

PAINTINGS—THEIR RESPONSE TO TEMPERATURE, RELATIVE HUMIDITY, SHOCK, AND VIBRATION

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ABSTRACT: *This review of the mechanical properties of paintings places the conservation literature in the broader context of the industrial paint and polymer literature. The layers in paintings that create and carry most of the tension (varnish, paint, ground, and size) are all amorphous or semi-amorphous polymers. Short times (such as shock and vibration), low temperature, low humidity, high pigmentation, and aging increase both the stiffness and the likelihood of cracking of these layers, and the unifying concept is the glassy/rubbery transition. The stiffness data on oil paints, glue, acrylics, and resins is charted in terms of this transition. Low temperature and low humidity also shrink materials, and this data is summarized. All the tension models—experimental, simple equation, and computer—are consistent in their predictions. Extreme but plausible conditions of shock, temperature, and humidity may exceed the strengths of some new materials, but unfortunately the tolerance of old and weak paintings to moderate conditions remains unclear.*

If a stream of warm and dry air enters a gallery just below the pictures, the canvases, frames, and panels become altered in shape and size each day, returning more or less to their original state each night. Thus the colored films of the painting are submitted to an injurious strain, which may end, as the binding medium of the pigments becomes more brittle, in a multitude of minute fissures, and the final flaking off of portions of the paint.

Professor Church, c. 1872¹

INTRODUCTION

For over a hundred years, most of the causes of cracking have been bandied about: humidity and temperature, expansion and contraction, strain, paint embrittlement, and multiple cycles. The symptoms were obvious—cracking and paint loss—but the causes were not: the literature to this day is marred by haphazard measurements and naive conclusions. In 1982 Mecklenburg² reported the first systematic unraveling of painting mechanics, others including researchers at the Canadian Conservation Institute (CCI) followed.³ Aside from our own slowly accumu-

lating experimental evidence, we have discovered much useful literature from disparate fields. The methodical study of shock and vibration began with several British researchers such as Sitwell⁴ in the 1980s, but the emphasis lay on crate performance. It was not until Green's⁵ work that the difficult problem of painting response was addressed, then CCI and others followed. Many of the relevant phenomena have emerged, certainly not in complete detail, but positioned in context. Other papers in this volume will examine segments of the pattern in detail, but here

I wish to map out interrelations, to sketch boundaries between risk and safety, and to demonstrate how broad the base of information has become.

The only way unequivocally to prove that we know the mechanics of paintings will be to predict and then cause specific damage in real paintings. After the "exceptionally dry weather of 1929" and increase in the "flaking and blistering" of the panels at the National Gallery, London, a study was commissioned that included ten Flemish and Italian panels of "small intrinsic value."⁶ These were sawn into strips and tested in various ways to humidity and bending. Alternatives are hindsight and modeling. In hindsight, one observes extant damage, considers all the forces that have acted on the painting, then relates the two. As will be seen, this can be a very powerful tool for humidity because, (a) there is extensive humidity damage in old paintings and (b) the history of humidity exposure can be known with reasonable accuracy. Temperature and shock allow some hindsight analysis, but vibration eludes the approach completely because large-scale exposure is so recent. Modeling solves this shortage, via experimental paintings or mathematical simulations. In any event, whether the paintings are real, almost real, or unreal, their study begins with a study of constituents.

TIME-TEMPERATURE-HUMIDITY INTERRELATION

The list of painting materials is short and familiar: resins, drying oils, egg, glue, acrylics, pigments, canvas, and wood. All the media are amorphous or semi-amorphous polymers. If rubbery they stretch without harm, but if glassy they break with very little stretching. It is this simple dichotomy—glassy/rubbery—that clarifies the interaction of temperature, humidity, shock, vibration, and age of the painting.⁷

Amorphous polymers have long, kinked molecules entangled like spaghetti. Some, such as linseed oil are crosslinked, i.e. here and there adjacent molecular strands are stapled to each other by a chemical bond. Tem-

perature of the polymer determines the degree of molecular vibration: higher temperature, more vibration. If the polymer is warm enough and tension is applied slowly enough, the molecules bump past each other enough to let their kinks straighten out. The network can be pulled to twice its length without breaking, hence rubbery behavior. Glassy behavior occurs when the molecules don't vibrate enough to bump past each other during the application of stress. Note that time and temperature are intertwined: glassy behavior can arise from either too low temperatures or too little time.⁸

The transition from glassy to rubbery is also known as the "leathery" region. From a practical point-of-view for paintings, leathery behavior is often sufficient to avoid cracking, since as the term implies, considerable stretch is possible.

In the glassy regime, about three percent elongation is the elastic limit, beyond which the polymer either cracks (brittle) or flows and then cracks (ductile). Even ductile polymers become brittle if cold enough. The brittle/ductile transition is especially important in explaining the sensitivity of some acrylics to cold. It comes about if the molecules have secondary motions that assist slippage when forced, but which eventually become too slow to help.⁹

At long enough times or high enough temperature, rubbery behavior may give way to rubbery flow. This is very important to paintings since it represents a mechanism of permanent "forgiveness" to long-term strain, such as age shrinkage. Rubbery flow only occurs in uncrosslinked or lightly crosslinked polymers: the entangled molecules don't just unkink, they slide past each other to new positions. The net effect is similar to ductile flow, but there is no minimum force required, no yield point to reach.

Some solvents plasticize polymers by entering the molecular network and disentangle through "lubrication." Thus they allow the material to behave rubbery at lower temperatures and faster times. There may be added plasticizer in emulsion paints, naturally occurring plasticizer in oil paints, and inadvertent plasticization of many materials

by humidity. Even when moisture absorption is fairly small, the effects on transition can be profound, especially in size, glue grounds, and oil paints.

EFFECT OF PIGMENTS ON STIFFNESS

Pigments and fillers stiffen the material.¹⁰ In a glassy binder the particles act as inert links between bits of polymer. Stiffness increases up to fivefold with pigmentation levels typical of artists' paints. (In leaner mixtures, stiffness decreases because of voids between particles.) In the transition and rubbery regime pigment effects are much greater. Each particle adsorbs a layer of polymer about 3 nm thick¹¹ which then acts more glassy, only the remaining binder acts rubbery. Paint manufacturers have long known that above about 30% pigment volume concentration (PVC) paints become much more brittle.¹² At this concentration, particle separation is about one-third of the average diameter, so the adsorbed layers coalesce if the particles are very fine, such as some blacks and Prussian blue (0.015 μm).¹³ Unfortunately, recipes below 30% PVC are runny, useful as glossy house paints¹⁴ but not artists' paints. Artists' paints are 30%-60% PVC if buttery. (Artists' glazes, on the other hand, are similar to enamels, 1%-20% PVC.)

Fortunately, it is unnecessary to survey artists' manuals, or to analyze samples to estimate pigment concentration in artists' paints. The very method of traditional manufacture, grinding small amounts of oil into a pile of pigment until it formed a buttery paste, became the basis of the industrial *oil absorption test* and much data is available. The test determines the mix at which binder just fills the spaces between particles, also known as the critical pigment volume concentration (CPVC). It is typically in the range of 40%-60% PVC,¹⁵ so artists' paints would have been at this ratio if stiff, or slightly lower if brushable. Glazes would be much lower, oil grounds with tooth would be slightly higher, and glue grounds (gesso) rise to 90% PVC.¹⁶

STRENGTH, ELONGATION, AND AGING

For over fifty years, the paint industry has been divided over whether to emphasize elongation at break or strength when predicting cracking. The issues become even more polarized because pigmentation generally increases strength but reduces elongation at break.¹⁷ Intuitively, we know stiff materials tend to be strong but ultimately breakable with very little "give" (elongation at break). On the other hand, rubbery materials stretch a lot, then break, all with little force. The relevance of each to paintings can only be clear when specific events are considered.

Aging tends to make paints more glassy by chemical changes: crosslinking and loss of plasticizer. Glassier materials are stronger, all else being equal, but aging also degrades microstructure. Ultraviolet in daylight or exposure to damp can notch the surface or break the pigment-medium bonds, thus weakening the paint. In lead white oil paint, for example, elongation drops from leathery to almost glassy values during the first three months of outdoor exposure, and strength increases severalfold, as expected for a curing oil film. After three months, however, strength falls rapidly, while elongation remains low.¹⁸ Microscopic flaws are developing. Thus all of the strength data on artists' materials to date must be seen as representative of unweathered paintings. Although paintings don't experience full rain and sun, centuries of moderate daylight along with the harsh cleaning of the past will have weakened them. Exactly how much needs to be studied.

Finally, time has one last effect on amorphous polymers, called "physical aging."¹⁹ The randomly arranged molecules slowly rattle into a more closely packed system, resulting in a stiffer, glassier network.

SHRINKAGE

When the humidity drops, water molecules leave hygroscopic solids. The solid shrinks by an amount equal to the lost water. In isotropic solids such as glue and paint, shrinkage of each dimension is simply one-third of

volume shrinkage.²⁰ By 70% RH, oil medium has adsorbed 2.5% moisture, one molecule of water for each molecule of oil.²¹ Since artists' paints are only half medium by volume (50% PVC), the net shrinkage coefficient between 70% RH and 0% RH becomes 0.006% per percent RH. Of course, this is an average figure. As Mecklenburg has shown, specific paints range from triple this value to one-half for lead white.²² The pigments change the water absorption behavior of the oil medium.²³ Above 70% RH, moisture clusters in the oil medium and builds up on the pigment surface, so swelling is much greater.²⁴ Paints can also show anomalous behavior on the first few cycles,²⁵ or react differently along each dimension.²⁶

For glue shrinkage below 70% RH, the various length change curves determined by Mecklenburg have slopes of 0.023-0.040% per percent RH,²⁷ whereas the weight change data implies 0.045-0.060% per percent RH.²⁸ Apparently, glue films shrink less in length than thickness, due to orientation effects during drying. If 0.03% per percent RH is taken as typical of glue, it is five times that of the average oil paint.

Shrinkage of glue ground has been modeled by the author,²⁹ consistent with the mechanical data of Mecklenburg.³⁰ The whiting particles are slightly separated by the glue bonds, not touching, so that shrinkage of the ground is proportional to these bond lengths. For typical gesso recipes, shrinkage is about one-twentieth that of glue alone, i.e. several times less than oil paints.

Wood's response to humidity is well documented and simple;³¹ therefore museums have understood its significance. Canvas, on the other hand, has caused considerable confusion, because the fabric usually shrinks when its fibers swell. In 1924, Ramsbottom (Royal Aircraft Establishment, United Kingdom)³² correctly identified that in painted canvas at moderate humidity, the paint "is primarily responsible for the tautness" whereas at high humidity "tautness is apparently dominated by the fabric and increases as the fabric further contracts." By the 1940s, industry knew that it was crimp in the woven yarns that made the textile shrink

when the fibers swelled.³³ In 1964, equations for tension in restrained fabrics appeared, along with ample data,³⁴ but it was not until Mecklenburg³⁵ presented the same arguments in 1982 that our field comprehended linen. The important fact is this: in a painting, at all but the highest humidities, linen in the warp direction is slack and in the weft direction usually slack. (Sometimes the weft threads have negligible crimp, so shrinkage in length at low humidity becomes significant.)³⁶ In most old paintings, however, the other layers in the painting generate and carry the tension. The linen just bridges the fragments.

Shrinkage by low temperature can easily be generalized: in the glassy state, polymers shrink 0.007-0.014% per degrees C (0.004-0.008% per degrees F). In the rubbery state this coefficient doubles.³⁷ The shrinkage of pigments (minerals) is typically 0.0007% per degrees C (0.0004% per degrees F),³⁸ negligible in comparison. Thus artists' paints around 50% PVC would shrink half as much as pure medium.³⁹ Overall, varnishes, media, and size, at or near their glassy state, will shrink about 0.010% per degrees C (0.006% per degrees F), artists' paints will shrink about 0.005% per degrees C (0.003% per degrees F).

Glue as a glassy polymer should shrink about 0.010% per degrees C (0.006% per degrees F) but Mecklenburg and Tumosa have measured a value at 5% RH of only 0.0025% per degrees C (0.0014% per degrees C).⁴⁰ At a fixed relative humidity, the moisture content of many hygroscopic materials increases slightly at lower temperatures, e.g. wood (but not oil media).⁴¹ In the case of wood, this "side effect" overrides thermal shrinkage completely.⁴² In the case of glue, this swelling side effect amounts to a little less than thermal shrinkage itself, a fortuitous balance. Thus any reference to shrinkage at low temperature must stipulate whether humidity or moisture content is fixed.

The shrinkage of glue ground with low temperature has not been measured, but it can be estimated. Whiting particles shrink 0.0007% per degrees C (0.0004% per degrees F). The glue bonds are typically one-

twentieth the length of the particles,⁴³ given the response of the glue, the contribution of the bonds must be only 0.0001% per degrees C (0.00007% per degrees F), i.e. negligible compared to the whitening.

STIFFNESS

Oil Paints, Oil Ground

In the 1920s, Nelson⁴⁴ began the scientific study of the mechanical properties of oil paint, first investigating the role of time then of humidity. Unfortunately, very little information appears after him until the 1950s, and by the 1960s alkyds and emulsions had dis-

placed oil as the media of interest. It is not until 1982 when Mecklenburg reported his studies of artists' oils that further data emerged.

In Figure 1, all the data on the effect of relative humidity on stiffness has been compiled on a master curve.⁴⁵ Although pigment radically alters paint stiffness as given by the pigment factor in Table 1, it does not change the shape of the curve: all oil paints double their stiffness between 70% RH and 0% RH. Above 70% RH the curves diverge depending on water sensitivity of the pigment. The least sensitive is titanium white, the most sensitive are zinc white, lead white, Prussian blue and azo red. (With complete wetting,

Table 1
Legend for Figures 1 and 2

Label No.	Description	Scale Source (Figure No. 1)
1	Artists' Prussian blue, safflower	(x 1100)
2	Artists' azo red, safflower	(x 580)
3	Artists' burnt umber, safflower	(x 370)
4	Artists' titanium white, linseed	(x 340)
5	Artists' lead white, linseed	(x 210)
6	Zinc white, linseed, 14% PVC	(x 180)
7	Artists' burnt umber, linseed	(x 58)
8	Lithopone, linseed, 20% PVC	(x 22)
9	Lead white, linseed, 21% PVC	(x 16)
10	Clear linseed	(x 1)
11	Clear stand oil	(x 1)
11E	Clear stand oil, minus leachables	(x 10)
A	Same paint as #3; TMA data	
B	Same as #6; creep data	
C	Leaded zinc, linseed; creep data	
D	Artists' burnt sienna; DMTA data	
E	Same as D, but acetone leached	
F	Same as #10; creep data	

1-5, 7: Mecklenburg 1982.

6, 8-10: Nelson and Rundle 1923a.

11, 11E: Talen; 1962.

A: Michalski 1989, unpublished.

C: Gutfreund 1965.

D: Hedley et al. 1990.

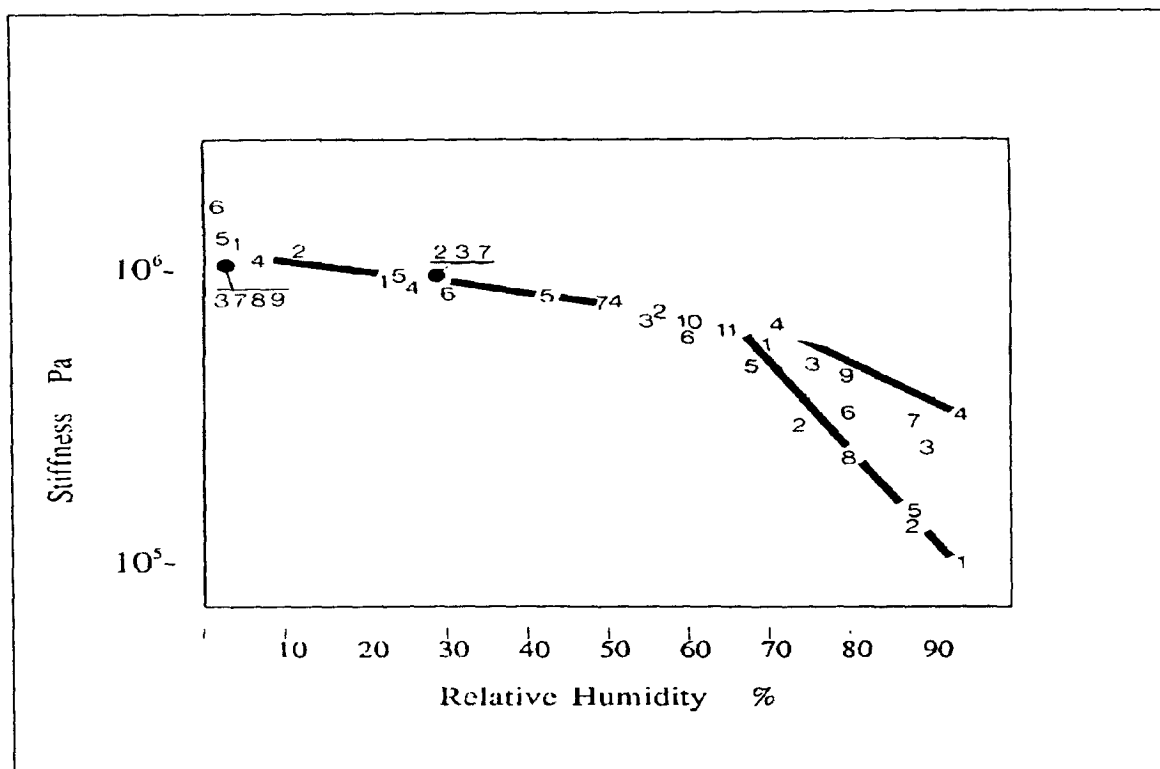


FIGURE 1
Change in stiffness of oil paints with relative humidity. Description, scale factor, and source for numbered points are given in Table 1.

zinc white is unique in its enormous swelling⁴⁶.)

Despite a spotty collection of data, the glassy/rubbery transition in oil paint can be pieced together in Figure 2. Nelson and Rundle⁴⁷ first looked at the transitions by measuring creep over time, as did Gutfreund⁴⁸ thirty years later. Brunt⁴⁹ provides the first (and only) measure of the time/temperature equivalence, and together with the creep data allows an estimate of the scales for Figure 2. Finally, in the last three years both Hedley and Odlyha,⁵⁰ and CCI have begun the modern thermo-mechanical studies necessary to clarify oil paint behavior. Complementing the mechanical data is the calorimetric (DSC) data by McGlinchey,⁵¹ which confirmed that the fundamental glass/rubber transition starts near -30°C (-22°F) and ends before 0°C (32°F) for linseed, walnut and poppy oil, with or without pigments, with or without aging.

In Figure 2 several important features emerge. Full glassy response occurs only

when linseed oil is very cold (-30°C [-22°C] for a ten-second event). The speeds typical of shock (0.01 s) are not fast enough to reach this behavior at room temperature. At room temperature, pure medium is fully rubbery but artists' paints show a stiff leathery behavior at best, especially very fine pigments such as Prussian blue. At one day to a week, a forgiving region of rubbery flow occurs in some paints (zinc white) due to the noncrosslinked fraction of the oil. This flow is not indefinite, but stops as the crosslinked portion asserts itself (much like behavior of polymer blends).⁵² As Hedley and Odlyha⁵³ showed, this behavior can be erased by leaching, and presumably by age as well. The strong "dryer" lead white shows no such flow. Overall, oil paint is leathery over a wide range of conditions. Both cold and the rapid elongations of shock and vibration will cause much stiffer behavior, but full glassy response is unlikely.

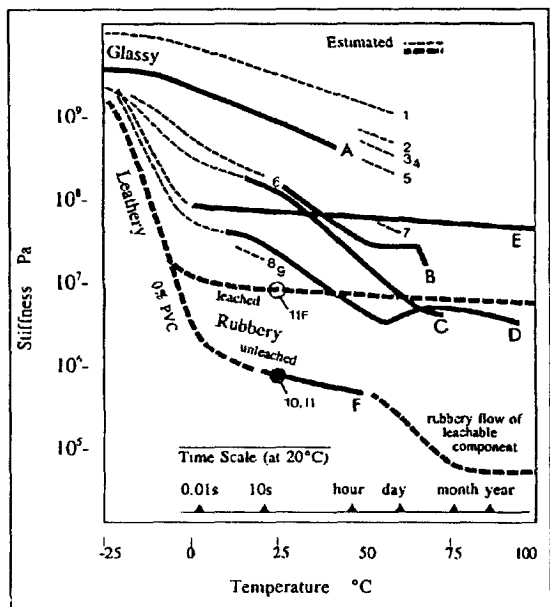


FIGURE 2
Change in stiffness of oil paints with time and temperature at 50% RH. Numbered data points and lettered graphs described in Table 1.

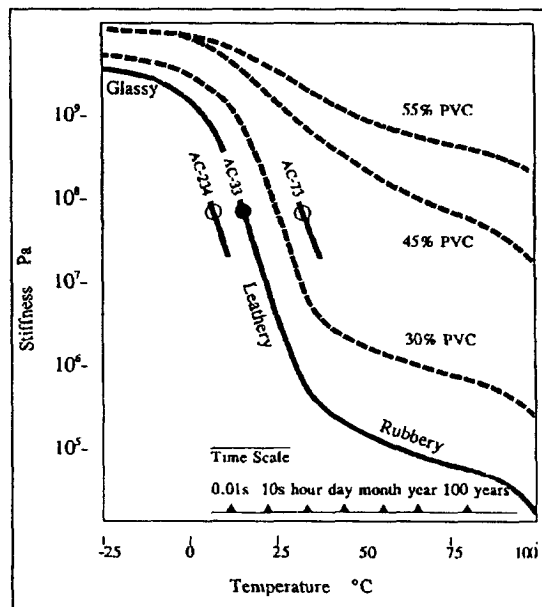


FIGURE 3
Change in stiffness of acrylic paint, AC-33, with time, temperature, and pigmentation (titanium white). Horizontal shift in curves shown for other common acrylics. (Estimated from Zesl 1980 and Rohm and Haas 1981.)

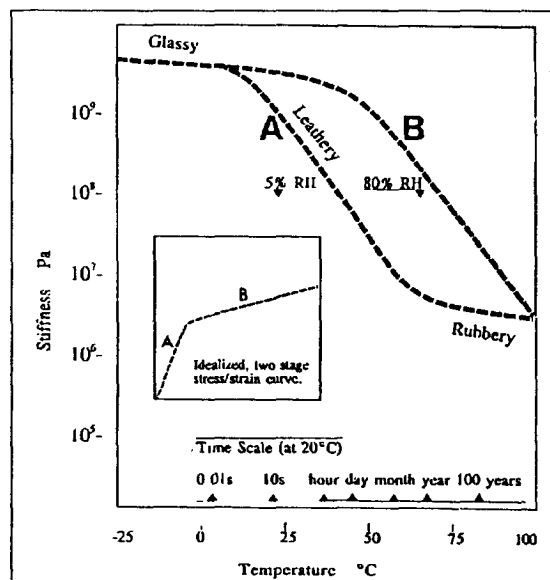


FIGURE 4
Change in stiffness of glue with time and temperature, assuming moisture equilibrium with 50% RH and room temperature (20°C, 68°F). Horizontal shift in curves shown for low and high humidity conditions. (Estimated from Yannas 1972, Bradbury and Martin 1952, Eliassaf and Eirich 1960, Ueno and Ono 1963, and Mecklenburg 1988.)

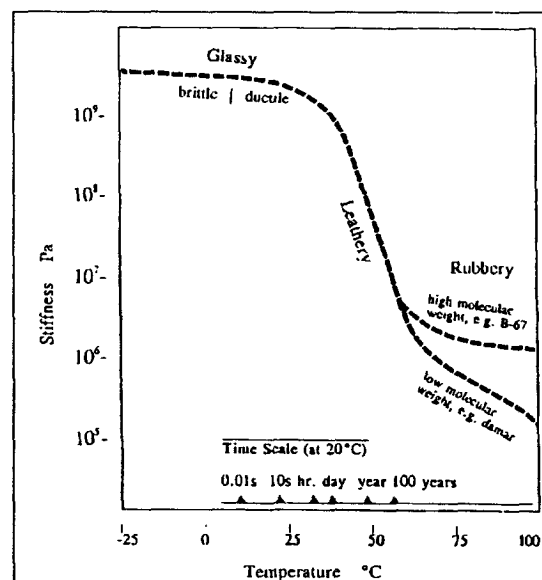


FIGURE 5
Change in stiffness of resin varnishes with temperature and time. The curve is representative of dammar, shellac, mastic, sandarac, and B-67 acrylic. (See notes 70, 71 for further information.)

Acrylic Paints, Ground

"Acrylic" refers to a family of polymers, and none of the pure acrylic polymers makes a particularly good paint medium; they are either too glassy or too rubbery. Therefore acrylic paints are formulated as copolymers that behave leathery to a moderately slow strain at room temperature. The different molecules are not just side by side as distinct chains, but combined into single chains. Although the softer component is referred to as an "internal plasticizer," it is not a leachable molecule.

Probably the singlemost common acrylic paint used over the last forty years is a copolymer of 40% methyl methacrylate and 60% ethyl acrylate, known as Rhoplex AC-33 in the United States or Primal AC-33 in the United Kingdom.⁵⁴ Based on Zosel's data for a similar acrylic, Figure 3 shows the equivalent times and the effects of titanium white pigment.⁵⁵ Stiffness increases markedly above 40% PVC and peaks at 55% PVC, the very region of artists' paints. Iron oxide red behaved similarly, but other pigments, iron oxide yellow, carbon black, and phthalocyanine blue⁵⁶ had even greater effects.

The brittle/ductile transition is known in acrylics better than any other polymer, because of studies by Wu.⁵⁷ He found it in a variety of acrylics 30°-50°C (54°-90°F) below the glass transition.

Over months and years, acrylics enter almost indefinite rubbery flow because they are not crosslinked. (Great age may crosslink them.) Together with their negligible humidity sensitivity, they should crack very little, however, artists' acrylics become glassy by about 5°C (40°F) or 0.01 s. This represents a serious vulnerability during transit, especially since acrylics seem so resilient to us at room temperature. In extreme but not impossible conditions, e.g. a .01 s shock at -10°C, the brittle/ductile transition may be broached as well.

Glue (Size) and Glue Ground (Gesso)

The behavior of glue (size, gelatin) is complicated. Stress-strain curves follow two stages,

idealized in the inset of Figure 4 as A and B. This is not a simple ductile yield curve, but as Mecklenburg and Karpowicz have shown, it is two stage elastic behavior.⁵⁸ At moderate humidity, and time periods of a day, phase B takes over near 0.8% elongation. These two phases have been plotted as separate stiffness curves in Figure 4, with the shape of the curves based on the work of Yannas⁵⁹ and their dependence on humidity and time a synthesis of Mecklenburg⁶⁰ and several others.⁶¹ Gelatin is also the only historic artists' material to have its stiffness measured biaxially,⁶² and its delamination stresses monitored during drying.⁶³ These studies confirm the approach taken by our field.

The humidity response of glue is shown as a shift in the horizontal scales of Figure 4. Both phases, though, are glassy to shock and vibration at moderate humidity. Elsewhere in this publication Mecklenburg and Tumosa report particularly brittle behavior to shock at very low humidity and low temperature, indicating a brittle/ductile transition. For humidity fluctuations, it is the fact that phase A remains glassy for months at low-to-moderate humidity that dominates response.

Glue physically ages in hours in its rubbery phase, apparently due to reformation of some of the original collagen structure or crystallites,⁶⁴ not just loss of free volume. Pharmaceutical research showed the effect in terms of increased stiffness after exposure to high humidity.⁶⁵ Physical aging as measured quickly during high humidity is important not only as a direct effect, but also as an indicator of the much slower aging possible at lower humidity.

Altogether, three separate mechanisms can increase tension in glue after a high humidity cycle.

(a) If the glue layer is prevented from swelling by an adjacent layer, it may plastically compress while soft, then try to shrink on return to moderate humidity.

(b) It may physically age, not just by compaction of a random network but by formation of crystallites.

(c) Many months prior to the high humidity

cycle, the glue may have been stretched quickly to a high tension and held (e.g. keyed-out). Over many months it would eventually behave rubbery, so the tension would disappear ("stress relax") but the elongation remains unchanged. If the glue were released at moderate humidity, the old stretch would seem "frozen in" but if released at high humidity, the glue will quickly recover the "old" stretch as well as swelling due to moisture gain.

Karpowicz⁶⁶ showed this same phenomena for "old" drying strains, as large as 5% elongation, and the author found a similar 3%-4% strain frozen in the glue bonds of gesso.⁶⁷ Given the estimates of Figure 4, it does not appear that such strains are erased by rubbery flow for centuries at moderate humidity.

The short-term stiffness of grounds has been measured by Mecklenburg.⁶⁸ A model developed from the data predicts the inter-particle glue bond dimensions as a function of recipe. A typical recipe, 85% PVC, has a glue bond length 0.05 times the average particle diameter and 0.07 times its area.⁶⁹ The net result is that gesso appears to have similar stiffness to glue, but any calculated prediction must consider whether the elongation in the glue bonds enters phase B response. Given the small relative size of the glue bond, such elongations occur at very small total elongation of the ground.

Resin Varnishes

None of the natural resins has been characterized as to the width of their leathery region, or their time characteristics, but several authors have measured the temperature of the transition by other means, and 50°C (122°F) is typical.⁷⁰ Fortunately, the synthetic resins, i.e. acrylics, have been well characterized, and their behavior is taken as representative. The curve in Figure 5, represents both the most important varnish historically, dammar, and also the glassiest of the commonly used acrylic varnishes (iso-butyl methacrylate, B-67).⁷¹ All other acrylic varnishes are softer.

Clearly varnishes are the glassiest layer in

paintings and although they might be dismissed as a sacrificial layer, the real risk lies in the initiation of cracks in the paint film below, especially with a heavy varnish. Fortunately, varnishes are not pigmented, so elongation at break can be upwards of three percent. Cold and shock may exceed the ductile/glassy transition in acrylics, whether or not dammar has such a transition is unknown.

Resin plus Oil

These mixtures were a very important part of nineteenth-century paintings, both as varnish and medium.⁷² Although the mechanical data is sparse, parts of it are remarkable. The results of Nelson and Rundle⁷³ are graphed in Figure 6. With any mixture, the glassy-rubbery transition lies between that of its constituents, and since the oils and resins are so far apart, small changes in recipe make large changes in the transition temperature of the mix.⁷⁴ In fact, the old varnish terms *long-oil* and *short-oil* refer to varnishes long on oil (over two-thirds oil) and short on oil (less than one-half oil), and these mixtures were recognized as very different compromises between hardness and flexibility.⁷⁵ The long-oil mixes in Figure 6 are in rapid transition between glassy and rubbery states, because of strong plasticization by water and because the mix has its transition at room temperature. Hess documents an example of very wide "alligatoring" in a "too short oil" topcoat over a "too long oil" primer on interior furniture. It occurred only after "one winter in an unheated room."⁷⁶ Whether it was the low temperature that embrittled the top layer or damp that allowed the bottom to enter rubbery flow, or both, is unclear. In either case, very large drying strains must have been present due to solvent evaporation, which would only arise in paintings of poor technique.

PAINTING RESPONSE TIMES

Shock and vibration cause immediate mechanical response in the painting. Since paintings on canvas resonate in the range of

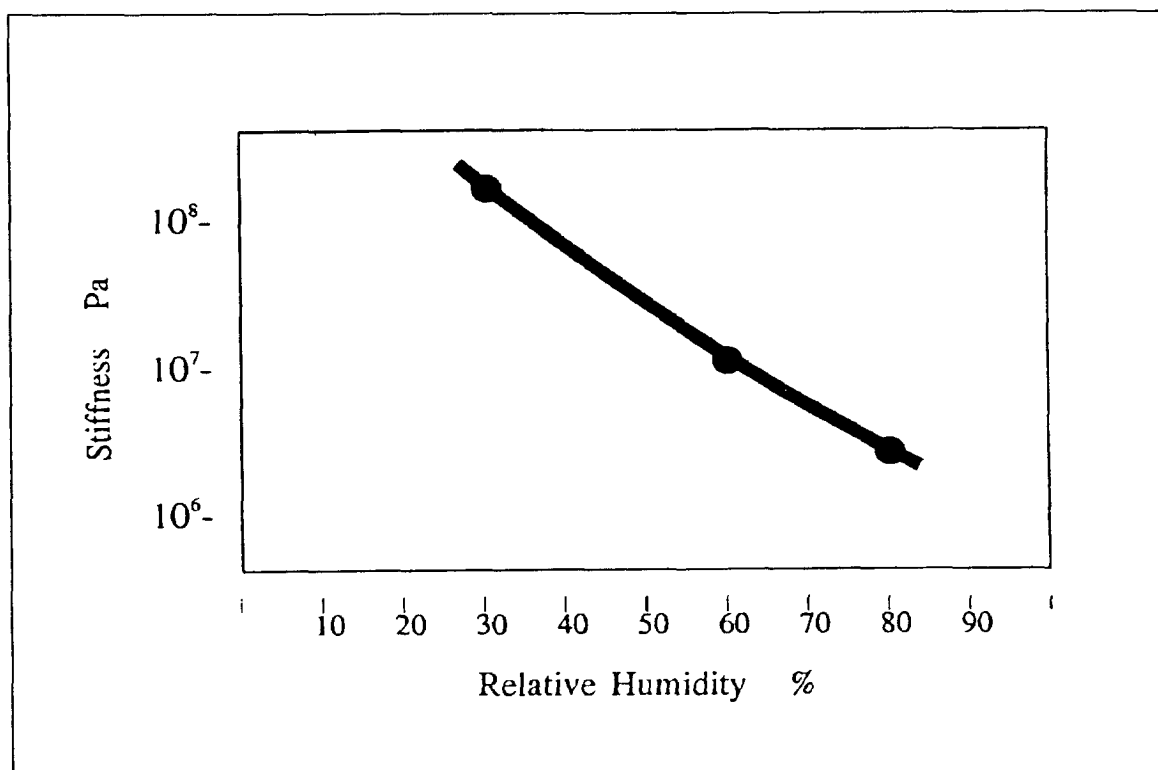


FIGURE 6
Change in stiffness of linseed oil and fossil resin mixture (2:2:1) with RH. (Nelson and Rundle 1923b.)

5-50 Hz, the duration of each tension fluctuation is on the order of 0.1-0.01 s. Shock impulses tend to the short end of this same spectrum, i.e. about 0.02 s.⁷⁷

Temperature and humidity response times are most conveniently expressed as the time required for half of full response, i.e. half-times. This has two advantages: it avoids the imprecision of the asymptotic and frequently anomalous approach to equilibrium, and it emphasizes the rapid first half of the response. As an approximation three times the half-time gives about 90% of equilibrium.⁷⁸

If thermal response times are calculated by well-established engineering procedures, the effect of thickness, the effect of room conditions, the location of temperature gradients, and many other parameters become clear.⁷⁹ Direct experiments confirm the techniques.⁸⁰ For the most common change, fluctuations of air temperature at the front, the half-time of low impasto paint and ground layers (1 mm [.04 in.]) is ten minutes. The whole paint layer warms and cools with negligible gradient, i.e.

the front and back maintain similar temperature throughout the change. A stretcher bar or wooden panel (2 cm [.79 in.]) is ten times slower, about two hours, and experiences some gradient (20% of total). If heating occurs by radiation, e.g. direct sunshine, these times will be much shorter and gradients very steep. Once inside an insulated crate, paintings follow the response time of the whole crate, which tends to be many hours, as discussed by Richard elsewhere in this publication.

The moisture response times can also be calculated⁸¹ and confirmed experimentally.⁸² Unlike the response to temperature, the response of different layers to humidity varies considerably. For practical purposes, however, the hygrometric half-time of linen, size, and glue ground ranges from minutes to hours, that of oil grounds and paints, hours to days, and finally stretcher bars and panels, days to weeks. Also unlike temperature, the most influential side of the painting is the back. In paintings on canvas, the linen and

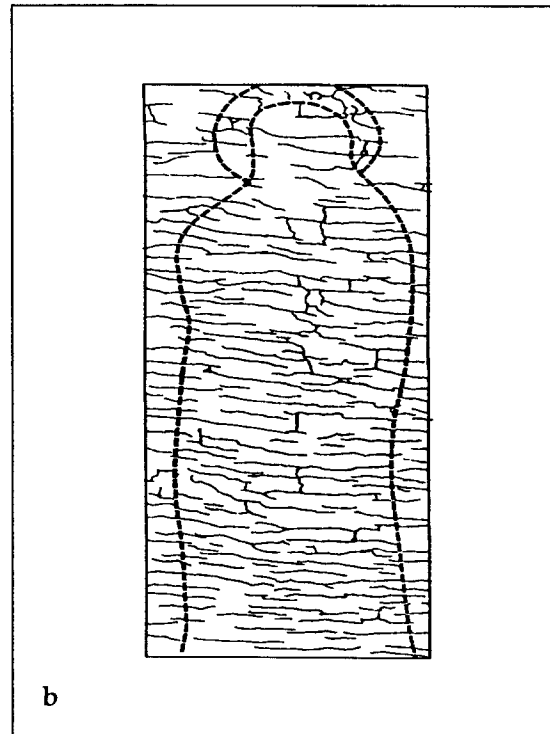
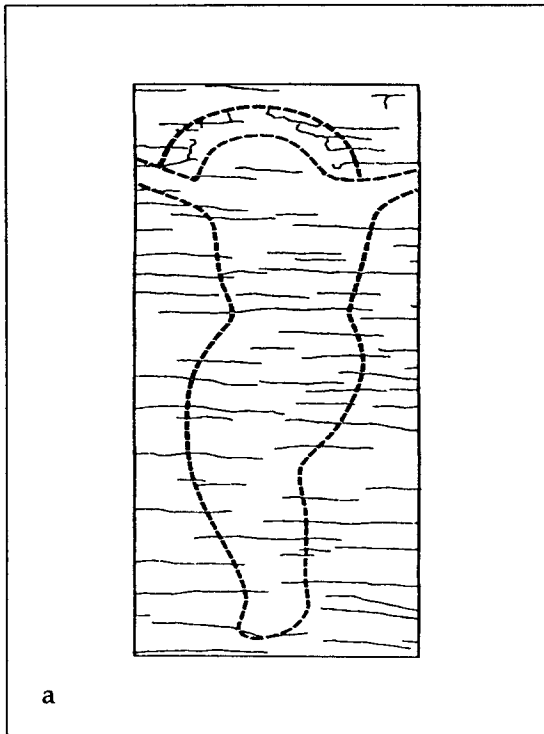


FIGURE 7
Visible cracks in parts of Di Cione's *The Crucifixion* (fourteenth century, egg tempera, glue ground, panel) National Gallery, London. (These drawings were made from photographs contained in Bomford et al. 1990.)

size layers respond in minutes if air circulation is good, but historically a painting on a wall, or with a partial backing board in a leaky crate, would take up to an hour or more to respond due to restricted circulation.⁸³ A tight backing board, tight bag, or tight crate can increase this time to days and weeks.⁸⁴ Similarly in panels with uncoated backs, the moisture response will penetrate the back significantly within a few hours, although half-time of the whole piece is days.⁸⁵

PATTERNS OF TENSION AND CRACKING

Extant Cracks in Paintings on Wood and Hardboard

The most striking feature of cracks on panel paintings is the rectilinear pattern, oriented

by the wood grain. The primary cracks run perpendicular to the grain, as in Figure 7a. Repeated here is a brief explanation of conclusions by the author:⁸⁶

(a) During any exposure to damp, (including the original application) the gesso is swollen, soft, and stress-free.

(b) Upon returning to the average humidity of the wood below, the gesso attempts to shrink, but cannot; tension arises in all directions.

(c) When both wood and gesso react to lower humidity, the wood shrinks across the grain and releases tension in the gesso, but not along the grain, hence, cracks form across the grain. Panels may also show secondary cracks along the wood grain (Figure 7b).

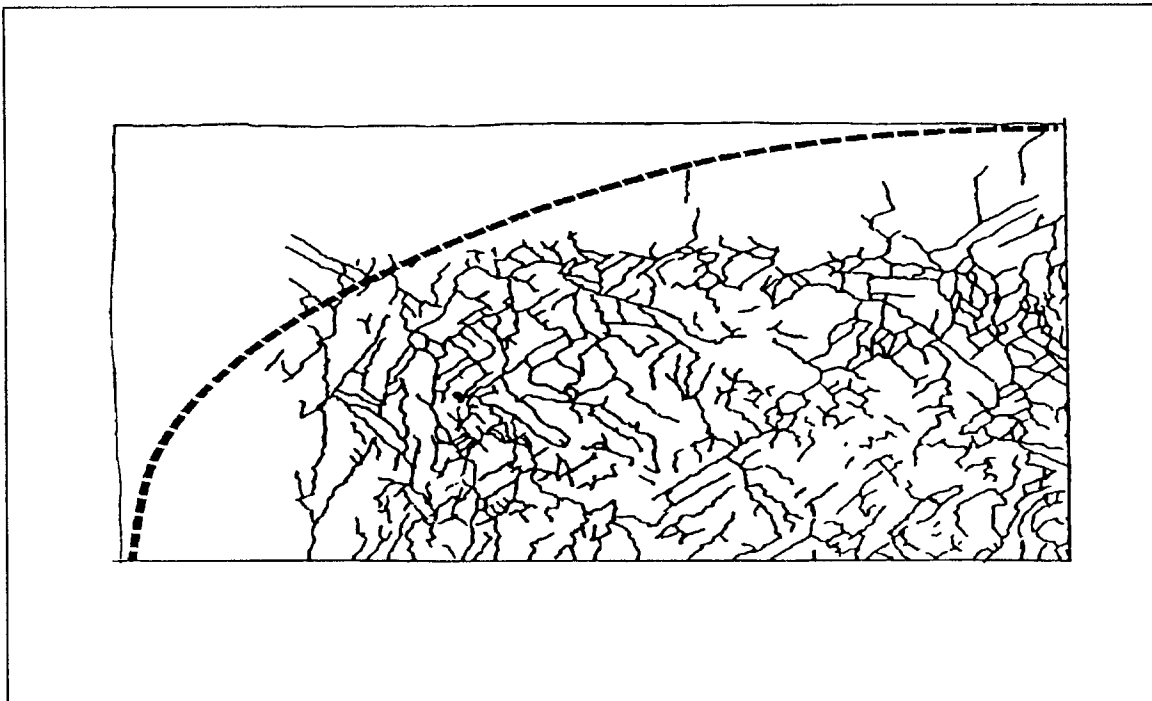


FIGURE 8

Visible cracks in top left quadrant of Krieghoff's *Jam of Logs on the Little Shawinigan* (nineteenth-century oil on canvas) Rideaugate, Ottawa. The dotted line represents the edge of the painted area and the edge of the oval frame liner.

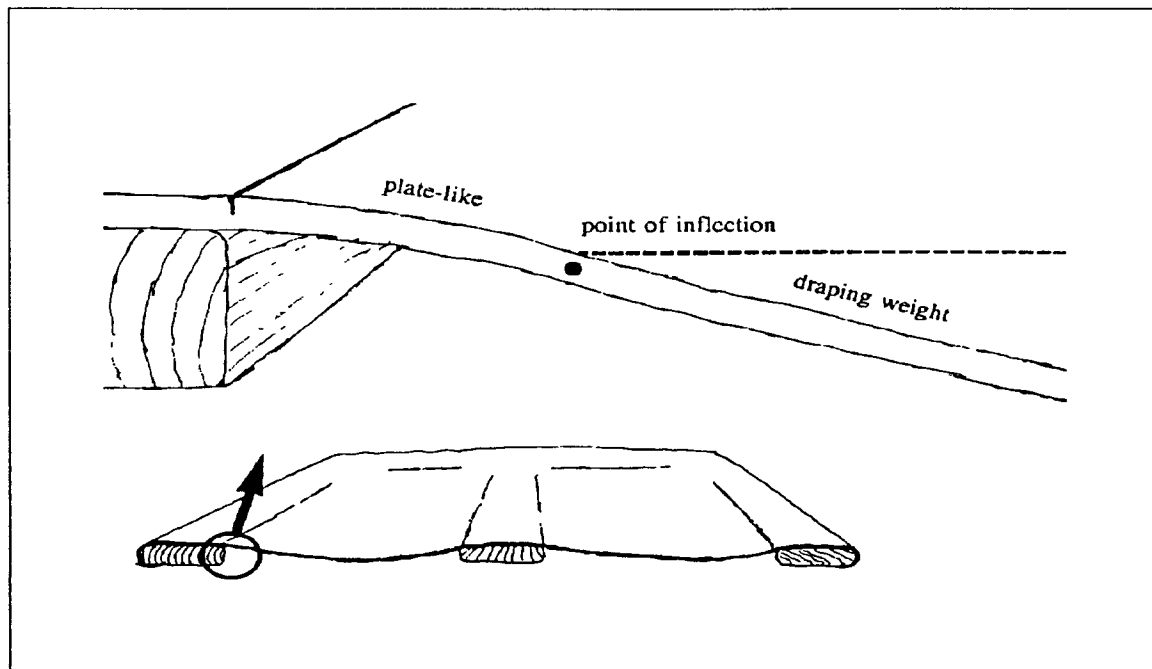


FIGURE 9

Cross section through a sagging painting on canvas. The painting drapes over most of its length, but near the bars it acts as a thin, stiff plate.

As noted by Hodge⁸⁷, a T-junction in cracks must have formed the top of the T first, so in Figure 7b the primary cracks formed first as in Figure 7a, then the strips of paint broke from side to side. The patterns in Figure 7a and b are particularly interesting because they come from the same piece of wood in Jacopo Di Cione's altarpiece, *The Crucifixion*.⁸⁸ Areas of the panel dominated by gilding, such as the sky and Christ,⁸⁹ respond to humidity primarily from the back of the panel, so the wood shrinks first, then the gesso reacts. Areas of gesso unprotected by gilding can react before the wood, so tension forms in both directions. Since gilding cannot influence any other agent so profoundly as it does humidity,⁹⁰ gilt panels like *The Crucifixion* are especially useful in establishing the historic importance of humidity to crack mechanisms.

In a description of Botticelli's *Primavera*, oil/tempera on glue ground,⁹¹ Baldini indicated that "all the paint layers seemed to be cracked and in poor condition, but the actual damage was found to be mostly at the level of the oldest varnish."⁹² This is not unusual, indeed cracks in varnish often run across the wood grain much like gesso cracks, but with much closer spacing. As to the paints, Baldini notes that the vegetation (mainly malachite) contains only fine, horizontal cracks.⁹³ Thus varnish, some paints, and ground all show the same primary crack pattern, but with variable spacing. The flesh tones in *Primavera* (mainly lead white) cracked quite differently: meandering primary and secondary cracks, or areas of fine cracks unrelated to the wood grain.⁹⁴ Many Y-junctions occur, which are the start of cracks, not the end like Ts. Lead whites had a poor reputation for checking in house paints too,⁹⁵ and these checks were often independent of wood grain. The stress cycle responsible for such independent cracking must be either faster or much larger than the cycling due to the wood, and specific to lead white. One fast possibility is overnight dewfall, not uncommon in historic buildings in Europe.⁹⁶ Alternatively, the problem may be lead white's inability to enter rubbery flow after curing (see Figure 2). Curing paints can develop up to three percent shrinkage,⁹⁷

easily the dominant stress if never dissipated.

Modern panel paintings are frequently on 0.6 cm (0.25 in.) hardboard. Unlike wood, hardboard shrinks uniformly in all directions when humidity drops, causing random directional cracking. The ground delaminates easily if painted on the smooth side so cracks tend toward wide separation (1 cm-5 cm [0.5 in.-2 in.]) with no cupping and large-scale blind cleavage.

Extant Cracks in Paintings on Canvas

Virtually all paintings on canvas crack, and the only universal characteristic is some relation to the stretcher bars behind. Two features arise: cracks may be reduced over the stretcher bars, and a prominent crack may form along the stretcher bar edge. The author observed a clear example of crack reduction in Cornelius Krieghoff's *Jam of Logs on the Little Shawinigan* (oil paint, oil ground, Figure 8). This is a good example for two reasons: the pattern shows no influence of the oval image, therefore only the linen, size, and ground are relevant; and it shows no crack along the stretcher bar. Therefore, stretcher bar crack has a different set of causes from crack reduction (though some causes may overlap).

Historically, the most common temperature and humidity fluctuations were diurnal. As discussed in the section on response times, the stretcher bars have a temperature half-time of two hours (or less if radiated heat) whereas their humidity half-time is many days. Over the course of twelve hours, the humidity in the small gap between the bars and the canvas would change only a small fraction of the fluctuation in the room,⁹⁸ so the size, ground, and half of the paint would be protected from the diurnal humidity cycle, but not the temperature cycle, as some have proposed.⁹⁹ Of course, paintings with a considerable gap between the bar and the canvas, or with lean, permeable paint layers, would show less and less benefit from the bars. The Krieghoff had an oval gilded frame liner that moderated humidity from the front, hence the exceptional condition in the corners. Although different

humidity scenarios could explain the cracks, all point to the benefits of stable humidity, especially at the back of the painting, hence the value of airtight backing boards. In another location, a fine spiderweb crack pattern with no out-of-plane deformation is noted with a dimple of similar radius nearby showing no associated cracking. These damages represent glassy and brittle behavior in one instance and rubbery flow in another. The spiderweb crack may have been caused by a quick blow (0.01 s) from a blunt object at 5 °C (40 °F), and the dimple may have been caused by a hook from another painting pressing the painting while stacked in storage. In the first few minutes, the entire painting would have stretched elastically, but over many days, rubbery flow would occur. These incidents represent the two extremes in oil paint behavior (see Figure 2).

Although stretcher bar crack might result from the discontinuous humidity response, simple bending against the bar is more likely the cause. Historically, bending probably occurred when the painting was leaned against a wall, or held horizontal. In Figure 9, the loose painting drapes. Near the stretcher bars, however, it resists bending (Figure 9). The distance over which this inflexible behavior persists can be estimated as the point of inflection shown in Figure 9, and the strain in the paint at the edge of the bar can then be calculated.¹⁰⁰ For a medium-size painting (1 m [3.3 ft.] wide) of low impasto (0.1 cm [0.04 in.] horizontal and loosely sagging in the middle by 1 cm (0.4 in.), inflexible behavior acts for 7 cm if all layers are glassy, and elongation reaches 0.08%, not enough to crack in one event. Changing all layers to a typical leathery oil paint value shortens the inflexible distance to 1.6 cm and increases paint elongation to 0.36%, not enough to crack leathery paints. If, however, the painting is dropped a short distance on its back against the wall or floor, even 10 cm (4 in.), the effective weight of the painting increases forty times for one moment,¹⁰¹ and paint can crack along the stretcher bar. Booth describes several improvements for old and new stretchers that the Tate Gallery has used to avoid such damage; they are blind stretchers, pan-

els, loose lining, and chamfering.¹⁰²

Modeling of Humidity and Temperature Effects

The first useful model of paintings on canvas was developed by Mecklenburg¹⁰³ for tension versus humidity. Having measured the humidity dependence of each painting material as noted above, he calculated the tension in each layer and summed them. Despite being the simplest form of laminate model (additive elastic equilibrium) it predicted the tensions he then measured in a strip of a century-old painting. The success lay in his appropriate time scale: measurements were carried out over several days, so that the oils reached equilibrium in the rubbery plateau, while the glue remained glassy. Hedley¹⁰⁴ carried out similar measurements on other old paintings, confirming the model. In particular, he demonstrated the dramatic difference in pre- and postindustrial linens, due to the differences in crimp, as shown in Figure 10.

The paint industry has also begun modeling the effect of humidity and temperature on paint tension. Perera and Vanden Eynde¹⁰⁵ have not only produced graphs identical to those in Figure 10 for paintings, they have shown the same effect for decreasing temperatures. Bender¹⁰⁶ monitored tension in a stretched, two-coat paint layer. He demonstrated that the glassier layer dominated tension and that percent relaxation over time was independent of thickness. Although these studies do not use orthodox artists' media, their analogous results and emphasis on glass transition complements the approach taken by our field.

Daly and Michalski¹⁰⁷ modeled paintings physically with samples prepared in every stage of completion to compare the effect on each additional layer and different media (see Figure 10 for some of the results of this modeling). They demonstrate the negligible response of acrylic to low humidity. The short-term results resemble other studies, but the long-term data indicates new effects.¹⁰⁸ First, the tension dropped significantly over the first year as the glue and acrylic entered

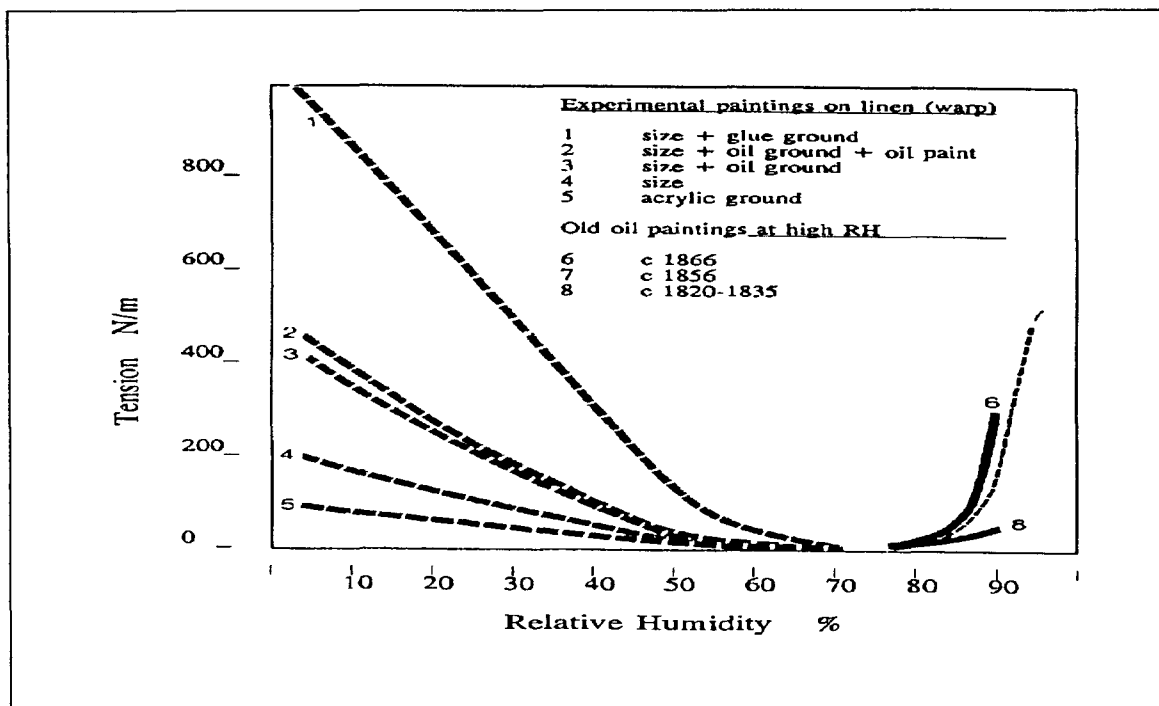


FIGURE 10
Change in tension of paintings with relative humidity. (From Daly and Michalski 1987 and Hedley 1988.)

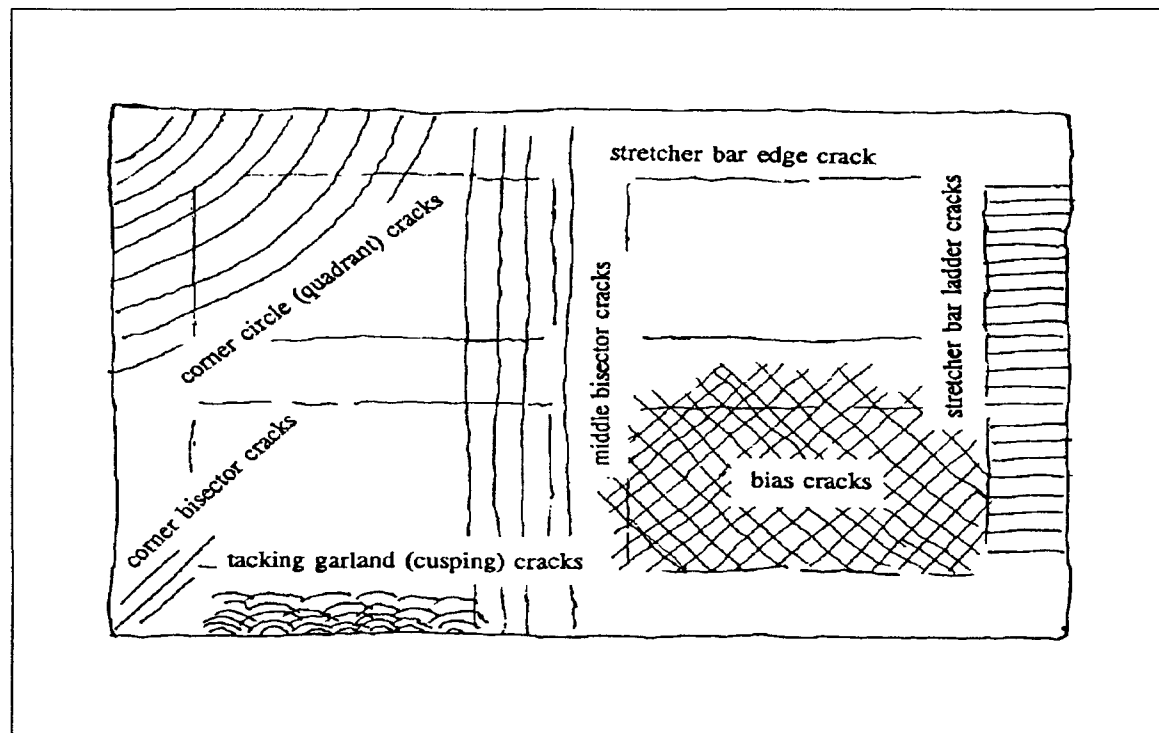


FIGURE 11
Typical large-scale crack patterns in paintings on canvas.

rubbery behavior. As a result, the oil assumes a larger proportion of the tension. (The samples were never taken above 70% RH over the years so the glue was not “reset” in tension.) Second, the tension began to climb after the first year, which in the oil, probably represents further curing. In the glue, it implies that physical aging supersedes any tendency to rubbery flow at these conditions (50% RH, 21 °C [70 °F]).

Berger and Russell¹⁰⁹ published considerable tension data from model and old paintings. Their early data from linen primed with an epoxy/gesso mixture shows little humidity response until the linen gets damp,¹¹⁰ but some response to temperature, as expected for a coating dominated by epoxy. Indeed, the response to a large temperature shift agrees with the work on epoxies by Shimbo et al.¹¹¹ Later results by Berger and Russell¹¹² with acrylic and oil paint conform to the humidity response pattern in Figure 10.

Computer modeling was first introduced for paintings in the work of Colville, Kirkpatrick, and Mecklenburg.¹¹³ Their humidity model predicted most of the initial stages in the crack pattern of Figure 11 that shows tacking garlands (cupping), keying-out cracks, parts of the circular corner cracks, and the orientation of center cracks parallel to the short dimension. It was a powerful proof not so much of the method (common engineering by then) but of the assumptions and material coefficients Mecklenburg had provided.

Modeling of Shock and Vibration

Virtually all the published work appears in this volume. Unlike the modeling of humidity, modeling of shock and vibration often leads to the unfamiliar, so its validity will depend on the reliability of the method rather than the emergence of familiar cracks. Fortunately, the success of the humidity and temperature models helps to provide this reliability.

If elongation or stress is applied in many small cycles, such as vibration, a crack can grow by imperceptible increments until it reaches a critical length, then sudden breakage occurs. Figure 12 graphs the number of

cycles to reach this sudden breakage in a glassy acrylic, both as pure medium, and as a mix with whiting, similar to ground.¹¹⁴ The critical feature of Figure 12 is the threshold below which the material will tolerate almost indefinite cycling. In these and the many other polymers that have been studied, the threshold plateau begins at about ten million cycles. In terms of stress or elongation, the plateau does not occur lower than about one-fifth of the values for cracking in one cycle.¹¹⁵

Of course, these values are for flawless pieces, the effect of existing cracks cannot be analyzed without considering specific structures.¹¹⁶ At CCI, fatigue tests of model paintings are underway, starting with sized linen canvases (61 x 76 cm [24 x 30 in.]) brush-coated with an unusually lean glue ground (93% PVC). One was vibrated to an amplitude of 4 mm (0.16 in.) at its resonant frequency for one-hundred million cycles (25 Hz, 20 days). No cracking and no change in resonant frequency was observed. This result is plotted on Figure 12 as a point of “no effect” in terms of the approximate elongation in the ground.¹¹⁷ The same painting was then vibrated 9 mm (0.35 in.) and showed no effect at one-million cycles (28 Hz, 6 hours) but between one- and ten-million cycles extensive cracking developed throughout the central region, and resonant frequency fell to 19 Hz. Stretcher bar cracks also developed at the middle of each long side, where the canvas had slapped the bar edge. It is important to realize that this study was an attempt to locate the fatigue threshold, even if it required vibration levels far in excess of transit environments, which it most certainly did (2.5 G, 28 Hz continuous). Even the vibration that fell below threshold was extreme (1 G, 25 Hz continuous). Thus, a painting with the most conceivably brittle layer, vibrated continuously for three weeks at levels possible only with no cushioning and terrible transit,¹¹⁸ showed no damage.

Real panel paintings were incredibly “vibrated” in the 1931 National Gallery, London study.¹¹⁹ Although forced much slower than any natural resonance of the panels, the bending was carried out for a significant ten-thousand cycles (pieces cut from one Flemish

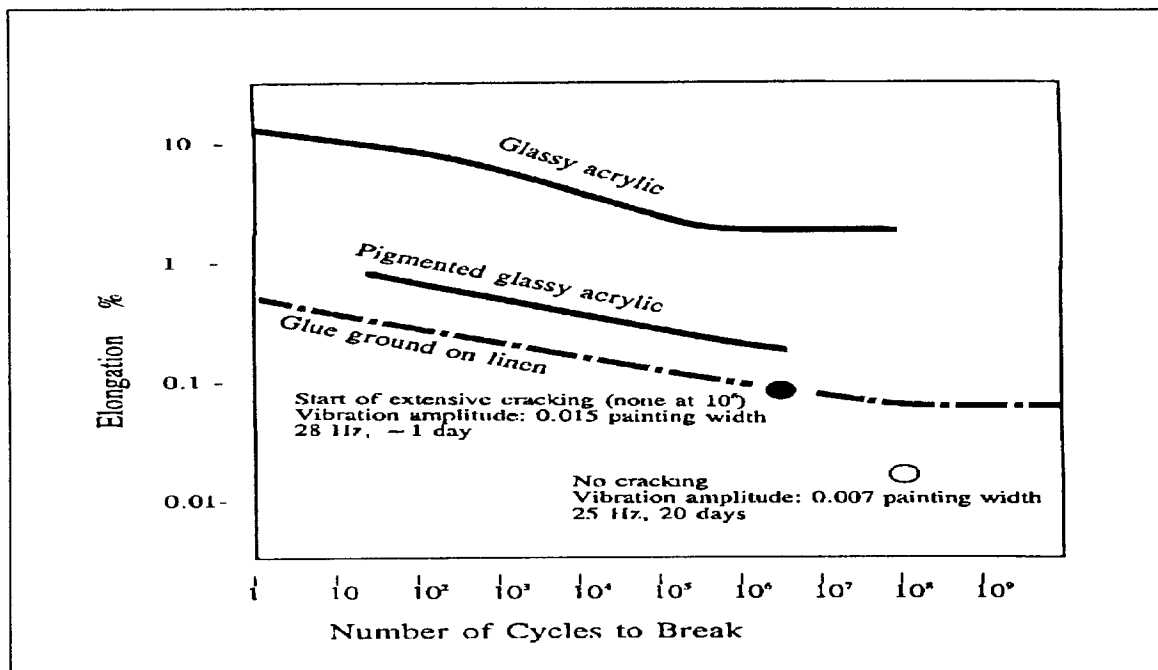


FIGURE 12
Number of cycles and elongations necessary to crack glassy materials by fatigue. (Acrylic data cited in Hertzburg and Manson 1980, gesso data by Michalski, CCI.)

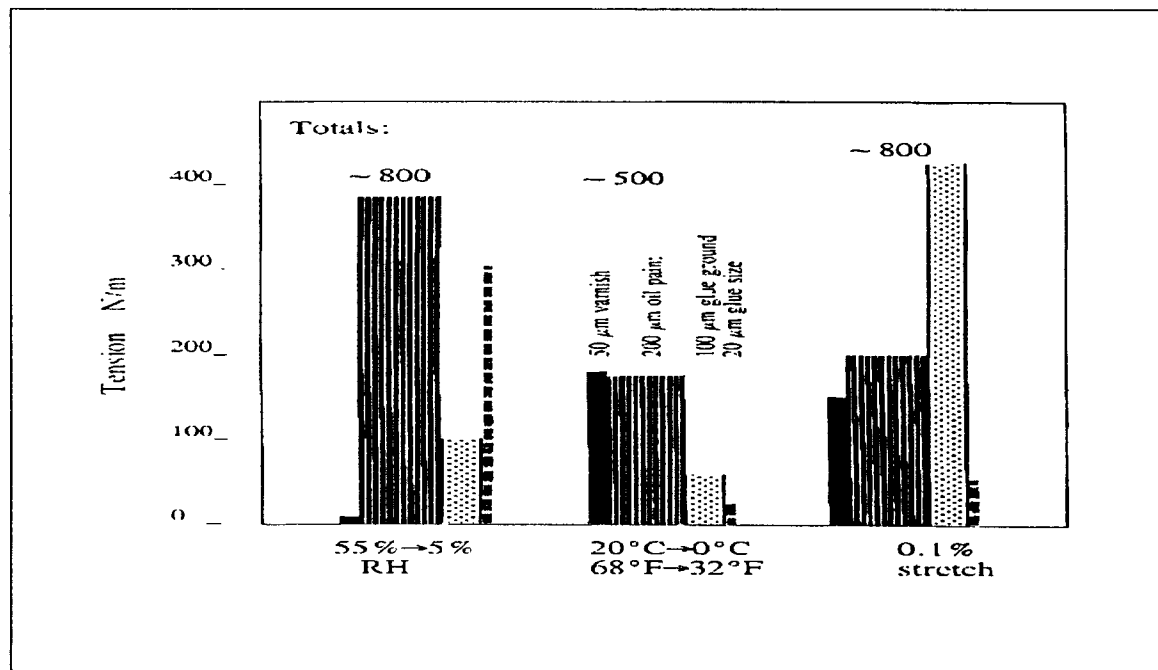


FIGURE 13
Histogram of tension increase in each layer of a "typical" oil painting after a drop in humidity, drop in temperature, or increase in stretch. This degree of stretch may occur by slight keying-out, moderate shock, or extreme vibration. It also occurs as a reduction in stretch when stretcher bars equilibrate to low humidity. Thus a painting exposed to daily low humidity increases tension as shown on the left, but if the low humidity is sustained for many days, this high tension is reduced by the approximate amounts shown on the right.

and one Italian panel, c. sixteenth century). No flaking or blistering was produced, despite bending of the same amount as the warping in the humidity tests. The researchers were surprised because the humidity tests had produced considerable damage, but the misconception lay in blaming curvature itself. It is the elongation of the paint that counts, and in this test as in any vibration of panels, it would have fallen well below threshold for fatigue. Vibration of panels, just as with canvas, remains a problem of indirect effects: abrasion, slapping, and dislocation of loose fragments.

Drop tests with experimental paintings modeled by Marcon and computer modeling by Mecklenburg (elsewhere in this publication) show some unprotected corner drops to be catastrophic to paintings on canvas. During impact, momentum forces the stretcher bars to scissor, which in turn stretches the painting violently. Thus, there are several unfortunate ironies in painting mechanics—the stretcher becomes a liability and not a support during impact, the canvas provides little support during humidity and temperature fluctuations, therefore the layers applied by the artist support the image both figuratively and literally.

Summary of Modeling

Some general equations emerge for tension in paint layers:

- (a) *Painting tension*=sum of tensions in each layer
- (b) *Each layer tension*=sum of tensions from all previous events
- (c) *Tension from each event*=(shrinkage or stretch) \times (stiffness for that humidity, temperature, and time interval)

Shrinkage occurs at curing, then later by physical aging and chemical aging (loss of mass). Fast shrinkage occurs with humidity drop and temperature drop.

Change in stretch of canvas paintings can be caused by keying-in/out, dilation of the stretcher bars with humidity change, slippage in the linen between cracks, shock, and

vibration. For panels, expansion of the wood stretches ground and paint.

In Figure 13, these equations have been applied to a theoretical model painting. It contains a natural resin varnish, a low impasto oil paint, a glue ground, and a size layer. The linen layer is ignored because usually it contributes nothing. The painting is assumed to have no tension in any layer at 55% RH and 20°C (68°F). Then three different events are modeled; drop in humidity to 5% RH over the course of one day, drop in temperature to 0°C (32°F) over the course of one hour, and stretching of 0.1% over a period of one second. The various parameters are taken from the data presented as typical values in this review. The oil paint is assumed to be one of the stiffer varieties (see Figure 2), and the resin varnish is assumed to have little response to low humidity. Figure 13 illustrates several key points:

- (a) Humidity, temperature, and stretching (shock and vibration) can cause similar total tension, but the individual layers responsible vary markedly.
- (b) At low humidity, the tension is mostly in the oil paint and the thin glue layer.
- (c) The only layer to come anywhere near its elongation (or stress) at break as a new material is the glue ground at 0.1% stretch. Thus any stretch phenomenon is risky, e.g. shock, vibration, and keying-out.

Some crack patterns have been predicted by modeling (Figure 11). Tacking garlands were anticipated, but radial corner cracks are subtle. They occur due to the bias introduced by shrinkage of the stretcher bars. Their expansion and contraction with humidity can easily add or subtract the 0.1% stretch modeled in Figure 13, but they do so unevenly with patterning the result.

Figure 13 covers the common range of climate conditions, and the tensions are similar to those found by all researchers, but none exceed typical strengths of new materials. Some other phenomena must be a work:

- (a) Fatigue cracking can occur at one-half to

one-fifth ultimate strength as long as the cycles occur quickly enough for the layer to act glassy. Daily temperature and humidity cycles would be eligible. This could explain crack reduction over stretcher bars, but experimental proof is lacking.

(b) Outdoor aging reduces oil paint strengths to one-fifth or less in about a year, as well as shrinking them markedly. The effect of being indoors for centuries is presently unknown.

(c) Curing strains can remain almost indefinitely in glue, ground, fast-drying oil paints, and varnish; modeling to date has not acknowledged this. Although much information has been ascertained, many questions remain.

CONCLUSION

What has the above revealed? It is not about the obvious—spearing by a forklift, six inches of water in a crate, or theft. The issues here are subtle, and the damage may easily be overlooked each time a painting is transported. Overall, four elements conspire to make paintings vulnerable to cracking: glassy behavior of the materials, pigmentation, fatigue, and the defects of age.

A temperature drop of 20°C shrinks paint layers, but it also significantly stiffens leathery polymers, i.e. oil, acrylic, and oil/resin paints. Combined with the speed of shock, these layers will act fully glassy and may also pass through a brittle/ductile transition; tension in the painting will increase.

Humidity fluctuation appears to be the historic cause of most extant cracks and dela-

mination in paintings. At the very least, humidity fluctuations should be kept well below the range routinely experienced by the painting in the past, so that a few transit cycles become an insignificant part of many thousands.

Shock threatens paintings the most and is the agent most capable of damage in one event. It is also the agent most peculiar to transit. Avoiding the range of shock that reaches dangerous values is discussed in detail by others in this publication.

Experiments concerning vibration indicate that canvas paintings do not stretch enough to damage even the most fragile new gesso unless the canvas is subjected to unrealistically high levels. By this point, displacements are so large that indirect effects such as stretcher slap are the main problem, especially on large paintings.

The most mechanically vulnerable material in paintings is the ground because of overpigmentation. Glue grounds are glassy to all transit forces, oil and acrylic become glassy if subjected to cold and shock. As the layer with the lowest elongation at break, grounds are the first to crack. Because the layer is hidden, cracking from transit may not penetrate the paint layer until years later. For panels, elongation in the fragile ground layer depends solely on moisture, therefore panel paintings require moisture control much more than temperature control. Shock in panels is a risk to the wood rather than a direct risk to the paint. □

NOTES

1. Professor Church, "Chemistry of the Fine Arts-VI," *Cassell's Technical Educator* 3 (London, c.1872), 246-248.
2. Marion F. Mecklenburg, "Some Aspects of the Mechanical Behavior of Fabric Supported Paintings," (Washington, 1982) unpublished manuscript.
3. Debra Daly and Stefan Michalski, "Methodology and Status of the Lining Project, CCI," *ICOM Committee for Conservation 8th Triennial Meeting Preprints*, Sydney (1987), 145-152.
4. Christine Leback Sitwell, "Transporting Works of Art on Paper—Shock Test Results," *Conservation News* 32 (March 1987). Contains a bibliography of other British authors.
5. Timothy Green, Tate Gallery, personal communication of test results.
6. S.T.O. Stilwell and R.A.G. Knight, "An Investigation into the Effect of Humidity Variations on Old Panel Paintings on Wood," Appendix I (July 1931), in *Some Notes on Atmospheric Humidity in Relation to Works of Art* (London, c.1934). A limited edition distributed by the Courtauld Institute. A committee was formed in 1929 under the direction of the National Gallery, London. The Forest Products Research Laboratory (United Kingdom) carried out these tests. The paintings came from private donors approached by the gallery. The booklet also contains the first attempt to recommend a relative humidity for paintings (55%) made, ironically, by a public works engineer, J. Macintyre in "Some Problems Connected with Atmospheric Humidity," 7-16.
7. A. Zosel, "Mechanical Behaviour of Coating Films," *Progress in Organic Coatings* 8 (1980), 47-79. For a less technical and brief guide to the concepts of viscoelasticity applied to paint, see Loren W. Hill, *Mechanical Properties of Coatings* (Philadelphia, 1987). Given the recent date of the latter, it illustrates how unfamiliar the approach still is to industrial paint technologists.
8. Friedrich R. Schwarzl, "Viscoelasticity," in Vol. 17 of *Encyclopedia of Polymer Science and Engineering* 2nd ed., H. F. Mark and Jacqueline Kroschwitz, ed. (New York, 1989), 587-665. The best review of all the parameters that have been used to characterize viscoelasticity: creep, compliance, modulus, relaxation, retardation, etc. See pages 643-648 of the time-temperature shift superposition principle.
9. Souheng Wu, "Effects of Strain Rate and Comonomer on the Brittle-Ductile Transition of Polymers," *Journal of Applied Polymer Science* 20 (1976), 327-333. Wu has measured the activation energy of the brittle-ductile transition and finds that it falls between that of the α and β transitions.
10. Zosel 1980, 67-68.
11. Temple C. Patton, *Paint Flow and Pigment Dispersion* 2nd ed. (New York, 1979), 167. Patton calculates that the layer of linseed oil on carbon black is 2.5 nm thick, two layers of coiled linoleic triglyceride molecules. Zosel 1980, 65, found a range of 0.5-50 nm for the adsorbed layer.
12. Adolf C. Elm, "Some Mechanical Properties of Paint Films," *Official Digest* 25 (November, 1953), 751-774, and particularly 758-759.
13. Patton 1979, see spacing calculation, 136, and example of a fine carbon black, 138, with data on page 142; see also M. F. Dix and A. D. Rae, "The Structure of Prussian Blue and Analogues," *Journal of the Oil and Colour Chemists' Association* 61 (1978), 69-74.
14. Patton 1979, 186 shows enamels 15%-30% PVC, gloss paints 30%-40% PVC, semigloss 40%-50% PVC, flat paints 60%-70% PVC.
15. Patton 1979, 148, 161-169.
16. Stefan Michalski, "Crack Mechanisms in Gilding," in *Gilding Conservation* (Winterthur, 1991 [in press]).
17. A. Toussaint and L. D'Hont, "Ultimate Strength of Paint Films," *Journal of the Oil and Colour Chemists Association* 64 (1981), 302-307. For further discussions on alkyd and acrylic paints see: Fred B. Stieg "Pigment Binder Geometry," *Pigment Handbook* 3, Temple C. Patton, ed. (New York, 1973), 205.
18. E. J. Dunn and C. H. Baier, *Official Digest* (1948), beginning on 743 for a study that measured recoverable elongation. See H. W. Talen, "The Influence of Pigments on the Mechanical Properties of Paint Films," *Journal of the Oil and Colour Chemists Association* 34 (October 1951), 455-472 for discussion on the curing period. See R. L. Eissler and L. H. Princen, "Effect of Some Pigments on Tensile and Swelling Properties of Linseed Oil Films," *Journal of Paint Technology* 40 (no. 518, March 1968), 105-111 for discussion on strength of zinc white linseed oil paints and titanium whites, after water exposure.
19. L.C.E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Amsterdam, 1978).
20. The linear expansion coefficient $\alpha' = 1/(1+\alpha''')^{1/3}$ where α''' is the volume expansion coefficient, but for typical small values this simplifies to $\alpha' \approx 1/3 \alpha'''$.
21. Harley A. Nelson and George W. Rundle, "Further Studies of the Physical Properties of Drying-oil, Paint and Varnish Films," *Proceedings, American Society for Testing*

- Materials* 23, Part 2 (1923a), 356-368, they discuss nine white linseed oil paints.
22. Mecklenburg 1982, also, Mecklenburg and Tumosa elsewhere in this publication, "Mechanical Behavior of Paintings Subjected to Changes in Temperature and Relative Humidity."
 23. F. L. Browne, "Swelling of Paint Films in Water, III Absorption and Volumetric Swelling of Bound and Free Films From Air of Different Relative Humidities," *Forest Products Journal* 5 (February 1955), 92-96. Browne measured weight gain and expansion. The 65%-97% RH data clearly shows lead white swells least of all because it absorbs the least water.
 24. Stefan Michalski, "A Physical Model of the Cleaning of Oil Paint," *Preprints of the IIC Dresden Conference* (1990), 85-92.
 25. F. L. Browne, February 1955. At 80% and 90% RH, first time exposure of oil paints causes variable "springback" equivalent to as much as 50% of moisture expansion. I have plotted his data: the springback totals 1.0% paint volume, or 1.4% oil volume (30% PVC). Oil alone sprung-back 2.3% volume, so pigments did constrain the effect.
 26. F. L. Browne, "Swelling of Paint Films in Water, V Effects of Different Pigments," *Forest Products Journal* 5 (June 1955), 192-200. With water immersion total swelling was generally equal to the volume of water absorbed, but the expansion in thickness, length and width varied depending on several other factors, such as curing stresses in the paint and brushstroke direction. These effects would probably show in the 70%-100% RH response of paint, but not 0%-70% RH.
 27. Mecklenburg 1982. Figure 4: 0.023% per percent RH, taking midpoint between hysteresis at 70% RH; Marion Mecklenburg, "Some Mechanical and Physical Properties of Gilding Gesso," paper presented at the *Gilding Conservation Conference Philadelphia* (1988a), personal communication concerning graphs, see *Gilding Conservation* (in press 1991). Three full length cycles were monitored, my best fit to the curve in the range 5%-80% RH is 0.040% per percent RH; see also, Mecklenburg and Tumosa, "Mechanical Behavior of Paintings Subjected to Changes in Temperature and Relative Humidity" in this publication.
 28. A. S. Marshall and S.E.B. Petrie, "Thermal Transitions in Gelatin and Aqueous Gelatin Solutions," *The Journal of Photographic Science* (1980), 128-134. Figure 4, cold dried gelatin, 1/3 slope of EMC curve is 0.045% per percent RH in the range 10%-70% RH. Hot-dried film only 0.030% per percent RH in the range 0%-60% RH; Marion Mecklenburg, "The Effects of Atmospheric Moisture on the Mechanical Properties of Collagen under Equilibrium Conditions," *AIC Preprints of the Sixteenth Annual Meeting New Orleans* (1988b), 231-244.
 29. Michalski 1991. Bond lengths are $[(1-\text{PVC})/\text{PVC}+1]^{1/3}-1 \times$ particle diameter. Thus expansion coefficient gesso = expansion coefficient glue/ $(1+1/[(1-\text{PVC})/\text{PVC}+1]^{1/3}-1)$.
 30. Mecklenburg 1988.
 31. *Wood Handbook*, U. S. Department of Agriculture, rev. ed. (1987), see Table 3-4, page 3-11 for moisture content at different T, RH, Table 14-3, page 14-14 for coefficient of expansion of different species, in terms of moisture content.
 32. J. E. Ramsbottom, "Aircraft Fabrics," *Physical and Physico-Chemical Problems Relating to Textile Fibres* (London, June 1924), 73-80. The papers in this monograph are all reprinted from *Transactions of the Faraday Society* 59, 20, Part 2 (1924).
 33. F. T. Peirce, "Geometrical Principles Applicable to the Design of Functional Fabrics," *Textile Research Journal* 17 (March 1947), 123-147; G. E. Collins, "Fundamental Principles that Govern the Shrinkage of Cotton Goods by Washing," *Textile Institute Journal* 30 (1939), 46-61.
 34. N. J. Abbott, F. Khoury and L. Barish, "10—The Mechanism of Fabric Shrinkage: The Role of Fibre Swelling," *Journal of the Textile Institute* 55 (1964), T111-T127.
 35. Mecklenburg 1982.
 36. Daly and Michalski 1987, Figure 8, see also Collins 1939, for discussion of longitudinal yarn and fiber shrinkage.
 37. J.E.O. Mayne and D. J. Mills, "Structural Changes in Polymer Films. Part 1: The Influence of the Transition Temperature on the Electrolytic Resistance and Water Uptake," *Journal of the Oil and Colour Chemists' Association* 65 (April 1982), 138-142, see discussion page 142.
 38. *Mark's Handbook for Mechanical Engineers* 6th ed., Theodore Baumeister, ed. (New York, 1978), see Table 12 "Coefficients of Linear Expansion (Thermal)," 4-7.
 39. D. J. Mills and J.E.O. Mayne, "Structural Changes in Polymer Films. Part 2: The Effect of the Pigment Zinc Oxide on the Electrolytic Resistance and Transition Temperature; Some Comparisons with the Pigments Iron Oxide and Red Lead," *Journal of the Oil and Colour Chemists' Association* 66 (March 1983) 88-93, for discussion on expansion coefficients (dilatometer) of modified oil media that were unaffected by pigment.
 40. Mecklenburg and Tumosa, elsewhere in this publication, "Mechanical Behavior of Paintings Subjected to Changes in Temperature and Relative Humidity."
 41. N. A. Brunt, "Blistering of Paint Layers as an Effect of Swelling by Water," *Journal of the Oil and Colour Chemists Association* 47 (January, 1964), 31-42. For an alkyd resin:

EMC/RH curve showed *no effect of temperature* between 20°C and 35°C.

42. *Wood Handbook* 1987, see Table 3-4, page s3-11 for moisture content at different T, RH and discussion on pages 4-26. The wood shrinks first because thermal response is fast, then as moisture equilibrates, the wood swells.
43. Given the formula in endnote 29, at 85% PVC, particle separation is 0.056, about one-twentieth of particle diameter.
44. Harley A. Nelson and George W. Rundle, "Stress Strain Measurements on Films of Drying Oils, Paints and Varnishes," *Proceedings, American Society for Testing Materials* 21 (1921), 1111-1134; Nelson and Rundle 1923a; Harley A. Nelson, "Physical Properties of Varnish Films Indicated by Stress-Strain Measurements," *Proceedings, American Society for Testing Materials* 23, Part I (1923b), 290-299.
45. Mecklenburg 1982; 1984, personal communication of stress-strain curves for Prussian blue; Nelson and Rundle 1923a, Figure 2; H. W. Talen, "Some Considerations on the Formation of Films," *Journal of the Oil and Colour Chemists Association* 45 (June 1962), 387-415, Figure 16. All modulus values were derived from the above studies by drawing a tangent on the published stress strain curves, passing through the origin.
46. Browne, June 1955.
47. Nelson and Rundle 1923a, Figure 1.
48. Kurt Gutfreund, "Study of the Deterioration of Paint Films by Measurements of their Mechanical Properties," *Circular* 793, National Paint Varnish and Lacquer Association (Washington, March 1965), 37, Figure 22.
49. N. A. Brunt, "The Linear Visco-Elastic Behaviour of Paint Films as a Function of Time and Temperature," *Journal of the Oil and colour Chemists' Association* 38 (October 1955), 624-654.
50. Gerry Hedley, Marianne Odlyha, Aviva Burnstock, June Tillinghast, and Camilla Husband, "A Study of the Mechanical and Surface Properties of Oil Paint Films Treated with Organic Solvents and Water," *Cleaning, Retouching and Coatings, Preprints of the Brussels' Congress* (IIC London, 1990), 98-105. The thermo-mechanical analysis was carried out by Odlyha (Birkbeck College, London).
51. Christopher W. McGlinchey, "Thermal Analysis of Fresh and Mature Oil Paint Films: the Effect of Pigments and Driers and the Solvent Leaching of Mature Paint Films," *Material Issues in Art and Archaeology II*, P. B. Vandiver, J. R. Druzik, and G. Wheeler, eds., Materials Research Society Proceedings (Pittsburgh, 1991), 93-103.
52. Zosel 1980, 62, Figure 14.
53. Hedley et al. 1990, 20-21, Figures 19, 20. The viscous flow nature of the unleached transition at 50°C was strongly supported by their loss tangent data.
54. Ethyl acrylate/methyl methacrylate copolymer has been identified in artists' acrylic medium sold by Grumbacher, Liquitex, Stevenson, and Winsor and Newton by R. Scott Williams, in "Commercial Prepared Painting Varnishes and Mediums," *ARS Report* No. 2672 (Canadian Conservation Institute, Ottawa, 29 September 1989; see also, G. G. Schurr, "Exterior House Paint," *Formulations Part 1*, Vol. 4 of *Treatise on Coatings*, Raymond R. Myers and J. S. Long, ed. (New York, 1975), 299); see Samantha Hodge, *Cracking and Crack Networks in Paintings*. Courtauld Student Project (London 1987), 54.
55. T_i for AC-33 is 16°C (61°F) where T_i is the nominal inflection point in the log E vs T curve, measured as the point where torsional modulus is 30 MPa. *Rhoplex Acrylic Emulsions and Acrysol Thickeners for the Adhesives Formulator*, Rohm and Haas (Philadelphia, August 1981); for the shape of the curve see Zosel 1980, 60, Figure 11; Wu 1976, 328, Figure 1; and Zosel 1980, 66, Figure 17, 53, Figure 6.
56. Zosel 1980, 68, Figure 18.
57. Wu 1976, 329.
58. Mecklenburg 1988b, Figure 9; Adam Karpowicz, "In-Plane Deformations of Films of Size on Paintings in the Glass Transition Region," *Studies in Conservation* 34 (1989) 67-74. "Frozen in" drying strains up to 5% were rapidly recovered by exposure to high RH. The terminology A, B, was coined in Michalski 1991 and has no molecular correlate however, I. V. Yannas, "Collagen and Gelatin in the Solid State," *Journal of Macromolecular Science—Reviews in Macromolecular Chemistry* C7, No. 1 (1972), 49-104 and pages 60-62 refer to gelatin and collagen as a block copolymer, and suggests multiple transitions in mechanical properties are to be expected.
59. Yannas 1972, Figure 15, curve 0.85.
60. Mecklenburg 1988b, Figures 8, 9.
61. My Figure 4 is slightly different from my earlier version based on an estimate of 5°C shift for each decade of time (Michalski 1991) due to better values of the time-temperature shift located in: Wataru Ueno and Ikuzo Ono, "Creep of Gelatin," *Journal of the Society of Materials Science Japan* 12 (1963), 341-346. See in particular Figure 4: between 28°C and 50°C the horizontal shift is about 6°-8°C per decade of time. Note also Figure 2, log E versus EMC, which shows the two phases A and B; E. Bradbury and C. Martin, "Mechanical Properties and Structure of Gelatin Films," *Proceedings of the Royal Society A*, 214 (1952), 183-192; J. Eliassaf and F. R. Eirich, "Creep Stud-

- ies on Gelatin at 100% Relative Humidity," *Journal of Applied Polymer Science* 4, No. 11 (1960), 200-202.
62. Richard C. Weatherwax, Beverly Coleman, and Harold Tarkow, "A Fundamental Investigation of Adhesion. II. Method for Measuring Shrinkage Stress in Restrained Gelatin Films," *Journal of Polymer Science* 27 (1958), 59-66 outlines the equations for displacement and tension in a thin clamped plate.
 63. A. T. Sanzharovskii and G. I. Epifanov, "Internal stresses in Coatings. III. Internal Stresses in Gelatine and Acetylcellulose Films Applied to Solid Substratums," *Vysokomol. Soedin.* 2 (1960), 1709-1714; S. A. Shreiner and P. I. Zubov, "The Effect of Internal Stresses on the Adhesive Properties of Gelatine Films," *Kolloid Zhur.* 22 (1960), 497-502; P. I. Zubov and L. A. Lepilkina, "Determination of Internal Stresses During Film Formation of Gelatine Films," *Kolloid Zhur.* 23 (1961), 418-422. Partial translations from the Russian are underway and will be available from CCI, Ottawa.
 64. Yannas 1972, 59.
 65. Robert A. Castello and Jere E. Goyan, "Rheology of Gelatin Films," *Journal of Pharmaceutical Studies* 53 (July 1964), 777-782.
 66. Karpowicz 1989, Figure 3. Biaxial restraint (dried on aluminum, then delaminated).
 67. Michalski 1991. Biaxial restraint (dried on glass, then delaminated).
 68. Mecklenburg 1988a.
 69. Michalski 1991.
 70. Michael Schilling, "The Glass Transition of Materials Used in Conservation," *Studies in Conservation* 34 (1989), 110-116 has a discussion on preferred T values; W. Konig, 6th Congress FATIPEC, (Wiesbaden, 1962) cites much lower values from old literature, cited in the review by Emil Krejcar and Otakar Kolar, "Ageing and Degradation of Paint Film Media," *Progress in Organic Coatings* 1 (1972-1973) 249-265; and D. N. Goswami, "The Relationship Between Glass Transition and Melting Temperatures of Natural Resins," *Journal of the Oil and Colour Chemists' Association* 63 (March 1980), 101-102 cites much higher values.
 71. *Acryloid Thermoplastic Acrylic Ester Resins*, Rohm and Haas, (Philadelphia, May 1975), 12, Table 7; Schilling 1989, 114.
 72. Leslie Carlysle, Ph.D Thesis, Courtauld Institute, (London, 1991)
 73. Nelson and Rundle 1923b, Figures 3, 4, 5. All varnishes are 27 gal. (US) oil to 100 lb. resin, give a ratio of about 2.2:1 by weight or volume.
 74. Konig 1962 (endnote 70) Films of stand oil and "Albertol 11 L" resin mixtures were measured for index of refraction versus T. A sharp knee in the curves was identified as a glass transition. Oil -18°C (0°F); oil/resin 3:1, 8°C (46°F); oil/resin 1:1, 30°C (86°F); resin 80°C (176°F). A 2:1 ratio would therefore have a transition near room temperature.
 75. Manfred Hess, *Paint Film Defects: Their Causes and Cure* 2nd ed. (Chatham, England, 1965) 442. This is the European definition for traditional resins (fossil resins, called "gum"). The American definition is slightly different, and both become relative for synthetic resins that need less oil to be "long."
 76. Hess 1965, 318 and Figure 57.
 77. Masaji T. Hatae, "Packaging Design" in *Shock and Vibration Handbook* 3rd ed., Cyril M. Harris, ed. (New York, 1988) 41-3, Table 41.1. Approximate sinusoidal rise time for drop of a wooden box is 0.004 x, carton 0.006 s. A wooden panel or stretcher bar hitting a hard surface will experience similar conditions. Duration of a half-sine pulse will be approximately three times as long, giving ~0.01-0.02 s.
 78. Temperature and humidity response roughly follow an exponential decay function: $1 - \exp(-kt)$. The half-time occurs at $kt = -\ln 0.5$, and 90% of response occurs at $kt = -\ln 0.1 = -3.3 \ln 0.5$. Humidity response may deviate considerably from this function at the last stages due to variable diffusion coefficient.
 79. *ASHRAE Handbook: 1985 Fundamentals Volume* American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta 1985.) Jerald D. Parker, James H. Boggs, Edward F. Blick, *Introduction to Fluid Mechanics and Heat Transfer* (Reading, Mass. 1969.) *The following calculation assumes appropriate SI units throughout, as defined in ASHRAE Handbook 1985; A 1°-10°C temperature difference between wall and air in a room 2 m high causes turbulent convection at the painting ($GrPr = 10^8 L^3 \Delta T$ exceeds 108) so heat transfer coefficient will be $h = 1.31 \Delta T^{1/4} = 2.8$ for a 10° difference (ASHRAE 1985, 3.13.) Thermal conductivity of paints is 0.26 (ASHRAE 1985, 39.3) so for $L = 1$ mm thick with one exposed face $k/hL = 93$ (ASHRAE 1985, 3.5.) Since this ratio is large, the temperature gradient is almost entirely across the air layer, and times will vary directly as the thickness of the paint (up to several millimeters). From Heisler charts (Parker et al 1969, 461; those in ASHRAE 1985, 3.5 are inadequate) the back of the paint will reach half the temperature difference when $Fo = 60$. Thermal diffusivity α can be estimated as similar to acrylic resins and other polymers, 1.1×10^{-7} (Parker et al 1969, 587,) so $t = Fo L^2 / \alpha = 9$ minutes. For 2 cm of wood, $k = 0.12$, $\alpha = 1.3 \times 10^{-7}$ so $k/hL = 2.1$. Half temperature response at the back means*

- Fo=2, so $t=100$ minutes, and the Heissler chart for temperature gradient (Parker et al. 1969, 460) shows only 20% of the temperature difference occurs across the wood. For 90% of response, calculation shows Fo numbers triple, so t triples, as expected. For temperature changes three times smaller or larger, t changes by only ~50%, because h varies as the cube root of temperature difference.
80. R. Keylwerth, "The Variation of the Temperature of Wood During the Drying of Veneers and Sawn Wood," *Holz Roh Werkst* 10, No. 3, (1952), 87-91. Once corrections are made for dimension and heating two sides, the seven minute half-time for midpoint of wood 1.2 cm thick agrees with the calculation methods of the previous end-note.
 81. J. Crank, *The Mathematics of Diffusion*, 2nd ed. (Oxford, 1975); J. F. Siau, *Flow in Wood* (Syracuse, New York, 1971). The moisture transfer coefficient of air is negligible compared to wood and paint permeance. Half-times are therefore $0.2 L^2/D$, if one side exposed. See ASHRAE 1985, 5.10; see also Siau 1971, 4, 93; Crank 1975, 61, Figure 4.7 or page 239; ASHRAE 1985, 21.6; H. E. Ashton, "Predicting Durability of Clear Finishes for Wood from Basic Properties," *Journal of Coatings Technology* 52 (April 1980) 63-71; J. A. Berrie, "Water in Polymers," in *Diffusion in Polymers* (London, 1968) 259-313, Table 5.
 82. Daly and Michalski 1987, and unpublished data. Canvas, sized canvas, glue grounds in typical artists' thicknesses show 90% response on the order of ten minutes. Full response of oil paintings undergoing relaxation treatments at 80% RH 20°C (68°F) takes hours to days, depending on thickness. Wood panels have been studied by many authors, see in particular, Stilwel and Knight 1931.
 83. Stefan Michalski, "Leakage of Enclosures," in preparation. The hygrometric half-time of a leaky enclosure containing natural cellulosic buffer at room conditions is $t_{1/2}=250 \text{ pf}/N$ where pf is the volumetric packing factor and N is air exchange rate. The space between a canvas and a wall, or a partial backing board will leak at 50-500 changes per day, pf is 1 mm canvas/2 cm air, so half-times are 0.05-0.5 days. The stretcher bar is too slow to contribute at these leakage rates.
 84. Leakage rates of fairly tight enclosures are 2-20 exchanges per day. Using the equation in note 83, and considering canvas first, half-times are 1.3-13 days. This is slow enough for stretcher bars to contribute, so half-times increase to 2-20 days. Tests at CCI of a painting with various backing boards confirm these estimates.
 85. Crank 1975, 50, Figure 4.1 shows that at 0.1 and 0.4 of the half-time, moisture penetration is about 0.1 and 0.2 of the thickness. Based on information in note 81, 1 cm of wood will react 1 mm deep in 0.5 days at middle relative humidity, but at high relative humidity (overnight damp) this may increase to 2 mm. Refer to Stilwel and Knight 1931 (note 82) for further information on old panel curvature at 0.1 of half-time.
 86. Michalski 1991.
 87. Hodge 1987, 17.
 88. David Bomford, Jill Dunkerton, Dillian Gordon, Ashok Roy, and Jo Kirby, *Art in the Making: Italian Painting Before 1400* National Gallery (London, 1989). The line drawings in Figure 7 were sketched from closeup photographs of Plate 137 (Christ) and Plate 107 (St. John the Evangelist). The x-radiograph showing the single wood piece is Plate 100, and placement of the two figures Christ and St. John the Evangelist is in Plate 126.
 89. The wood under Christ's figure is in equilibrium with the adjacent gilded sky because the figure is relatively narrow compared to the thickness of the wood.
 90. Gilding would reduce heating by radiation, and photochemical degradation, but in that case Christ's figure would show secondary cracks, but it does not.
 91. Umberto Baldini, *Primavera, The Restoration of Botticelli's Masterpiece* (New York, 1986) 46-47, 49.
 92. Baldini 1986, 49.
 93. Baldini 1986, 74.
 94. Baldini 1986, 4, 74, 75.
 95. Schurr 1975, 285.
 96. F. L. Browne "Swelling of Paint Films in Water X. Rate of Penetration of Water, Permeability to Water Vapor, and Penetrability to Air in Relation to Water Absorption," *Forest Products Journal* 8 (April 1957), 145-154. Basic lead white paint permeated up to 150 μm in spots during thirteen hours. Burnstock's SEM photos showed pore formation peculiar to lead white exposed to water twenty-four hours, see Hedley et al. 1990.
 97. L. L. Carrick and A. J. Permoda, "Shrinkage of Some Organic Film Forming Materials During Aging," *Official Digest* 28 (November 1951), 692-600. Linseed oil, trilinolenin, trilinolenin with driers, on glass, were monitored for volume change (thickness) and all lost about 16% by volume, i.e. 5.3% each dimension if unrestrained, 3% for a 40% PVC paint. This would be a maximum value, since restrained curing will orient some molecules without residual stress. Browne 1955, found complex differences in area and thickness changes between free and bound oil paints.
 98. The moisture resistance ratio of three coats lead white in oil to 1 cm wood is $500/180=2.8$ (see note 81). Measured ratio in old panels was 5 (see Stilwel and Knight 1931).

Heat and mass transfer equations are analogous, so by the Heisler chart for temperature profile in Parker et al. 1969, 460, the surface of the wood near the canvas will change by only 10%-15% of the total humidity fluctuation during times less than the half-time of the wood.

99. Gustav A. Berger and William H. Russell "Deterioration of Surfaces Exposed to Environmental Changes," *Journal of the American Institute for Conservation* 29 (Spring 1990), 45-76. see Figure 14a for a good example of crack reduction in a nineteenth-century painting, it however states, "The area protected by the stretcher from fluctuations in temperature has not cracked." Their laboratory simulation Figure 14b, does indeed show crack reduction over the stretcher bars after temperature cycling. The priming (ground) is unspecified, but if it is either acrylic or the epoxy/ghesso mix of their earlier studies (William H. Russell and Gustav A. Berger, "The Behaviour of Canvas as a Structural Support for Painting: Preliminary Report," *Science and Technology in the Service of Conservation, Washington Congress* [IIC, London, 1982] 139-145) then it would indeed show only thermal sensitivity not humidity sensitivity. Besides, the heavy lacquer applied to indicate strain cracking is itself a glassy layer designed to crack at extremely low elongations (0.03%-0.05%) and for which "rapid cooling will result in crazing of the brittle coating," cited from *General Instructions for the Selection and Use of Tens-Lac Brittle Lacquer and Undercoating*, Instruction Bulletin 215-C, Measurements Group, Inc, [Raleigh, North Carolina, 1982]). If the temperature fluctuations were less than a few hours duration, then the stretcher bars could have a direct effect.
100. *Mark's Handbook* 1978, 5-28 for formulas.
101. Hatae 1988, 41-43, Figure 41.1, Wooden box rise-time 0.004 s, height 10 cm (4 in.) yields 60 G, carton rise-time yields 40 G. At CCI, a medium-size experimental painting was tested with an accelerometer sitting on the top face of the painting at the outer edge of the stretcher bar. It was laid on the floor, and one edge lifted 10 cm (4 in.) and dropped. Peak acceleration at impact was 40 G. The linen corner tucks were softening the impact, otherwise agreement with prediction was good.
102. Peter Booth, "Stretcher Design: Problems and Solutions," *The Conservator* 13 (1989), 31-40.
103. Mecklenburg 1982.
104. Gerry Hedley, "Relative Humidity and the Stress/Strain Response of Canvas Paintings: Uniaxial Measurements of Naturally Aged Samples," *Studies in Conservation* 33 (1988), 133-148.
105. Dan Y. Perera and D. Vanden Eynde, "Moisture and Temperature Induced Stresses (Hygrothermal Stresses) in Organic Coatings," *Journal of Coatings Technology* 59 (May 1987) 55-63.
106. Howard S. Bender, "The Stress Relaxation Properties of Free Films as a Function of Time, Temperature and Film Thickness," *Journal of Paint Technology* 41 (February 1969) 98-103.
107. Daly and Michalski 1987.
108. Daly and Michalski, 1991, CCI unpublished data.
109. G. A. Berger and W. H. Russell, "Investigations into the Reactions of Plastic Materials to Environmental Changes. Part I. The Mechanics of the Decay of Paint Films," *Studies in Conservation* 31 (May 1986), 49-63.
110. Berger and Russell 1982, 139, note to Table 1: "Stiff hand priming with a mixture of glue-ghesso and epoxy paint 1:1." In their Figure 4 a relative humidity change from 25% to 90% causes tension to drop from 140 N/m to 110 N/m (MD). Between 2.3 and 2.6 hours RH is kept high and tension climbs to 300 N/m as the damp linen takes over the tension. The linen takes 0.3 hours to extract all the moisture it needs from the air. This large stress change is not due to the small, coincidental temperature change, as Berger and Russell propose.
111. Masaki Shimbo, Mitsukazu Ochi, and Katsumasa Arai, "Internal Stress of Cured Epoxide Resin Coatings Having Different Network Chains," *Journal of Coatings Technology* 56 (No 713, June 1984), 45-51, and Figure 5; Berger and Russell 1982, 143, Figure 5 The 50 N/m spikes in hours 11-17 are implausible for a 1°C temperature fluctuation, and I believe they represent a 50°C temperature fluctuation due to the nearby electric heater cycling every fifteen minutes. The thermometer is too sluggish and too far from the heater to respond.
112. Berger and Russell 1990, 47-48, Figures 1 and 2.
113. James Colville, William Kilpatrick, and Marion Mecklenburg, "A Finite Element Analysis of Multi-layered Orthotropic Membranes with Application to Oil Paintings on Fabric," *Science and Technology in the Service of Conservation Washington Congress of the IIC* (London, 1982), 156-150.
114. Richard W. Hertzberg and John A. Manson, *Fatigue of Engineering Plastics* (New York, 1980), see acrylic (PMMA) data on page 60, Figure 2.19c, and acrylic bone cement data Figure 5.31, page 226.
115. Richard W. Hertzberg and John A. Manson, "Fatigue" in Vol. 7 of *Encyclopedia of Polymer Science and Engineering* 2nd ed., (New York, 1987), 378-453. See page 411. Most fatigue data is presented as RCP lines. These begin just after crack initiation and end near break, see Figure 14, page 391; Figure 25 page 403, Equation 23 page 414, also Figure 31, page 412. RCP curves typically begin around 10^{-6} mm/cycle at one-half to one-fifth of the critical stress intensity, hence it takes a million cycles at such levels just to pass through the early stages of crack

propagation.

116. Hertzberg and Manson, 1980, 227. The stress (or elongation) to break polycarbonate (both with and without glass fibers) in ten-thousand cycles at 10 Hz drops five-fold if a sharp notch is present.
117. Raymond J. Roark and Warren C. Young, *Formulas for Stress and Strain* 5th ed., (New York, 1975), 405-409. For a circular diaphragm radius a , without flexural stiffness, $\epsilon = .965 (y/a)^2$ at the center, where y is the displacement at the center. In terms of a painting, a is half the painting width. Roark and Young also give the more complex equations for rectangular thin plates, but the simple equation above is close, and conservative since it overestimates ϵ .
118. *An Assessment of the Common Carrier Shipping Environment* FPL 22, Forest Products Laboratory, USDA (Madison, 1979) 13, Figure 5 shows that the peak vibration for a flatbed truck traveling on a variety of roads (construction, railway tracks) near 10-20 Hz was 1 G. This would not be sustained level, in fact, 90% of the time levels fell below 0.1 G. My 1 G test is tantamount to damping the painting flat on the truck floor and driving on railway tracks for three weeks. This must not be confused with a loose painting bouncing around the same truck which would suffer severe damage from multiple shocks; see also, Paul Marcon, "Shock, Vibration, and Protective Package Design," elsewhere in this publication.
119. Stilwell and Knight 1931.