietta Laboratories in Arbutus, Maryland. Several intersection points are shown in each of these adhesives. Finally, figure 7, shows rabbit skin glue with five actual intersections and with extrapolation, six additional points. For these materials, plots in a 3-D coordinate system describe surfaces generated by the parameters stress (or force), length, and RH.

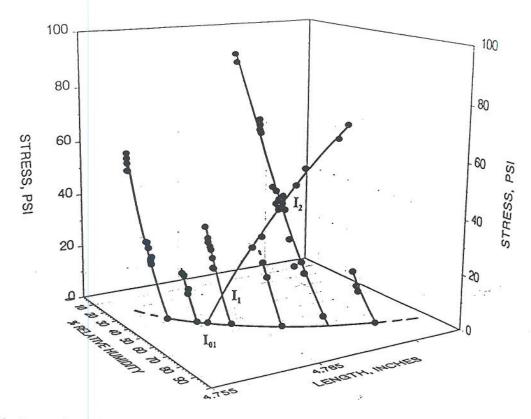


Figure 2. Stress-length-relative humidity plot for cadmium yellow alkyd paint showing mutual intersection points of stress starting at I<sub>o</sub>, and going to I<sub>1</sub> and I<sub>2</sub>.

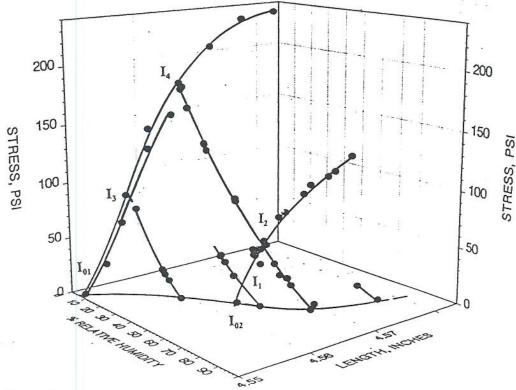


Figure 3. Stress-length-relative humidity plot for titanium dioxide oil paint showing mutual intersection points of stress starting at different points,  $I_{o1}$ ,  $I_{o2}$  and going to four different stress states  $I_1$ ,  $I_2$ ,  $I_3$ , and  $I_4$ .

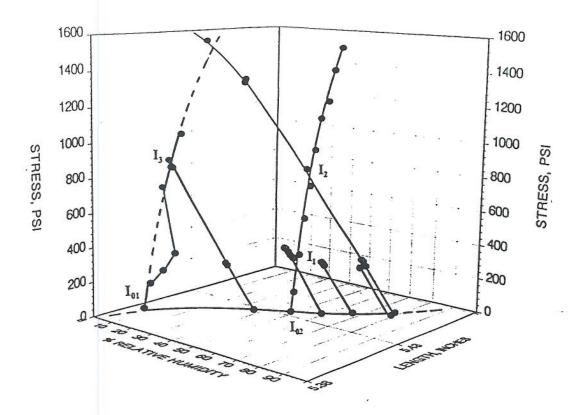


Figure 4. Stress-length-relative plot for epoxy adhesive HYSOL EA 9394 mutual intersection points of stress starting at different points, I<sub>01</sub>, I<sub>02</sub> and going to three different stress states I<sub>1</sub>, I<sub>2</sub>, and I<sub>3</sub>.

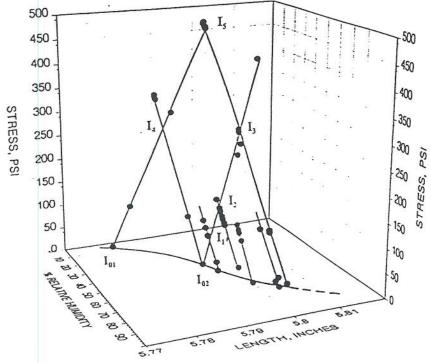


Figure 5. Stress-length-relative humidity plot for epoxy Adhesive 96 mutual intersection points of stress starting at different points,  $I_{o1}$ ,  $I_{o2}$  and going to five different stress states  $I_1$ ,  $I_2$ ,  $I_3$ ,  $I_4$ , and  $I_5$ .

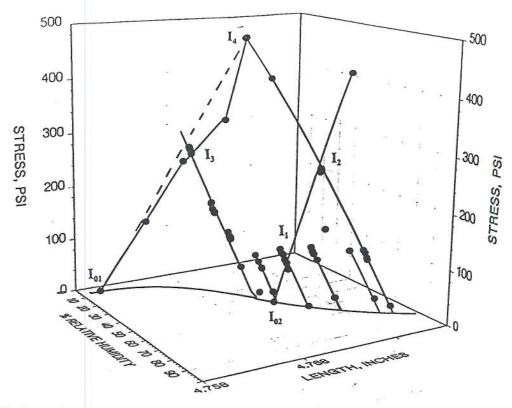


Figure 6. Stress-length-RH plot for epoxy Adhesive II 3H mutual intersection points of stress starting at different points,  $I_{o1}$ ,  $I_{o2}$  and going to four different stress states  $I_1$ ,  $I_2$ ,  $I_3$ , and  $I_4$ .

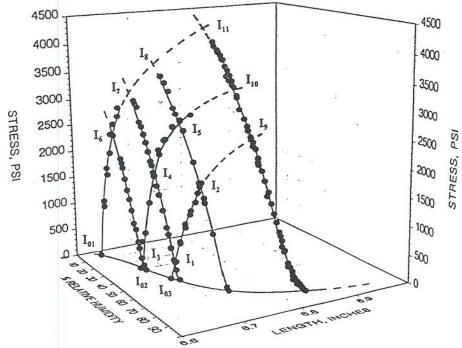


Figure 7. Stress-length-RH plot for rabbit skin glue mutual intersection points of stress starting at different points, I<sub>01</sub>, I<sub>02</sub>, and I<sub>03</sub> and going to five different stress states I<sub>1</sub>, I<sub>2</sub>, I<sub>3</sub>, I<sub>4</sub>, and I<sub>5</sub>. Six additional projected mutual stress points are shown at I<sub>6</sub>, I<sub>7</sub>, I<sub>8</sub>, I<sub>9</sub>, I<sub>10</sub>, and I<sub>11</sub>.

These materials represent both cross-linked and non-cross-linked polymer networks, yet the basic behavior is the same. So far no material tested has failed to follow this pattern. For these materials and perhaps many more, a fundamental relationship between the mechanical, dimensional and environmental behavior can be established.

# GENERAL MATHEMATICAL CONSIDERATIONS

The preceding data can be discussed in mathematical terms and it is possible to construct a theoretical model. In figure 8 the hypothetical paths are illustrated in the force, length, and relative humidity (F,L,RH) three dimensional coordinate system. The slope of the force-length equilibrium plot, (analogous to the stress-strain plot) at any point can be defined as  $(\partial F/\partial L)_{RH,T}$ . The slope of the length-relative humidity plot can be defined as  $(\partial L/\partial RH)_{F,T}$ , which is analogous to the coefficient of expansion when the force is zero, i.e., F=0. Finally the slope of the force-relative humidity plot is defined as  $(\partial F/\partial RH)_{L,T}$ . The subscripts refer to the fixed conditions when the partial differentials are taken. For any small increment of force (dF), the following holds:

$$dF = (\partial F/\partial L)_{RH,T}dL \tag{1}$$

and

$$dF = -(\partial F/\partial RH)_{L,T}dRH.$$
 (2)

The corresponding increment of length dL can be described as:

$$dL = (\partial L/\partial RH)_{F,T}dRH$$
(3)

Combining equations 1 and 3 will give:

$$dF = (\partial F/\partial L)_{RH,T} (\partial L/\partial RH)_{F,T} dRH$$
(4)

This equation can be combined with equation 2 such that:

$$(\partial F/\partial L)_{RH,T} (\partial L/\partial RH)_{F,T} = -(\partial F/\partial RH)_{L,T}, \tag{5}$$

and can be written as:

$$E^* \times \alpha^* = -\phi^*, \tag{6}$$

where:

$$E^{*} = (\partial F/\partial L)_{RH,T}$$

$$\alpha^{*} = (\partial L/\partial RH)_{F,T}$$

$$\phi^{*} = (\partial F/\partial RH)_{LT}$$

This equation relates the externally applied forces in a material to the environmentally induced forces. In addition, the stiffness, the equilibrium modulus, of a material as measured by externally loaded processes in a constant environment is the same stiffness that determines the forces developed by changes in relative humidity for a restrained material.