On Canvas

Preserving the Structure of Paintings

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Figure 2.17
John Latham (British, 1921–2006), *Film Star*, 1960. Mixed media on canvas and hardboard, 160 × 198.1 × 22.8 cm (63 × 78 × 9 in.). London, Tate.

canvas and eventual loss of tension? The answer remains open. Now, currently nearly sixty years old, the painting is still visually effective, although the canvas is a little browner and has an even layer of dirt. The canvas tension will probably remain for another fifty years or so before corner draws become apparent. These need not affect the appreciation of the image, since the tension in the middle of the canvas and the appearance of the cut will not be much affected. *Spatial Concept 'Waiting'* exemplifies the need for preventive measures but with minimal intervention.

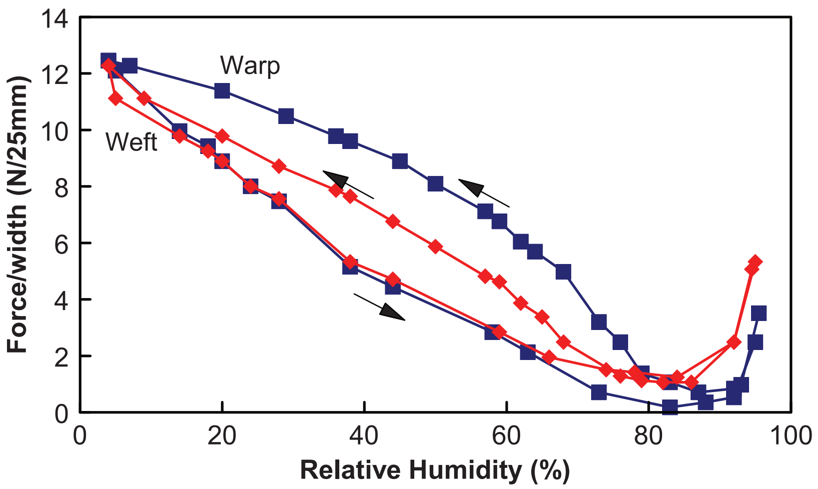
In *Film Star*, John Latham used the traditional format of stretched canvas as the basis for his exploration of unconventional allegorical images (fig. 2.17), incorporating books whose pages have been painted in twelve colors. Because the books can be opened at different pages, the work can exist in different states. It appeared in Latham's movie *Unedited Material from the Star*, consisting of a series of static shots of the opened books. During production, Latham would stop filming at various points, turn the pages of the books, and start filming again. When the film is shown, the books appear suddenly to open, close, and change color.

Figure 2.18
Details of *Film Star* (see fig. 2.17), showing vulnerable edges, attached plaster, wire, and book.

Latham attached damaged, painted, and sometimes burnt old books to his canvas, as well as other heavy materials, such a brittle plaster (Walker 1995). The books may be held in place only by the plaster, or they may have some added adhesive. Under the canvas, there is a solid board attached at the edges to provide some further support. Latham's methods of creating a work of art did not a take a very practical approach, since the added weight of material supported by the canvas put considerable localized tension on the unprimed stretched canvas support. The choice of paper books and exposed canvas makes the work light-sensitive and has led to limitations on lighting levels. The books themselves have proved to be susceptible to interference and have to be displayed behind a barrier. They are held open by attached metal wires, and more than one visitor has wanted to turn the pages. Even the artist seems to have had various ideas about how the works should be presented. In an interview conducted by Tate, Latham was inconsistent in his answers to the questions of curators and conservators perhaps because he did not want his work to be too readily or glibly interpreted, or perhaps because his best form of expression was visual.

The canvas is open-weave jute burlap without even a size layer to protect it or a ground to provide further rigidity. It is pinned to a hardboard panel (Masonite). So far, except for some losses of white gesso and further discoloration of the books, his work has survived reasonably well, but the construction and materials constitute what is sometimes called, in insurance terms, "inherent vice" (fig. 2.18). Latham's work of art has changed since it was put together and will continue to degrade and embrittle, presenting a good argument for preventive conservation. At some stage, the canvas will lose tension and will slump where the attached books pull it out of plane. Major components will then detach and will have to be reattached, but since the actual visual appearance is not precisely fixed, the tolerance for repair is wide. Latham's own views on the appearance of his paintings will remain enigmatic.

Figure 5.10
Stress (force/width) versus RH for hide glue on linen samples (Mecklenburg 2005).



depending on artistic technique, age, pigment type, and concentration. Ground layers are more consistent; they are usually higher in pigment concentration and therefore higher in stiffness.

Figure 5.11 shows the responses of three separate painting materials—linen, hide glue, and paint—and allows comparison of the different contributions from each material. Most important, at low humidity (say, 20% RH), the high-modulus E hide glue has shrunk considerably, creating high tensile stress that could cause cracking. At exceptionally high humidity, above 80% RH, canvas shrinkage creates high stress.

These measurements of the behavior of the individual components can be used to predict the behavior of the entire painting. Since the entire painting structure is made of several layers locked together, it can be considered a stressed laminate. The stretcher and initial stretching define the dimensions and initial stress. Part of the total stress is carried in each continuous layer, and their contributions can be combined to model the behavior of the composite. In a changing environment, each component introduces strains due to dimensional changes, causing shear stresses with adjacent layers and transferring some stress. The hygroscopic layers tend to contract and expand the most. The stiffer layers (those with high E) are least able to resist high strains. The stiffest layers, therefore, carry the most stress. For a specific painting, if it is available, data about the thickness of each layer, response time, and initial tension can be used to calculate predicted changes in behavior in response tochanging humidity.

Time is also a factor. As RH increases, some materials, such as animal glues, respond within minutes, absorbing large quantities of water. Others, such as cured oil paint, do so only slowly and to a limited extent. Drying oil paints and grounds are much less hygroscopic. They take much longer than 24 hours to approach equilibrium with their surroundings, and they absorb a smaller percentage of water by weight—therefore exhibiting less change in volume (Hedley 1993).

James Colville and Marion Mecklenburg measured strips of a complete painting (dated 1906) to demonstrate that the combined behavior of the individual materials can indeed describe the measured behavior of a real painting (Colville, Kilpatrick, and Mecklenburg 1982). Hedley repeated measurements on samples of the 1906 painting and also measured a glue-lined painting fragment and several samples of nineteenth-century primed canvases (dated 1856, 1862, and 1868) (Hedley 1988). The nineteenth-century samples were original loose linings (or auxiliary canvases) from well-characterized paintings in the Tate collection, essentially identical to the canvases and grounds of the actual paintings (fig. 5.12). In typical nineteenth-century loose linings made by London artists' suppliers, the canvas is a tightly woven linen sized with animal glue, and the lean ground is oil medium applied in two layers, both containing lead white and calcium carbonate; the top layer has a higher proportion of basic lead carbonate. Samples from loose linings have provided the opportunity to measure authentic nineteenth-century prepared and aged canvases. These and other

Figure 5.11
Stress (force/width) versus RH for individual constrained samples of linen, hide glue, and dried oil paints. Hide glue exhibits much more stress at 20% RH, whereas the linen shows most stress at 90% RH (Mecklenburg 2005).

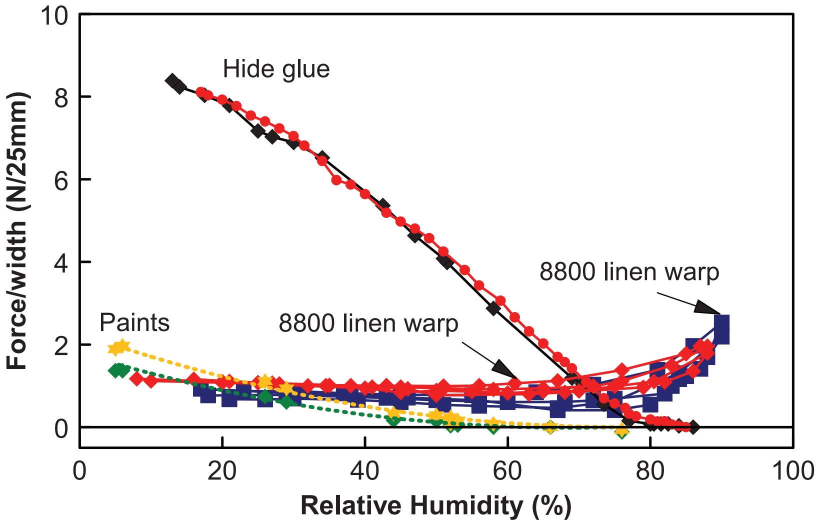
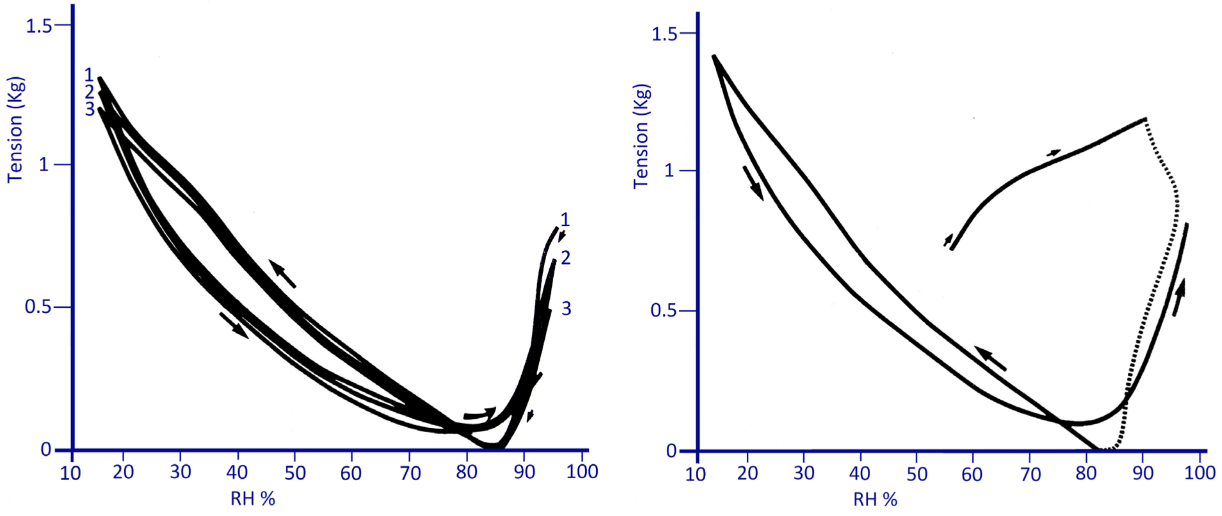


Figure 5.12
Tension versus RH of an original loose lining from W. P. Frith's The Derby Day (1856–58), primed and strained at 0.33% (Hedley 1988): (a) Tension development during 3 repeated RH cycles; and (b) a different initial response in the first cycle.



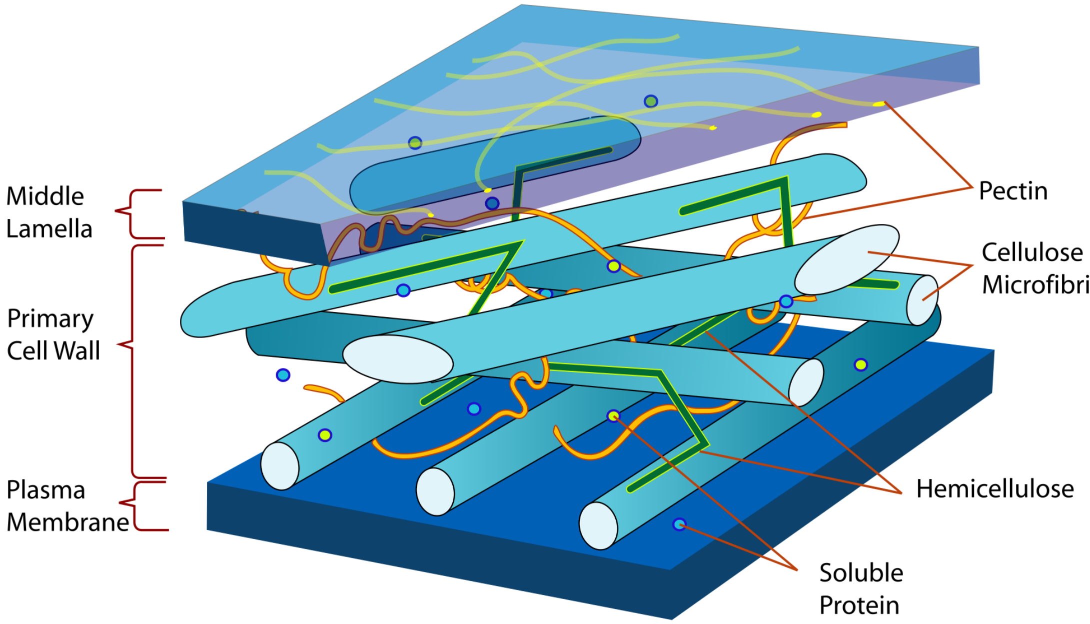


Figure 6.8
The long cellulose (I and II) molecules are embedded in a pectic matrix to form a microfibril. Microfibrils are aligned and bound together into fibril aggregates roughly 10–25 nm diameter, by a matrix of hemicellulose and either pectin or lignin (Fahlen and Salmen 2003; Donaldson 2007). This matrix is strong, and the amorphous adhesives provide flexibility, dispersing any stress concentrations in the structure.

Noncellulose Components

Celluloses are not the only type of molecule contained in bast fibers, other plants, and trees. Three categories are important in the growth of plants: hemicelluloses, pectins, and lignins, and each will have some effect on the behavior of yarns made from them. They are all less tightly packed together than is cellulose I and therefore more open to biological attack with enzymes. Their degradation causes darkening, contributes to acidity, and affects moisture response to some extent.

Hemicelluloses are a category of short-chain, amorphous polysaccharides, each with 500–3000 monomer units and acidic groups (Niklas 1992; Bodig and Jayne 1982). They include xyloglucans, xylans, glucomannans, and galactoglucomannans (Ebringerova, Hromadkova, and Heinze 2005). Lignin is an amorphous, complex phenolic compound (Boerjan, Ralph, and Baucher 2003). Pectins are a group of polysaccharides rich in galacturonic acid units (Ridley, O'Neill, and Mohnen 2001).

During cell growth, a plant maintains a lower yield strength in the primary cell walls, allowing a cell to deform significantly under pressure. Once growth is complete, the stiffness and strength of the cell wall increases, because adjacent cells are bound together by the middle lamella, which is initially high in pectin (Niklas 1992). Hemicellulose binds to the surface of the cellulose microfibrils, while pectin cross-links the hemicellulose molecules of adjacent microfibrils. Glycoproteins, a minor constituent of the cell wall, are also thought to be involved in cross-linking. A model has been proposed in which cellulose microfibrils, tethered by cross-linking hemicelluloses, are embedded in a pectic matrix (fig. 6.8) (Morvan et al. 2003).

After cell growth is complete, additional secondary layers are deposited. In bast fibers, and in the wood of larger structures like trees, lignification of the secondary cell wall layers increases their stiffness and strength, compared with unlignified primary layers. When flax is retted, enzymes destroy much of its hemicellulose, pectin, and lignin content, thereby releasing their grip on the cellulose fibers but preserving the microstructure. The cellulose fibers are typically oriented at different angles in each secondary layer; for example, in flax, the bast fiber is at about 7° to the direction of the stem.

Aging of Canvas

Linen is a very strong and stable substance that can last for hundreds of years in the right circumstances. When kept in the dark and under benign conditions, it will degrade only slowly by depolymerization of the long cellulose molecules.

For most canvases, exposure to strong light with a significant ultraviolet (UV) content is limited to its early days, before and perhaps during actual painting. Once finished, the back of a painting is likely to be shielded from light for most of the time, against a wall or perhaps behind a backboard. Exceptions are modern works in which areas of canvas are left unpainted. Such objects are light sensitive, but in practice, they are not always displayed for limited periods at 50 lux, since that would preclude their presentation alongside other works on canvas (fig. 6.9).

Figure 6.9
A mixed display at Tate Modern, London, where light-sensitive works are shown with other contemporary artworks (left to right): Sigmar Polke, *Untitled (Triptych)*, 2002; Roy Lichtenstein, *Reflections on Brushstrokes*, 1990.

The initial stages (autoxidation) are similar to those for cross-linking of drying oils (see chap. 7).

Energy of photon $E = h\upsilon$

Absorption of photon $h\upsilon + \text{photosensitizer} = \text{photosensitizer}^*$ (excited state)

The excited photosensitizer abstracts an electron from the covalent bond between a hydrogen atom and cellulose (designated *RH*), creating a free radical, $R\cdot$.

$$\text{photosensitizer}^* + RH = R\cdot + \text{photosensitizerH}$$

Propagation of many different free radicals takes place where electrons are removed from some species and added to others in a cascade of reactions. For example,

$$\mathrm{R\cdot + O_2 = ROO\cdot}$$
$$\mathrm{ROO\cdot + RH = ROOH + R\cdot}$$
$$\mathrm{ROOH = RO\cdot + HO\cdot}$$
$$\mathrm{2ROOH = ROO\cdot + RO\cdot + H_2O}$$
$$\mathrm{RO\cdot + RH = R\cdot + ROH}$$
$$\mathrm{2ROO\cdot = O_2 + 2RO\cdot}$$
$$\mathrm{R\cdot + H_2O = RH + HO\cdot}$$
$$\mathrm{HO\cdot + RH = R\cdot + H_2O}$$
$$\mathrm{HO\cdot + HO\cdot = H_2O_2}$$
$$\mathrm{H_2O_2 + 2HO\cdot = O_2^{-}\cdot + 2H_2O}$$

Various termination reactions can also consume two free radicals to make peroxides, breaking the sequence.

$$\mathrm{R\cdot + R\cdot = RR}$$
or
$$\mathrm{R\cdot + RO\cdot = ROR}$$
or
$$\mathrm{RO\cdot + RO\cdot = ROOR}$$

Water and oxygen are two important contributors to free radical reactions. By sequentially removing single electrons from water, it is possible to go from H_2O to $HO\cdot$ to H_2O_2 to $O_2^{-}\cdot$ to O_2, and by adding electrons to oxygen to regenerate water.

$$\mathrm{H_2O - e^- = HO\cdot - e^- = H_2O_2 - e^- = O_2^{-}\cdot - e^- = O_2}$$

$$\mathrm{O_2 + e^- = O_2^{-}\cdot + e^- = H_2O_2 + e^- = HO\cdot + e^- = H_2O}$$

In the complex environment of a cellulose-based material, such as linen canvas, it is impossible to specify in detail which of many competing reactions has occurred

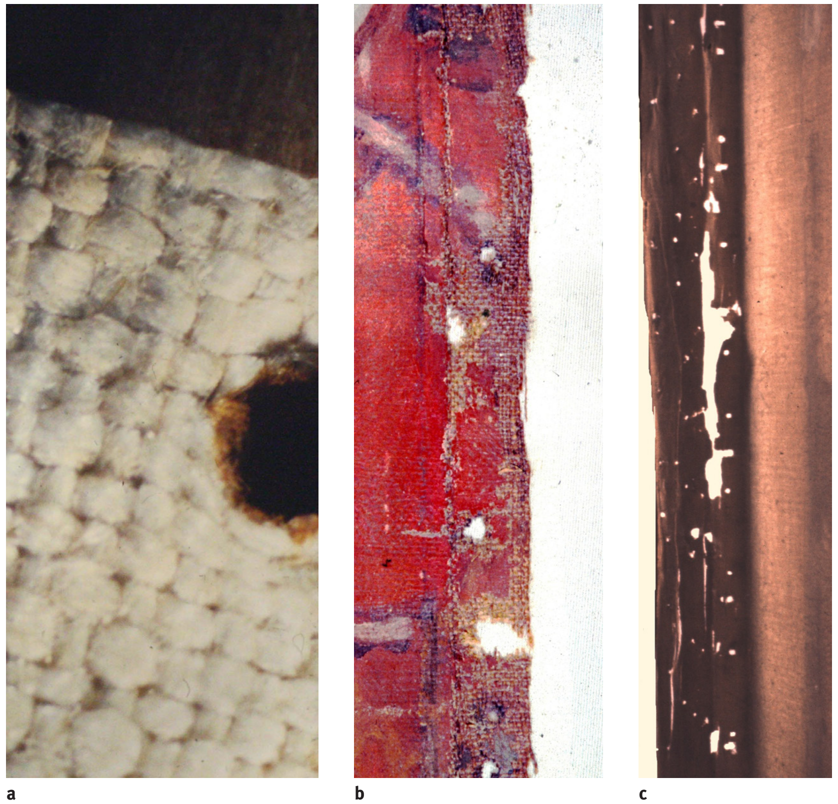


Figure 6.19
Oxidation of cellulose caused by rusted tacks: (a) Rust around a tack hole in relatively new canvas; and (b and c) two examples of canvas damage caused by rusted tacks due to the spreading of Fe++ ions from the tack location.

between each radical. Cellulose reactions take place only with species generated by free radicals. The radicals most likely to react with cellulose are the superoxide anion ($O_2^{-}\cdot$), the hydroperoxide radical ($HOO\cdot$), hydrogen peroxide (H_2O_2), and the hydroxyl radical ($\cdot OH$). The hydroxyl radicals in particular are very reactive, usually reacting with the first molecule they encounter (Zervos 2010), whereas the superoxide anion is less so and, as a consequence, more mobile over more bonding sites. Therefore, the use of chemical scavengers to remove hydroxyl ions might have some effect on the superoxide anions but is unlikely to be entirely successful.

A potentially important catalyst in the oxidation of cellulose is the presence of transition metals, such as iron (and, of lesser relevance, copper), which on a painting canvas may well be present in the form of iron or copper tacks, sprigs, or staples that attach it to a stretcher (fig. 6.19). Any rusting or corrosion of iron components will lead to soluble ferrous ions, which in the presence of UV radiation can cause the Fenton reaction, yielding reactive hydroxyl radicals that can oxidize cellulose (Potthast, Henniges, and Banik 2008).

$$\mathrm{Fe^{2+} + H_2O_2 = Fe^{3+} + HO\cdot + HO^-}$$

Further, the presence of the superoxide radical ($O_2^{-}\cdot$) can lead to a reduction reaction with Fe^{3+} to form oxygen and Fe^{2+}.

Driers

The addition of driers to the paint, such as salts of cobalt, chrome, manganese, iron, and lead, can accelerate the curing (drying) process. In the presence of a catalytic drier, thermal energy alone may suffice to initiate free radicals. Multivalent metal ions, such as the transition elements, which have more than one stable valency in air and can exist in more than one oxidation state, make good catalysts. Reactions with such elements produce free radicals, increasing the rate of oxygen uptake by forming complexes that lower the activation energy for the uptake reaction. For example,

$$\mathrm{ROOH} + \mathrm{M}^{\mathrm{N}} = \mathrm{ROO}\cdot + \mathrm{H}^{+} + \mathrm{M}^{\mathrm{N-1}}$$

The metal in its higher oxidation state, M^N, gains an electron or is reduced by a hydroperoxide to a lower oxidation state, M^{N-1}. This results in the production of a free radical ($\mathrm{ROO}\cdot$), as well as a proton (H^+) that can combine with anions to form an acid. This is an example of a redox (reduction/oxidation) reaction, where the M^{N-1} can then be oxidized back to M^N, perhaps by another free radical, releasing a hydroxyl ion and leaving the metal ion ready to repeat its catalytic role:

$$\mathrm{ROOH} + \mathrm{M}^{\mathrm{N-1}} = \mathrm{RO}\times + \mathrm{OH}^{-} + \mathrm{M}^{\mathrm{N}}$$

For a pigment to have drying properties, it must be in good contact with the oil; it also must be at least partly dissociated, in order to provide the necessary metal cations. Finer pigments will have more intimate contact with the medium. Oxygen must also be present, and its rate of diffusion through the paint affects curing times (Thomson 1978b). Thin paint films will cure more quickly than thicker ones. Very thick films containing cobalt drier may form a less permeable surface skin and remain liquid below the surface for many years. This condition leads to unresisted contraction and wrinkling of the paint skin.

Without the addition of a drier, cold pressed linseed oil would last longer in an opened tube, but each paint layer would need to be left for weeks to dry, slowing down the painting process excessively. The ability of multivalent metal compounds to catalyze the oxidation of oil to form a film also depends on their solubility and degree of dissociation in oil. In a sealed new paint tube in the absence of air, lead white pigment (basic lead carbonate) is nonionized and does not act as a drier. When painted out, however, it will combine with oxygen and water vapor in hydrolysis reactions, freeing its metal ions to take part in the curing process (Tumosa and Mecklenburg 2005).

Some metals, known as secondary or auxiliary driers, react with and remove any antioxidants that prevent the early buildup of peroxides; they therefore speed curing by shortening the initiation period without directly catalyzing oxidation (Feller 2002). Lead and some other multivalent metals work by both mechanisms.

Depending on their catalytic effects on curing, the various pigments employed in making paint have a significant effect on both the drying time and the ultimate mechanical properties of the paint (table 7.2) (Hedley 1988). For example, cobalt is an extremely good primary oxidative drier, being very effective at making a paint surface dry to the touch, since there is plenty of oxygen available at the surface. Lead is somewhat less effective at the surface but is very good at facilitating "through" drying of the film. It acts as an auxiliary drier to remove antioxidants, thereby sustaining the curing process in a limited-oxygen environment. Cobalt driers are therefore useful in thin decorator's paint, whereas lead is very useful in the thicker films of paint applied by artists. Lead white and various extenders are often added to grounds in order to ensure a solid surface for painting.

Table 7.2
The effect of pigment on the elastic modulus of cured oil paints (Mecklenburg, Tumosa, and Erhardt 2005).

Pigment	Age (years)	Azeleic acid (%)	Palmitic acid (%)	Stearic acid (%)	Elastic modulus of paint (MPa)
Raw umber	12.25	2.9	3.4	2.2	5
Red iron oxide	12.25	4.8	1.9	1.4	5
Malachite	12.25	4.6	1.7	0.6	89
Titanium white	14.5	9.6	3.3	2.2	140
Basic lead carbonate	14.75	6.6	1.9	0.9	300
Zinc white	14.5	1.9	4.4	2.6	1667

Not all pigments are useful driers. Many organic dyes have no catalytic effect and may behave as antioxidants, slowing the drying rate. The component antioxidants in dyes function in paints as they do in living plants, preventing autoxidation processes from occurring. Paint manufacturers attempt to modify the drying rates of various pigmented paints by the addition of an appropriate quantity of driers to reduce some of the variation among pigments. Since the pigment concentration is high in grounds and artists' paints, there are still noticeable differences in drying rates among different colors (Tumosa and Mecklenburg 2005; Mecklenburg 2005; Mecklenburg, Tumosa, and Vicenzi 2013). As fewer heavy metals are now used in paints, the effect of pigments on drying time has been reduced, and the addition of driers is more important.

Aging of Dried Oil Grounds

The mechanical behavior of individual oil films differ greatly depending on their composition and history. The relative rates of oxidation and hydrolysis reactions define the ultimate structure of the dried oil paint (linoxyn) film. Initially autoxidation dominates, but as the unsaturated bonds are consumed, the rate gradually decreases, whereas hydrolysis continues (Tumosa and Mecklenburg 2010). Hydrolysis can be a reversible reaction. If it is catalyzed by hydrogen ions that are generated by autoxidation, hydrolysis can continue at an increasing rate, especially in hot, humid, or acid conditions. Hence, the long-term structural behavior of the film (aging) is determined by the extent of continuing hydrolysis (Cotte et al. 2017).

The properties of a newly cured linoxyn film are determined by its initial composition, the nature of the oils, the range and concentration of pigments, pigment size and shape, the effect of individual pigments on drying times, the addition of driers, and the thickness of the film. Drying and subsequent aging are also affected by envi-

8

Physical Deterioration of Paintings and Canvas

A painting attached to a stretcher is subject to the initial strains applied in stretching; at its most extreme, this tends to create distortions near tacks or staples. Initial tension, which remains for many years, gradually relaxes until the painting is next keyed out and tensions are regenerated, predominantly at the corners. In addition, a painting is subject to internally generated strains caused by changes in moisture content and temperature. Also, on aging, most artists' materials undergo irreversible changes to their mechanical properties. Human interference from handling, transport, or accidents further exposes paintings to stress. Information on material changes and their mechanical consequences permits the development of a holistic view of the deterioration of paintings. Providing a model of possible behavior over time can also improve reliable identification and interpretation of flaws and damage.

Cracking of Oil Grounds on Canvas

In the absence of external forces, in restrained material such as stretched canvas paintings, cracks can be generated by changes in temperature or humidity.

Even when external stresses and strains remain fixed, changes in moisture content cause dimensional changes that lead to the development of internal strains in restrained hygroscopic materials, such as canvas and size. These can transfer to adhered materials that are less moisture responsive, such as oil grounds and paint films. In particular, shear stresses occur at boundaries, where the different dimensional changes of each layer are most evident, testing the adhesion between films and sometimes testing their cohesion. At low RH, overall contraction of a large area of canvas can set up tensile stresses that cause cracks to initiate at weaker points throughout the entire area, usually propagated in plane and at right angles to the stresses generated. This is the familiar craquelure.

A change in temperature in itself does not cause a large change in canvas dimensions; however, with a reduction in temperature, a large increase in elastic modulus of the paint can lead to stress development. On a fixed, effectively incompressible stretcher, on cooling there is only a small increase in strain, but because the elastic modulus increases significantly, the stress rises proportionally. Despite an increase in ultimate tensile strength, cracking may occur (fig. 8.1). A combination of low RH and low temperature is the worst scenario.

Figure 8.1
Cross section of a canvas and ground showing cracks in the ground.

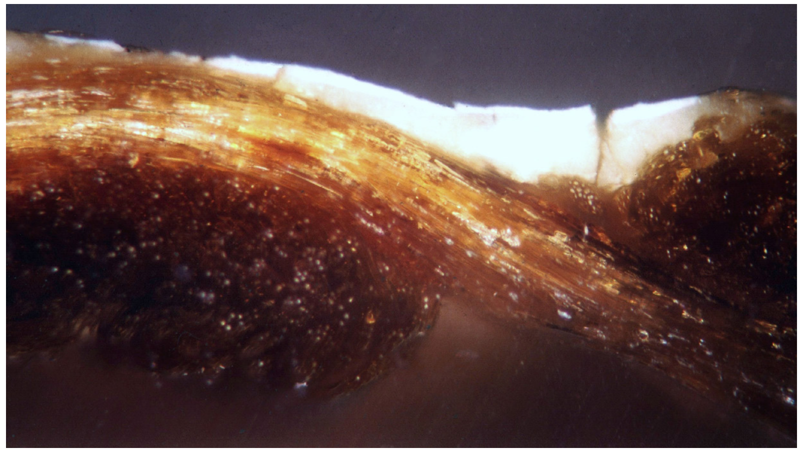
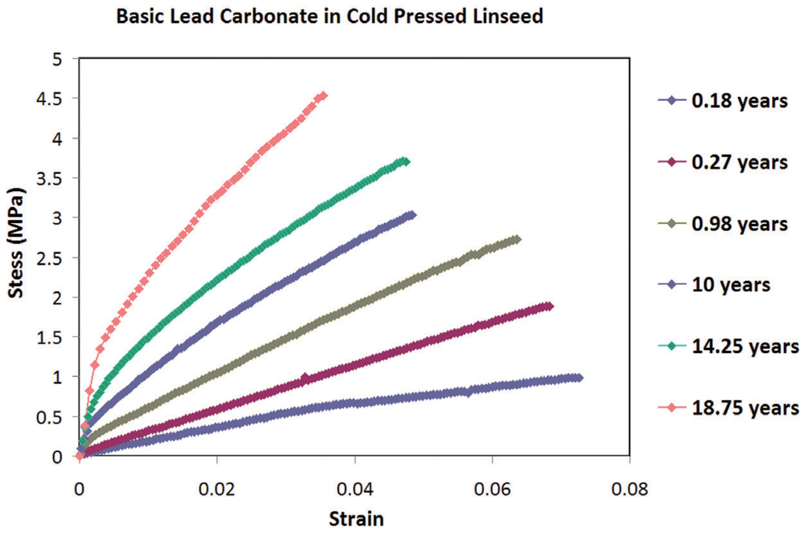


Figure 8.2
Changes in stiffness in lead white paint in cold pressed linseed oil as it ages to 0.18 (bottom curve) and 18.75 (top curve) years. A stretcher expansion of 1% results in 0.01 strain, which creates 0.2 MPa stress for the 0.18 year sample and 2.5 MPa for the 18.75 year sample (Mecklenburg, Tumosa, and Vicenzi 2013). The uniaxially measured ultimate strain for the 18.75-year-old paint is just over 3.5%. As the paint continues to age, this will reduce further.



A high-modulus material that breaks at low strain is said to be brittle. A brittle material, lacking flexibility, cannot absorb and disperse stresses (fig. 8.2). Instead, stress may be concentrated at specific points. This can be considered both in terms of the energy available to separate atoms and molecules and the energy released by the process. A high-modulus material is usually rigidly held by covalent, ionic, and/or hydrogen bonds, and the energy required to break such bonds may be very high. It is likely that any cracking can only be initiated at a fault in the material (of which there may be many) and where the energy available is concentrated at one point. At