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THE EFFECTS OF ATMOSPHERIC MOISTURE ON THE MECHANICAL PROPERTIES OF COLLAGEN UNDER EQUILIBRIUM CONDITIONS

M. F. Mecklenburg
Conservation Analytical Laboratory
Smithsonian Institution
Washington, D.C., 20560

Abstract

This paper examines the relationship between the mechanical properties of collagen samples and the stress and elongation behavior of this material due to changes in environmental relative humidity. The mechanical properties are determined by both rapid and equilibrium stress-strain testing at fixed environments whereas free swelling and restrained sample desiccation were used to examine changes in length and stress as a function of relative humidity. The data developed show that the changes in moisture can produce stress magnitudes in collagen nearly identical to those determined by the equilibrium stress-strain test.

Introduction

From 1978 to 1982, research conducted under the sponsorship of the National Museum Act as administered by the Smithsonian Institution examined the effects of relative humidity (RH) on the mechanical properties of the materials which are typically found in fabric supported oil paintings.(1) These materials include oil paint, linen and rabbit skin glue. The research program was designed to lead to a more complete understanding of the mechanical changes induced in this type of painting by changing environmental conditions. One phase of this research was to explore the response of a composite of those materials to fluctuating RH. Since 1982 additional information has become available which further clarify the link between environmental moisture and the mechanical (stress related) properties of artist materials.

To provide a background for discussion of current results a review of aspects of the earlier 1982 study is presented below. In one segment of that research, specimens of the separate component materials of oil paintings were restrained under tension at a nearly fixed length, then subjected to large cycles of RH at a fixed temperature of 71° F. In this way one can measure changes in tension in a restrained (stretched) material as a function of ambient moisture.

By comparing the response of the individual materials to that of an actual painting subjected to the same test, considerable information was gained regarding which layers of a painting were most likely responsible for humidity related damage. The comparison between individual components and the whole painting is made possible by superimposing the results of the individual material tests after correcting them for the thicknesses of the layers which would be found in an actual painting.

The oil paint used for this test was artificial vermilion in safflower oil which was allowed to dry for forty-two months as a film cast on mylar. The mylar was removed prior to testing. This paint was chosen since it showed twice the stiffness of white lead or titanium dioxide in linseed oil after comparable drying times. The fabric was an Ulster linen No.8800, 32 X 32 basket weave, and the hide glue was commercially available rabbit skin glue. Glue specimens were also cast on mylar. The test samples were cut to seven inch lengths and varied in both width and thickness from specimen to specimen. The width and thickness of each specimen was recorded allowing the calculation of stress (force per unit area) and providing the necessary information needed to compare component materials to the actual painting. A record of the sample tension was made after the specimen had equilibrated to a specified RH and before the RH was reset to a new value.

The RH cycles varied from a high of 95% to a low of 5%. Tension varied with the RH in each of the materials tested. These measurements are graphically presented in figures 1, 2 and 3.

In figure 1, force developed in a paint film is plotted as a function of RH. Here the tension indicated reflects a one half inch wide specimen with the paint thickness corrected to that found in a typical painting, about .005 in. In this plot it is seen that desiccation has a moderate effect of increase in tension. Note also that at an 80% RH level and above the paint will hold no tension. In the case of this paint, desiccation increases the stress level within the sample while high RH completely eliminates it. Figure 2 shows the response of the restrained fabric sample in the warp direction. This specimen was one half inch wide. Two distinct regions of response can be seen in this figure. From about 5% RH to 80% RH there is only a slight decrease in the tensile force. However from 80% RH to 95% RH there is a dramatic increase in force. Tests conducted in the weft direction of the fabric yielded very similar results. Traditionally, RH fluctuations and the associated dimensional response of fabric supports have been suspected to be the primary sources of mechanical damage to the design layers of paintings. Figure 2 shows this to be

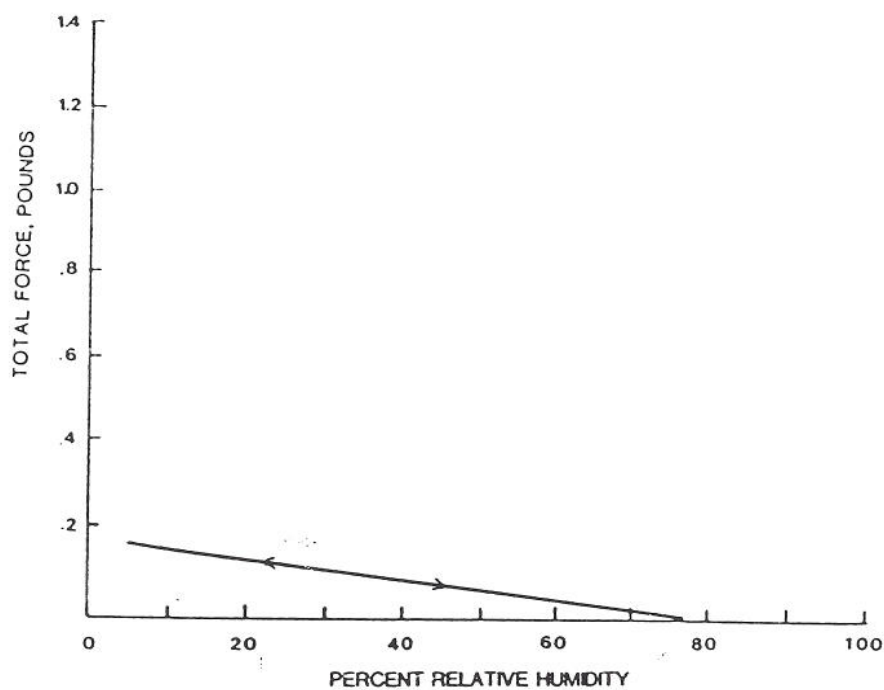


Figure 1. Restrained specimen force development vs. relative humidity at 71° F for artificial vermillion in safflower oil.

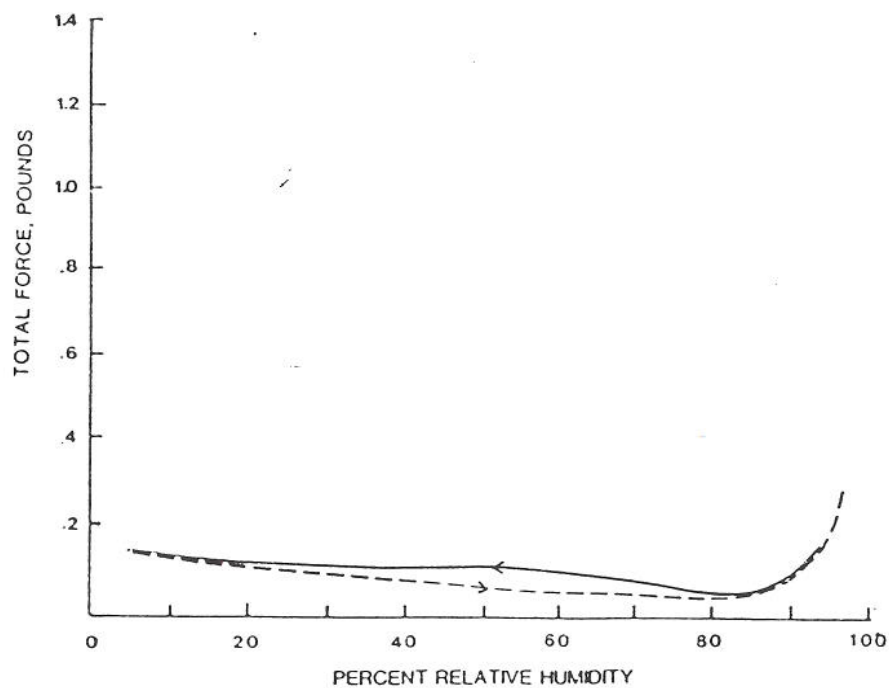


Figure 2. Restrained specimen force development vs. relative humidity at 71° F for linen in the warp direction.

the case only in the very high RH region, with very little response in the region of 80% RH and below. In other words at 80% RH and above any release in fabric restraint, such as loosening of tacks, will result in support shrinkage and in cleavage of the paint film and ground.

Figure 3 illustrates the response of the rabbit skin glue with changes in relative humidity. This plot is adjusted for a film of .00048 inches thick and one half inch wide. The increase in stress which the glue film is able to sustain under conditions of desiccation (from 80% RH to 10% RH) is quite dramatic, reaching force levels nearly six times that of the paint film alone and nearly seven times that of the fabric. As with the paint, the force nearly vanishes at RH levels above 80%. The response demonstrated by the glue film strongly suggests that this material is largely responsible for damage which occurs in paintings during periods of desiccation. In North America, wintertime heating of interior spaces without the addition of moisture to the environment can easily result in severe desiccation and consequent damage to paintings.

The data presented in figures 1, 2 and 3 are additive, so that when these data are combined the results should model the response of an actual painting constructed of a linen support, rabbit glue size and an oil ground and design layer.

Figure 4, then, is a plot of the added responses of all three materials. As can be seen, the model composite demonstrates two distinct response regions, one region from 5% to about 80% RH, and the other 80% to 95% RH. In both regions the composite exhibits considerable response to changes in environmental moisture with the highest force levels occurring at the extreme ends of the RH spectrum.

It is now possible to compare the composite plot with that of an actual painting segment. Seven by one half inch test specimens were cut from a painting, dated 1912, by the American artist Duncan Smith. This painting consisted of a linen similar to that previously described, a glue size, a white lead oil ground and a design layer composed of a thin scumble of ivory black. The painting was tested in both the warp and weft directions of the linen support, with the results being presented as figures 5a (warp results) and 5b (weft results). By comparing figure 5a with figure 4 it can be seen that the composite is an excellent model for the actual painting. The results illustrated in both figures are very similar.

While figure 5b, showing tension in the weft direction of the painting versus RH, describes results that are not quite the same as the composite, the results do reflect the behavior which was expected. In their research, Daly and Michalski find even greater differences in the different fabric

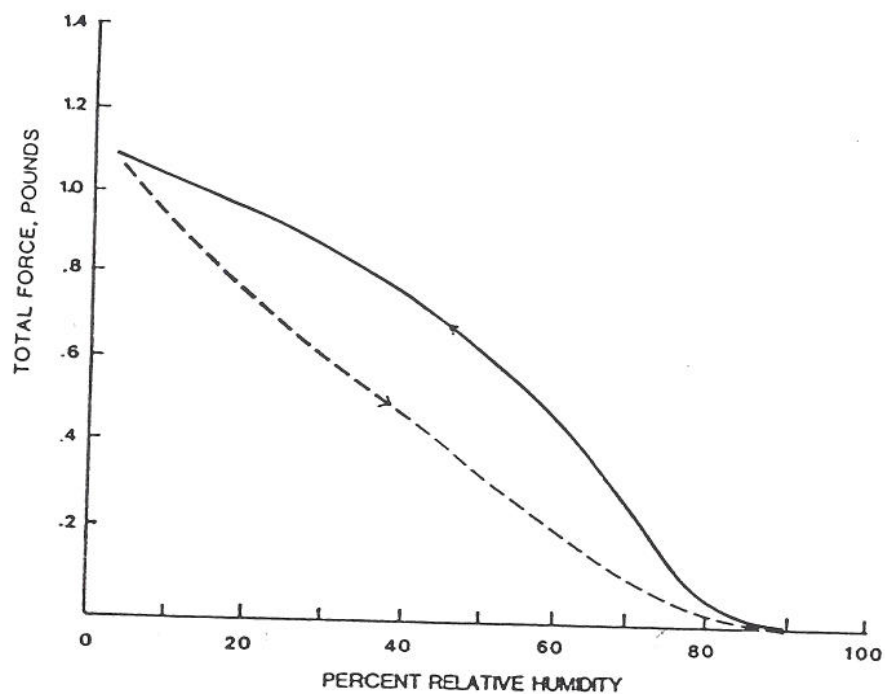


Figure 3. Restrained specimen force development vs. relative humidity at 71° F for rabbit skin glue .00048 inches thick.

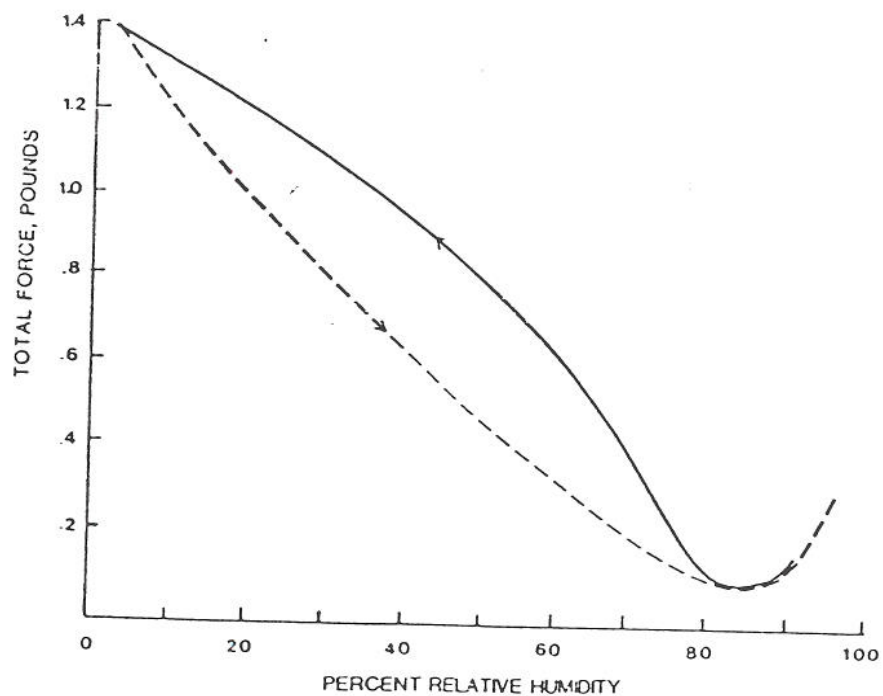


Figure 4. Composite of the data of figures 1 through 3 giving the total restrained specimen force of a model painting.

directions when conducting similar tests on their model painting. (2) It is also worth noting that the actual painting responded more severely to high RH than did the linen alone. The Duncan Smith painting chosen for this study is not unique in that the results described are indicative of any painting of similar construction. Between October 1984 and September 1985 Mr. Gerry Hedley, a lecturer at the Courtauld Institute of Art in London, spent a year at the Canadian Conservation Institute in Ottawa where he conducted similar experiments on several old paintings and prepared canvas samples. The results of his work are very similar to those illustrated in figures 4, 5a and 5b. (3) Mr Hedley also demonstrated that the residual amounts of hide glue which remain in the original fabric support after the removal of an old lining can severely increase the stress in the painting during desiccation.

What is clear is that of all of the components the glue layer exhibits the greatest changes in force over the largest spectrum of RH. Because of this dramatic behavior it is worth examining rabbit skin glue in more detail.

The main constituent of rabbit skin glue is collagen, which is a protein structure consisting of long chained, water bridged molecules. Collagen serves as one of the chief tensile stress-bearing materials for all mammals and fishes.(4) In addition to being found in innumerable forms of cultural and artistic works, when refined to gelatin it is found in photographic emulsions, medicine capsules and many food stuffs.

Collagen gains and loses large amounts of water with changes in ambient relative humidity. Figure 6 illustrates the shape of an equilibrium moisture isotherm (EMI) for this material. The specimen can be seen to lose as much as 35% of its dry weight as water going from about 85% RH to near total desiccation. Equally important, unrestrained collagen contracts in length about 3.6% when subjected to the same environmental changes as mentioned above. This is illustrated in Figure 7.

While neither the EMI nor the RH related dimensional change provide a real measure of the strength or damage potential of collagen in a painting these findings do establish a relationship between specimen size, water content and RH. Taken together, all of the previous plots provide an introduction to mechanical properties such as force, stress, elongation and strain. Stress and strain are by far the most common and useful parameters to describe the mechanical properties of materials. Stress is by definition, force applied to the specimen divided by the specimen cross-sectional area, and strain is the elongation or change in length divided by the original length of the specimen. If the relationship between stress and strain is linear, then the

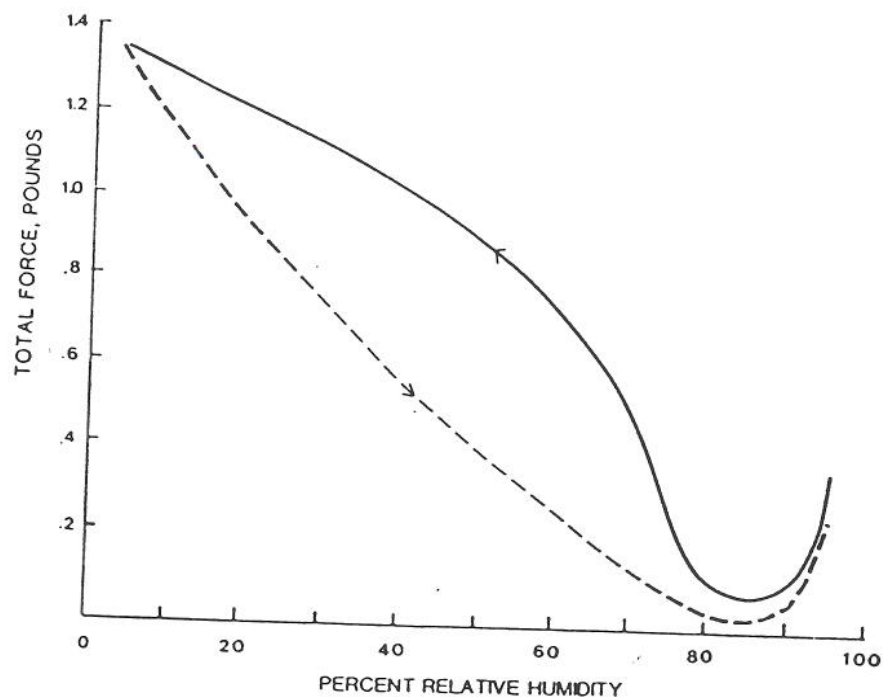


Figure 5a. Restrained specimen force development vs. relative humidity at 71° F for the warp direction sample of the D. Smith painting.

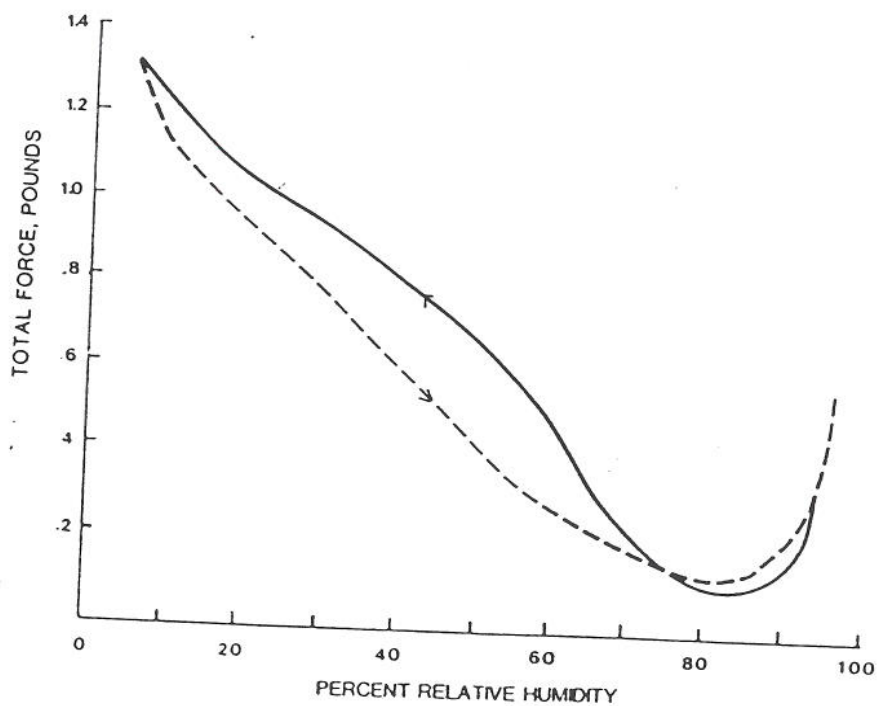


Figure 5b. Restrained specimen force development vs. relative humidity at 71° F for the west direction sample of the D. Smith painting.

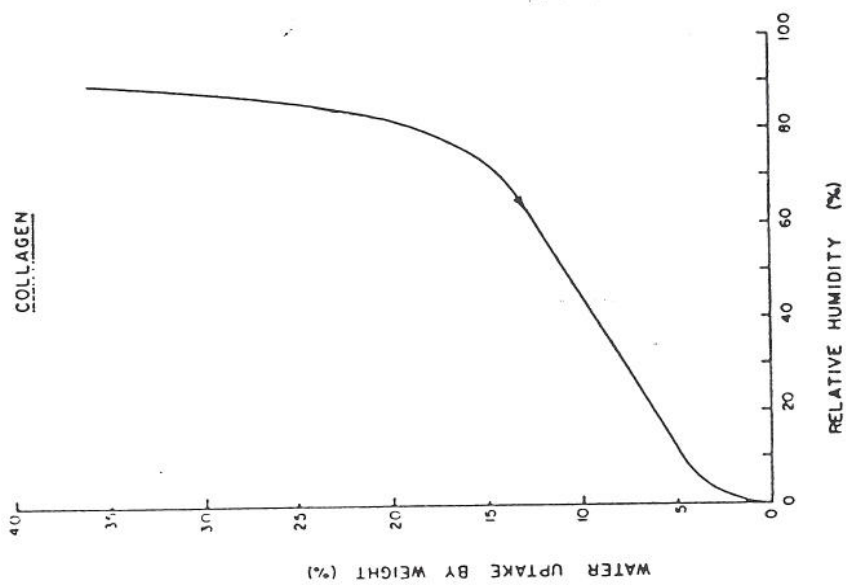


Figure 6. The equilibrium moisture isotherm for the rabbit skin glue specimen.

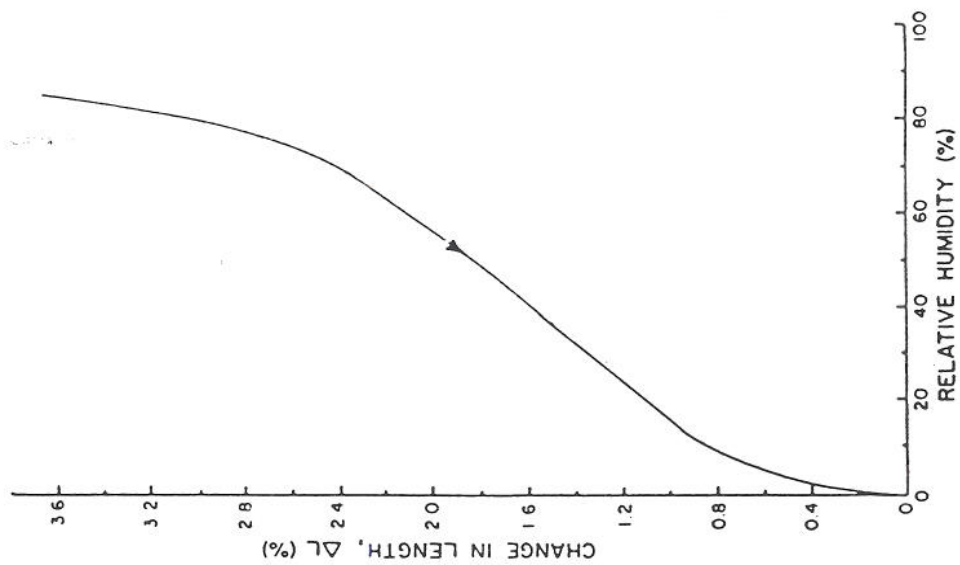


Figure 7. Dimensional changes vs. relative humidity for the rabbit skin glue specimen.

slope of a stress-strain plot is the modulus of elasticity, E . Figure 8 illustrates three stress-strain curves of rabbit skin glue specimens. Each is run over a period of about six minutes at the three different RH environments of 5%, 28% and 48%. The dotted lines drawn tangent to the origin of the plots represent the slope of the elastic portion of the curves and are, in fact, the modulus of elasticity of each of the curves. While there are differences in the modulus of each of the three plots, this difference is not as dramatic as might be expected. The plots can be considered to be the results from tests which were run moderately rapidly at their respective relative humidities. If instead a collagen strip is subjected to a fixed force over a long period of time it will "creep", or continue to elongate, either to failure or to equilibrium depending on the magnitude of the fixed force. If the same material is loaded and its length is fixed, then the force on the specimen will decay or "relax".

Figure 9 presents the results of an experiment in which the material was allowed to "stress relax" between increments of loading at the same RH values as before (5). Here the specimens were first rapidly loaded over a period of about one second and the strain fixed. Stress then was allowed to decay over a period of time until very little further decay was observed. The time required for this relaxation to take place was between 24 and 96 hours depending on the relative humidity and the amount of induced strain. All of the rapid loading paths were nearly parallel, and the relaxation points for each RH level formed well defined curves. This suggests that these curves represent "equilibrium stress-strain curves" in tension at extremely low strain rates. On the other hand the rapid loading path data are characteristic of behavior under cyclic, or impact, loading. As may be seen the differences described in figure 9 are considerably greater than those shown in figure 8.

It is clear from the above discussion that simply stretching (straining) a material, whether done quickly or slowly, will cause that material to become stressed. On the other hand, it was shown that restrained drying of collagen also induces stress. Since collagen is an important source of environmentally induced stress in a painting, further testing of restrained collagen is in order.

Figure 10 is a plot of stress versus RH for four specimens of collagen restrained at initial RH levels of 87%, 70%, 50% and 30%. The magnitudes of the stress attained by each of the samples at around 10% RH is related to its initial RH. For the specimen initialized at 87% RH, the stress reached nearly 4000 pounds per square inch (psi). If the initial starting RH was lower then the restrained specimen stress reached at 10%

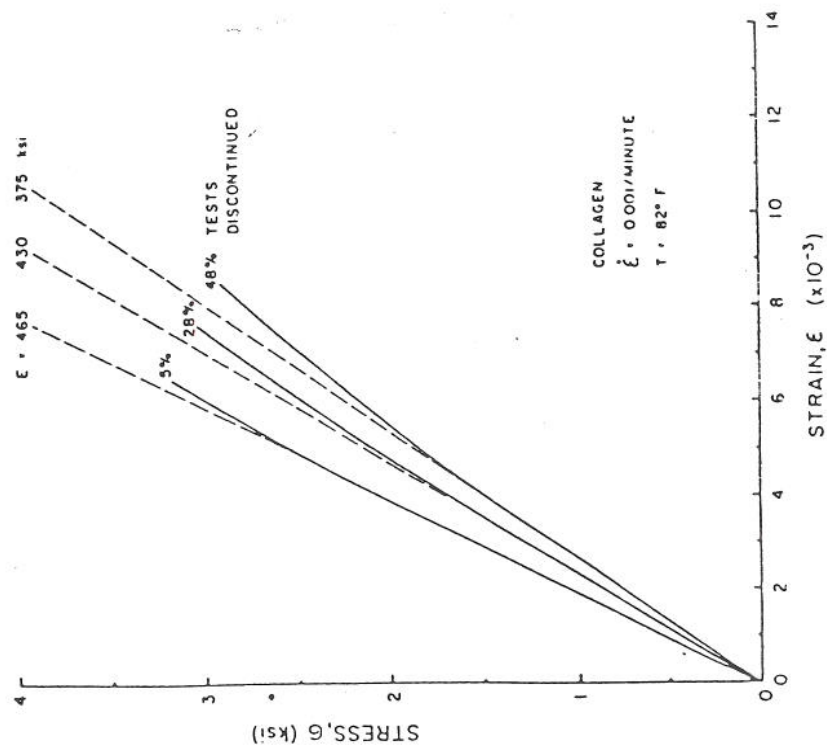


Figure 8. Rapid loading stress-strain curves for rabbit skin glue.

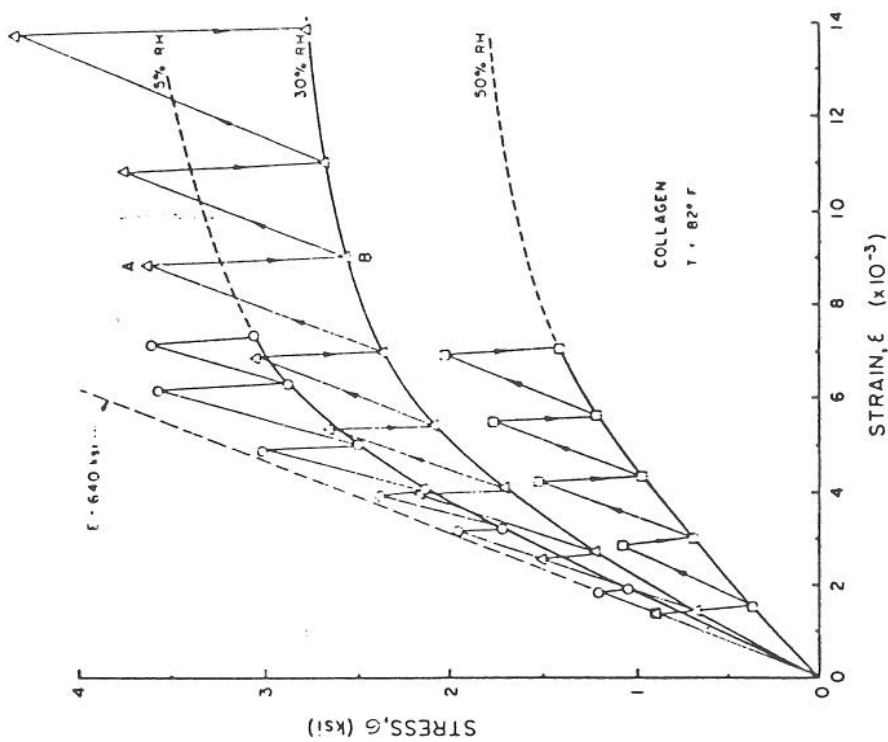


Figure 9. "Equilibrium" stress-strain curves for rabbit skin glue.

Figure 10. Restrained specimen force development vs. relative humidity for several glue specimens initiated at different relative humidity values.

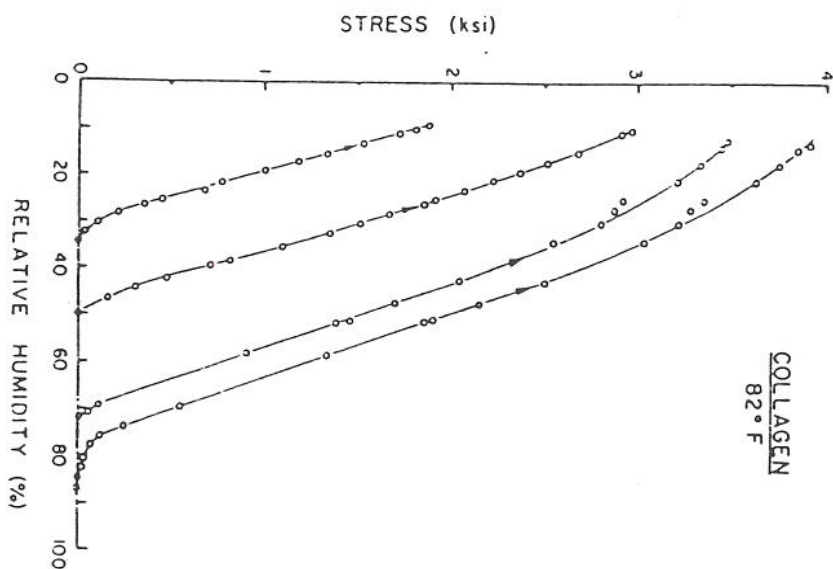
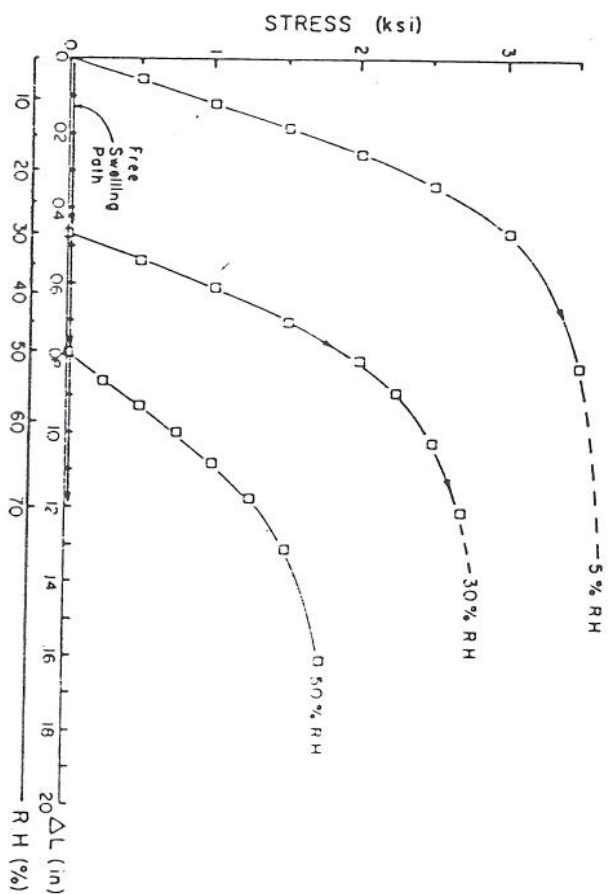


Figure 11. Equilibrium stress-elongation curves for rabbit skin glue.



is lower. If four collagen specimens of identical length had been used in this experiment, one would have found, that prior to restraining them, the lengths of the specimens, due to swelling, would increase going from a common low RH to each initialization level. In fact one would have found that the higher the initial RH starting point the longer the specimen. The actual size of the specimens could either be measured or calculated from the data presented in figure 7, length change versus RH. It can be said then, the potential for developing stress in the restrained test is related to the swelling of the specimen. The data from figure 7 are useful in another important way. The stress-strain curves of both figures 8 and 9 have been plotted in a traditional manner in that all are normalized to the origin of the graph. What these plots do not illustrate is the relative zero stress change in strain induced by different moisture content. In other words, if the origin of the equilibrium stress-strain curve run at 5% RH in figure 9 were taken as the absolute origin then the curves representing data taken at 30% and 50% would have their origins off-set to the right by the amount of elongation caused by increasing the RH levels. In figure 11 the plots of figure 9 are reconstructed in terms of stress and elongation, and have been off-set to reflect the zero stress elongation caused by RH swelling. Added to this figure is a RH scale below the elongation scale to provide further clarification concerning the starting points of the stress-elongation plots.

It is now possible to add even further information to figure 11. Any restrained desiccation test data can be added to the new diagram provided the data are initialized to the correct points on the elongation scale. Since there is no change in length, and only a rise in stress with a loss of moisture, then the restrained test data would appear only as vertical lines as illustrated in figure 12. This figure now combines the equilibrium stress-strain data, the RH induced free swelling paths, and the restrained specimen desiccation data. Along the restrained desiccation paths the points of stress and elongation at 5%, 30%, and 50% RH are indicated. It is noteworthy that these points fall close to the same values of stress, elongation and RH as measured previously by the equilibrium stress-strain curves. Although all the specimens used to generate the data for figure 12 were cast from the same lot of material, the consistency of the results is still remarkable since the results incorporate several different specimens cast at different times.

What is strongly suggested by the results of figure 12 is that a relationship exists between the purely mechanical properties of collagen and environmentally induced material behavior. This should not be too surprising since every point on this plot represents a material strain energy level at a specific RH and temperature, and these energy levels can be reached

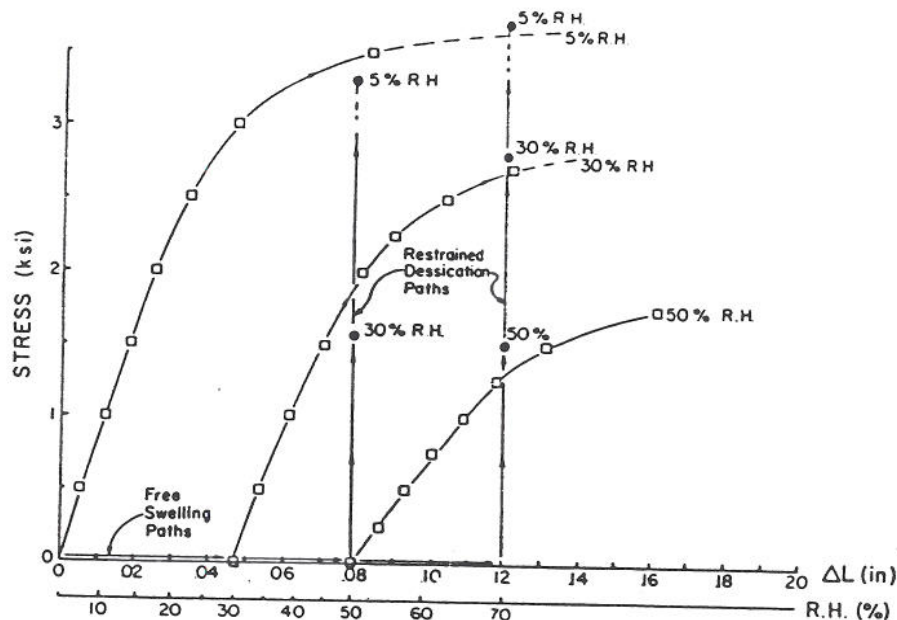


Figure 12. Comparison of tensile stressing and environmental stressing of rabbit skin glue.

by different paths, either mechanically or environmentally.

Conclusions

Cracking, cupping and flaking of the design layer of a "fabric supported" oil painting must be considered to be a result of displacement of that layer, high stress development in that layer or both.

While all of the materials found in such a painting respond to changes in environmental moisture the glue layer, or size, is the most significant, particularly in the region from 80% RH to 0% RH. This material seems to be the source of much of the mechanical damage to the paintings described during periods of desiccation.

The fabrics examined, both separate specimens and those part of paintings, showed considerable response to moisture in the region from 80% RH and above. This behavior strongly suggests that fabrics are largely responsible for damage done to paintings in wet environments.

Both material displacement and stress development can be a result of mechanical stimulus such as stretching of the painting or changes in environmental moisture. There exists a relationship between the mechanical properties and the environmentally induced behavior of rabbit skin glue such that changes in stress levels in the glue specimens are independent of the path of the stimuli.

If in fact, damage to paintings is largely confined to the high force levels shown to exist at the extremes of the RH spectrum, then future research might determine that there are central RH regions where paintings may safely be exhibited and stored.

It seems that the potential for developing stress under restrained testing lies in the degree to which the material wants to shrink upon desiccation. The magnitude of the developed stress seems to relate to the modulus of the material at any given RH.

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