Painted Wood: History and Conservation

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Proceedings of a symposium organized by the
Wooden Artifacts Group of the American Institute
for Conservation of Historic and Artistic Works
and the Foundation of the AIC, held at the Colonial
Williamsburg Foundation

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Edited by Valerie Dorge and F. Carey Howlett

Contents

PART FIVE

Ethical Considerations

Foreword

THIS VOLUME is probably one of the most ambitious publications projects undertaken to date by the Getty Conservation Institute and certainly the largest in the GCI's Proceedings series. And it is quite appropriate that it be so because the subject matter requires a comprehensive outlook. The importance of painted wood, its beauty, its many forms, and its complexity in the context of conservation required such an approach, particularly given the rapid advance of our knowledge in this area in the past few years. The book had its origin with the symposium organized by the Wooden Artifacts Group of the American Institute for Conservation of Historic and Artistic Works. This was a landmark event that required a full treatment of its contents.

Under the dedicated, disciplined, and enthusiastic editorship of Valerie Dorge and F. Carey Howlett, the present volume encompasses a wealth of material representing the breadth and depth of contributions to that symposium. From the mechanisms to understand and identify the materials that make up painted wood objects to the various factors affecting objects and surfaces, through the multiple analyses, techniques, and treatments of the diversity of painted wood surfaces, this publication attempts to provide an up-to-date compilation of information that would be welcomed by conservators, scientists, art historians, curators, artists, and all those interested in the fascinating array of painted wooden objects created since the earliest times.

One of the Getty Conservation Institute's goals is to contribute information and knowledge about cultural heritage to all those engaged in the conservation and protection of the cultural heritage. This publication is an example of the Institute's commitment to making that information available in ways that are illustrative, accessible, and relevant to the field.

We are delighted to have joined our effort to those of the AIC to bring this volume to professionals and students alike. The contents of the publication, the fine quality of its illustrations, and its format will hopefully be a significant contribution to the study of painted wood. We welcome your comments and hope that you will find as much joy and fascination in the publication as its designers, authors, and editors brought to its creation.

Miguel Angel Corzo
DIRECTOR
The Getty Conservation Institute

Preface

THE UNION OF WOOD AND PAINT is as old as the human desire to protect an object, or simply to decorate a surface," notes Bruce Hoadley in this volume. Indeed, throughout history, artists and artisans have combined a myriad of pigments, binders, and woods in countless forms. Whether made from common, locally found materials or from exotic commodities obtained through elaborate trade networks, such creations may reflect the inventive fancy of an individual or the formulaic conventions of a rigidly structured tradition. The function of the painted wooden object ranges from the practical to the profound: it performs utilitarian tasks, it conveys artistic whimsy, it connotes noble aspirations, and it embodies the highest spiritual expressions.

Whatever their composition, design, or purpose, however, all painted wooden surfaces share a common problem—they all endure the erosive effects of time, that continuum described by the Roman poet Ovid as a ceaseless "devourer of things." Use, exposure, response to physical change, chemical interactions, neglect, and a host of other damaging factors act as time's relentless agents. The condition of a painted wooden object, then, is the telltale gauge of its endurance, a gauge adjusted only by attempts to halt, slow down, or disguise the inevitable effects of time.

The past ten years have seen a wealth of innovative scholarship on the subject of painted wooden objects. Three distinct but interrelated perspectives contribute to this scholarship: the methods of inquiry of the curator or historian, the analytical techniques of the scientist, and the research and treatment practices of the conservator. Much of the best current scholarship incorporates all three of these perspectives with enlightening results. At times, this interdisciplinary approach confirms long-held assumptions about painted wooden objects. In other cases, it forces us to reinterpret their origins, meanings, materials, and methods of manufacture. In all cases, a comprehensive approach increases our understanding of these objects, and leads us to ever new avenues of inquiry.

To both document and further encourage this interdisciplinary exchange, the Wooden Artifacts Group of the American Institute for Conservation of Historic and Artistic Works (AIC) and the Foundation of the AIC sponsored a symposium in 1994 entitled Painted Wood: History and Conservation. This publication, the edited proceedings of the symposium, presents a sampling of painted wooden objects, addressing their historic significance, composition, deterioration processes, and methods

developed to preserve them. The conference had two main goals: (1) to look at paint and wood as interdependent and interactive materials, and to examine the preservation problems these interactions present; and (2) to look at painted wooden objects within a cultural context, and to explore the interpretive roles of all who are involved in their study and care.

Most of the papers presented at the symposium and appearing in the proceedings were drawn from a pool of more than seventy submitted abstracts. In addition, articles by Hoadley; Erhardt; Newman; and Mecklenberg, Tumosa, and Erhardt were commissioned to "set the stage" with reviews of the physical and chemical nature of paint and wood. A fifth article, by Martin, was commissioned for the publication to address the examination techniques alluded to in many of the chapters, and is an extension of the demonstration he presented at the symposium.

As an indicator of the collaborative nature of current scholarship, a significant number of articles in this volume were prepared jointly by related professionals—curator and conservator, conservator and conservation scientist, among others. See, for example, the article by curator Hastings and conservator Bigelow, which describes a treatment plan informed by interpretation in order to both "preserve the objects and improve their appearance for presentation within the context of a historic house." In other instances, a single author presents the results of interdisciplinary research, as exemplified by curator Safford's study, where paint analysis by conservators and scientists provided "tantalizing evidence [of intense color] that had long aroused the author's interest and curiosity" and resulted in a new understanding of the decorative qualities of Early American painted furniture.

Other articles encompass a diversity of painted wooden surfaces, including a German late-Gothic sculpture by Tilman Riemenschneider (Marincola and Soultanian); Baroque chapel decor in Minas Gerais, Brazil (Souza and Avila); eighteenth-century English painted garden furniture (White); Northwest Coast totem poles (Todd); and a twentieth-century American carousel figure (Parker and Sixbey). Despite differences in subject matter, most authors address universal concerns in the study and treatment of painted wood. These include questions of authenticity, problems of interpretation, ethical dilemmas confronted during treatment, and technical challenges to the conservation of deteriorating painted surfaces. Interesting contrasts arise because of differing approaches for various object types. Compare for example, the selective inpainting of losses to the polychromy of fifteenth-century Belgian altarpieces (Serck-Dewaide) versus preservation of the weathered surface of a nineteenth-century American trade sign (Hunt). In the same vein, juxtapose the careful stabilization of early decoration on European japanned cabinets (Webb) with the large-scale replication of original paint colors on nineteenth-century American houses (Gilmore; Gordon).

Because of the now prominent role of scientific analysis in the examination and treatment of works of art, one might assume that a thorough investigation is essential to the success of any undertaking. Yet real-world concerns—financial constraints, access to a laboratory, the intrusion of sampling—often preclude extensive scientific analysis. Fortunately, the resourceful investigative methods of the curator and conservator may make extensive analysis unnecessary. This perhaps is best illustrated by contrasting two approaches to the study and treatment of ecclesiastical

architecture in this volume. Because of budget constraints, Hulbert's research and subsequent treatment of alterations to the painted ceiling of Saint Helen's Church in Abingdon, England, were carried out with minimal scientific consultation. Payer and coworkers, on the other hand, report on a large-scale project supported by two major Canadian conservation facilities to investigate alterations, analyze early coatings and remove overpaint from sections of the interior of the Ursuline Chapel in Quebec City. Both projects were highly successful efforts to understand and preserve the painted wood components of elaborate church interiors, yet they differed significantly in their reliance on scientific analysis.

Beyond their focus on the history and conservation of painted wooden objects, these writings share another common element: the exhilaration of discovery. Several articles address promising innovations in conservation techniques and materials (Michalski et al.; Wolbers, McGinn, and Duerbeck), while a number combine historic research with scientific examination to rediscover historic painting techniques (Ballardie; Gold; Mussey; Portsteffen; Shelton; Thornton). Rediscovery also is a fascinating product of conservation examination and treatment: aged layers of overpaint and darkened varnish often cover intricate original decorative schemes (Parker and Sixbey; Williams, Ferrell, and Baker), and their removal sometimes leads to unexpected revelations, as in Ferrell's study of the painted omnibus, the Grace Darling, where conservation "returned the piece to a condition in which its original artistry could be visible and appreciated and . . . led to the discovery of the artist responsible for its extensive ornamentation."

Ultimately the discoveries presented here—the collaborative work of the scientist, curator, art or architectural historian, and conservator—add new layers of meaning to these objects. We hope you will make many exciting discoveries of your own within these pages, and that *Painted Wood: History and Conservation* will give new insight into the complexity, the beauty, the meaning, and the preservation of painted wooden objects.

Editors' Acknowledgments

A symposium and subsequent proceedings of this magnitude are the result of the long-term commitment of a small group of dedicated people, along with the support of many colleagues and many institutions. Though the list is long, the editors wish to acknowledge the contribution of each person and each institution to this project, and apologies are extended to anyone who may have been missed.

In 1992, the Wooden Artifacts Group of the American Institute for Conservation began discussing plans for a symposium on the subject of painted wood. Early the following year, a symposium planning committee was formed, consisting of F. Carey Howlett, the Colonial Williamsburg Foundation, as symposium director; Valerie Dorge, the Getty Conservation Institute, as program chair; with David Bayne, New York Bureau of Historic Sites, Peebles Island; Elisabeth Cornu, Fine Arts Museums of San Francisco; Gregory J. Landrey, the Winterthur Museum; Steven Pine, Fine Arts Museum of Houston; Michael Podmaniczky, the Winterthur Museum; Sarah Z. Rosenberg, executive director of the American Institute for Conservation; and Christine Thomson, then of the Society for the Preservation of New England Antiquities Conservation Center.

This core group was assisted by a symposium advisory board whose members contributed their specific expertise toward the development

of the program and the presentation of the conference. Members of the board were Ian C. Bristow, architect and historic buildings consultant, London; Wendy A. Cooper, then curator, Decorative Arts Department, Baltimore Museum of Art; Pamela Hatchfield, head conservator, Department of Objects, Museum of Fine Arts, Boston; Richard Newman, research scientist, Museum of Fine Arts, Boston; Jack Soultanian, conservator, The Metropolitan Museum of Art and The Cloisters, New York; and Richard Wolbers, associate professor of paintings conservation, Winterthur/University of Delaware Program in Art Conservation, Winterthur.

Following the symposium, the publications committee—Dorge, Howlett, Bristow, Cooper, Cornu, Newman, Soultanian, and Thomson—began the process of guiding the forty symposium papers through to publication.

The editors are grateful to the many people who provided invaluable comments in the manuscript review process. They are William Adair, David Arnold, Mark Aronson, Agnes Gräfin Ballestrem, David Barquist, David Bayne, Geoffrey Beard, Judy Bischoff, Sharon Blank, Susan Buck, Bodo Buczynski, Doris Couture-Rigert, Rene de la Rie, Jane Down, Robert Feller, Nancy Goyne Evans, Frances Halahan, Martha Hamilton, Pamela Hatchfield, Ronald Hurst, Gervase Jackson-Stopps, Paul Jett, Aldona Jonaitis, Patricia E. Kane, Manfred Koller, Gregory J. Landrey, Carl Lounsbury, Lee Miller, Mark Minor, Matthew Mosca, Cynthia Moyer, L. Cleo Mullins, Claire Munzenrider, Robert Mussey, Scott Odell, Steven Pine, Michael Podmaniczy, Bettina Rapael, Richard Renshaw-Beauchamp, William Robbins, Wendy Samet, Emily Sano, F. Christopher Tahk, Valentine Talland, Peter Volk, John Watson, Marianne Webb, Carolyn Weekley, Frank Welsh, James E. Wermuth, Paul Whitmore, and Richard Wolbers.

The following people contributed to the symposium poster session, and the editors regret that due to the size limitations, their presentations could not be included in this publication: William Adair, Keith Bakker, Jan Braenne, Ina Brousseau Marx, Claudina Maria Dutra Moresi, Richard Ford, William Gauthier, Helen Hughes, Mark Kutney and Philippe Lafargue, Caroline Marchand, James Martin, Alejandro Reyes-Vizzuett and Krassimir Gatev, Henning Schulze, Robert Snowden, and Valentine Talland. Demonstrations during the symposium were presented by Margaret Ballardie, Ina Brousseau Marx, James Martin, and Carole Dignard and David Arnold.

Other people and institutions making important contributions to either the symposium or the publication process include Margaret Whitchurch, Patricia Bare, Bonnie Baskin, Pamela Gladding, Rose Kerr, John Larson, Virginia Lascara, Carol Noel-Hume, Albert Skutans, Lynne Spencer, Christopher Swan, Thomas Taylor Jr., The Agecroft Association, Golden Artist Colors, members of the Virginia Conservation Association, and colleagues at the Colonial Williamsburg Foundation and the Getty Conservation Institute.

The editors are grateful for the encouragement and support of AIC President Deborah Hess Norris, the AIC Board of Directors, all of the staff of the AIC office, and the editors' colleagues in the Wooden Artifacts Group of the AIC, particularly Deborah Bigelow who generously shared her experiences as project director for the previous conference, the Gilded

Understanding and Identifying Materials
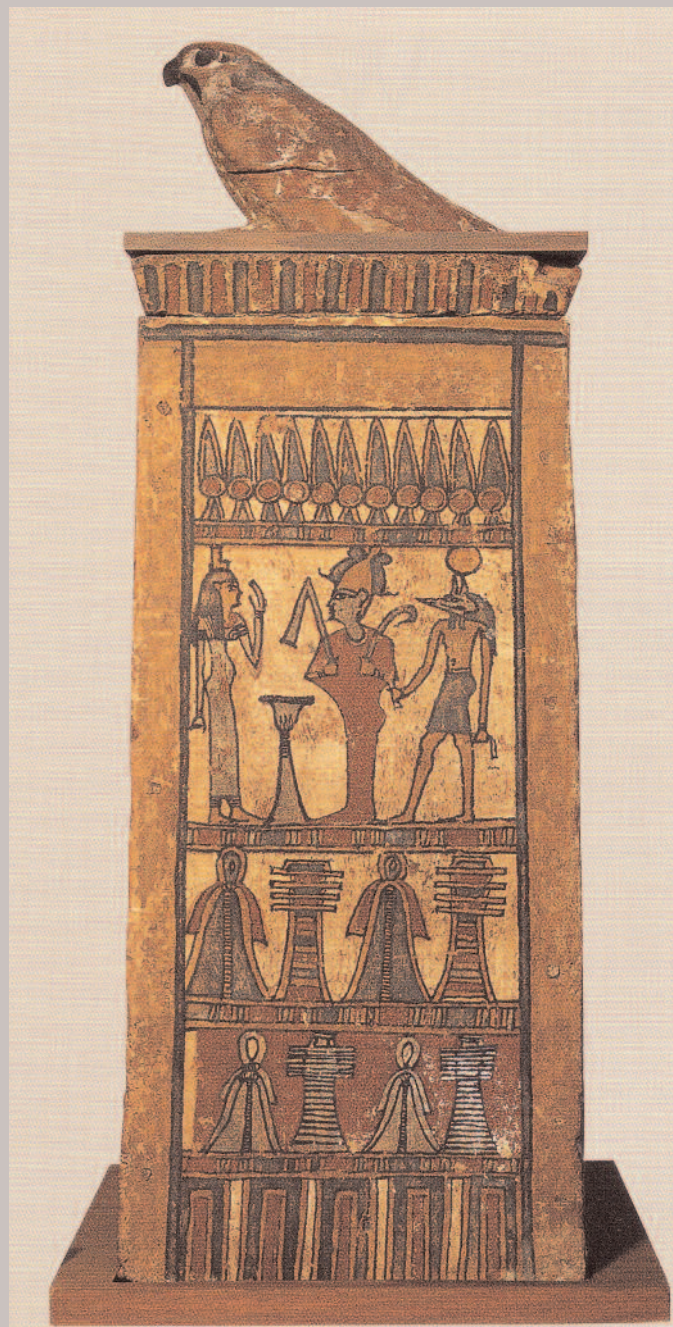
Wood as a Physical Surface for Paint Application

R. Bruce Hoadley

W OOD HAS ALWAYS BEEN a vital factor in human existence and has provided an array of blessings, from basic needs to fanciful luxuries. It is not surprising that as we survey our heritage, we find deep involvement with artifacts of wood, both utilitarian and decorative. In the study of decorative arts, attention is easily focused on design and aesthetics, as is so often the case with painted wood, while the wood itself may well receive the least consideration.

To explore wood is to realize its complexity, its diversity, and its variability. That a material with such a simple designation as *wood* could in fact be so complicated is part of its fascination. On the one hand, wood is a straightforward and simple material, a delightful bounty of nature, to be used at will. On the other hand, wood has its ability to remain enigmatic and troublesome. The union of wood and paint is as old as the human desire to protect an object, or simply to decorate a surface. The link between paint and wood is therefore at the heart of any approach to conservation of these objects. To the conservator, the analysis of conditions and problems involves a familiarity with the physical structure of the wood as a material and with its surface interaction with the applied paint, as well as with the behavior of the wood after paint application.

Evaluating a wood surface begins by exploring the wood itself, with the realization that every surface is different from the next and cannot be predicted in detail. This article will therefore focus on the basic anatomical structure of wood tissue to provide an understanding of potential surfaces generated by cutting through it. In addition, pertinent physical properties will be summarized, with particular attention given to the wood's response to variation in atmospheric humidity and resulting dimensional changes.

The Universe of Wood

Wood is the tissue of stems and branches of higher order plants—trees—within the division of the plant kingdom known as the spermatophytes, which includes all seed plants. Within the spermatophytes are two classes, the gymnosperms and the angiosperms. Taxonomically, these classes are further arranged into orders, families, genera, and finally species. Throughout the world there are well over one hundred thousand species of woody plants, but fewer than one percent are utilized in any significant quantity.

Among the vast array of tree species, the most familiar and most used woods are obtained from trees that we know as hardwoods and softwoods. The angiosperms are grouped into two subclasses, the monocotyledons (which includes palms, rattans, bamboo, etc.) and the dicotyledons, the source of the woods we know as *hardwoods*. The woods we call *softwoods* are from trees of the gymnosperms, principally in the order Coniferales; thus these trees are also known as *conifers*. The traditional terms hardwood and softwood have no accurate reference to the relative hardness and softness of the wood, and should therefore be interpreted simply as designations for the two major botanical groups they represent. Although tree stems of both hardwoods and softwoods have many similar characteristics of form and gross features, there are categorical differences of anatomical detail between the two groups of woods.

The Tree Stem and Its Wood

The tree has a main supporting stem or trunk, the portion most commonly used for lumber and veneer. When a cylindrical log is removed from the stem by crosscutting, the exposed ends of the log reveal the outer layer of bark. Interior to the bark, and comprising the bulk of the stem, is the wood, characterized by its many growth rings arranged concentrically around the central pith. Between the bark and the wood is a microscopically thin layer of living tissue, the cambium, whose cells divide during the growing season to produce new wood cells to the inside, bark to the outside.

Wood cells and tissues

The cell is the basic structural unit of plant material, and, accordingly, wood tissue is a physical structure of countless cells. Wood cells are typically elongated, although the proportions of length to diameter vary widely among cell types, from short barrel shapes to long needle-like cells.

Wood tissue consists mainly of elongated cells whose long axes are oriented vertically in the tree and are referred to as *longitudinal cells*. These cells are mostly too small in diameter to be seen without magnification, but in a few species, such as ash (*Fraxinus* spp.), chestnut (*Castanea* spp.), and mahogany (*Swietenia* spp.), the largest can be seen with the unaided eye. The direction of these dominant longitudinal cells gives wood its *grain* direction, parallel to the stem axis.

Scattered through the wood are cells called *ray cells,* whose axes are perpendicular to the longitudinal cells. These cells occur in flattened, ribbonlike groups called rays; the *ribbons* lie horizontally in the tree (the plane of the ribbon vertical), extending inward from the cambium toward the pith. Individual ray cells and even smaller rays are too small to see, but rays vary in size according to the number of cells contained within them, and in some species, such as oak (*Quercus* spp.) and beech (*Fagus* spp.), the largest rays are easily seen on wood surfaces.

Each wood cell consists of an outer cell wall surrounding an inner cell cavity. The cell wall is about 70% cellulose and hemicellulose, the remainder mostly lignin, and typically 1–5% extractives (as will be discussed), mineral traces, et cetera. The cellulose is oriented within the layered cell wall in a manner to give the greatest strength and dimensional stability parallel to the cell axis (Fig. 1).

Figure 1
Diagrammatic representation of a typical longitudinal wood cell, such as a coniferous tracheid or a hardwood fiber, showing the layering of the cell wall and the organization of cellulosic molecular structure into fibrils with crystalline and amorphous arrangement.

Structural diagram of longitudinal wood cell
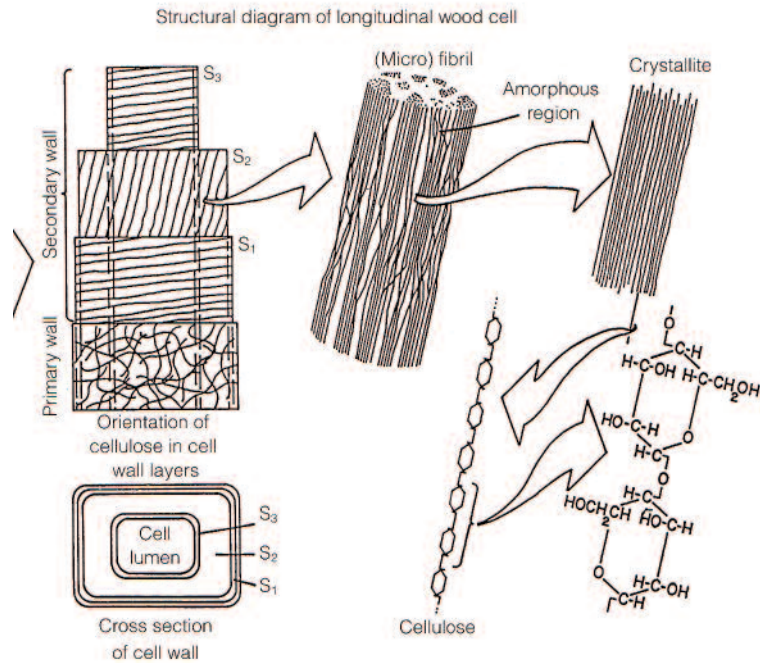
In considering wood as an interface for paint, it is important to recognize that a wood surface is the aggregate of severed or fractured wood cells whose physical configuration depends on the dimensions and orientation of the cells involved and whose surface chemistry reflects the chemical structure of the cell wall and the cell contents, as well as exposure to environmental pollutants.

Sapwood and heartwood

In the living tree, as new wood cells are being added to the latest growth ring by division of the cambial cells, the living protoplast disappears from the cavities of most wood cells as they become specialized for conduction or support of the tree. A few cells retain a living protoplast and continue as living cells, with the capability of metabolizing and storing food for the tree. The most recently formed rings of growth to the inside of the cambium and bark are called *sapwood,* which has the capability of transporting sap and storing food. The sapwood, the cambium, and the last-formed inner bark constitute the living portion of the tree. As a tree stem increases in diameter, the entire stem is not used to supply the crown with sap. The central wood of the stem ceases to function in vital activity and transforms to *heartwood*. This conversion to heartwood is usually accompanied by the deposition of materials called *extractives* on and within the cell walls. Extractives may alter properties and behavior of the wood. For example, it is the pigmentation of extractives that gives the heartwood any characteristic color it may have.

Growth rings

One recognizes wood by its growth rings, which are revealed in recognizable patterns on exposed wood surfaces. In temperate regions of the world, the growth cycles are yearly and produce annual rings. The distinctiveness of the growth ring is a species characteristic determined by cell

structure, usually by the variation of cell diameter or by the distribution of different types of cells. Where there is visual contrast within a single growth ring, the portion formed in the spring is called *earlywood,* the remainder *latewood.* In species such as larch (*Larix* spp.) or oak, the contrast between earlywood and latewood is conspicuous, and the wood is said to be *uneven-grained.* In other species, such as sweetgum (*Liquidambar styraciflua*) or holly (*Ilex* spp.), there may be little variation within each growth ring, perhaps requiring magnification with lens or microscope to discern the individual growth rings. In such cases, earlywood and latewood cannot be designated, and the wood is said to be *even-grained.*

Structural Arrangement within the Tree Stem
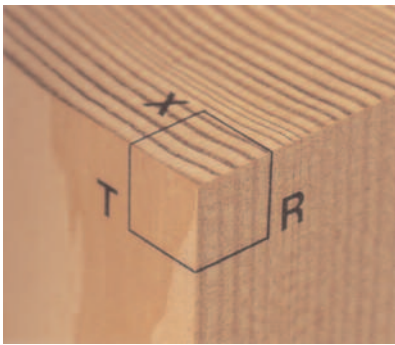
Figure 2
A block of Douglas-fir sawn to show the characteristic appearance of transverse, or cross-sectional (X), radial (R), and tangential (T) surfaces.
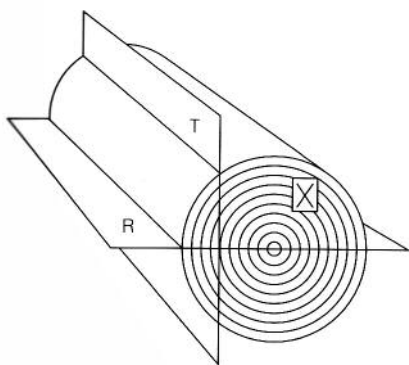
Figure 3
The fundamental structural planes of wood, as indicated in Figure 2.

In view of the concentric arrangement of growth rings around the central axis of the tree, as well as the orientations of longitudinal and ray cells, it is appropriate to consider wood tissue as a three-dimensional structure. The organization of the wood tissue thereby provides a basis for designating coordinate directions and structural planes within the wood. The three fundamental planes of wood are the transverse (cross-sectional), radial, and tangential planes. These terms equally apply to the surfaces that are exposed by cutting the wood in the respective planes, or to thin sections removed for microscopic study. The letters X, R, and T are commonly used to designate transverse, radial, and tangential planes, respectively, as well as corresponding surfaces or sections (Fig. 2).

Viewing a tree stem (or log) as a cylinder, any plane perpendicular to its length is a *transverse plane,* or *cross-sectional plane,* typically observed as the end of a log or board (X in Fig. 3). A plane that bisects the cylinder lengthwise through the center of the log, or the pith, is called a *radial plane* (R in Fig. 3). Any lengthwise plane that does not pass through the pith forms a tangent to its growth-ring structure and is called a *tangential plane* (T in Fig. 3). Because of growth-ring curvature, this plane is most accurately tangential where it intersects and is perpendicular to a radial plane. In preparing a small cube of wood for study, however, the curvature of the rings is usually insignificant, so the cube can be oriented to contain quite accurate transverse, radial, and tangential surfaces.

In wood harvested for use, the surfaces of boards or other components are usually cut parallel to the log axis and therefore are crosscut to transverse surfaces at the end. Their *side-grain* surfaces may not be specifically radial or tangential but intermediate to the two, or even a combination of both. Any board or outer slabbed face of a log is loosely accepted as a tangential board or surface.

Terminology applied to lumber and veneer is derived in some cases from the structural orientation within the log and, in some cases, from the manner of sawing the material. Tangentially cut boards and veneer—and their surfaces—are termed *plain-grained, flatsawn* or *flat-grained,* or *slash-grained.* Radially cut pieces are said to be *vertically grained, edge-grained,* or *quartersawn.*

Softwoods and Hardwoods

The tree-stem and cellular characteristics of wood discussed here are applicable without regard to specific type, but further investigation of the nature and properties of woods is best done in recognition of some of the distinct differences between the softwoods and hardwoods.

Specific gravity

Relative density, or specific gravity, is an important physical property of wood. It is related to strength and dimensional behavior and it affects paint application, as well. In comparing softwoods and hardwoods, it is valuable to consider the ranges of specific gravity represented by the two groups. Wood density is expressed as oven-dry weight per unit volume. Specific gravity of a given wood is determined by comparing the density of the wood to the density of water, which is 1 g cm^{-3}. For example, a wood weighing 500 kg m^{-3} would have a specific gravity of 0.5.

Figure 4 shows a number of representative woods listed opposite their respective average values of specific gravity. Note that the range of softwoods is approximately from 0.3 to 0.65, the heaviest little more than twice the density of the lightest. Among hardwoods, however, the range is from 0.15 to 1.3. It is evident that the traditional terms softwood and

Figure 4
The specific gravity of selected softwoods and hardwoods.
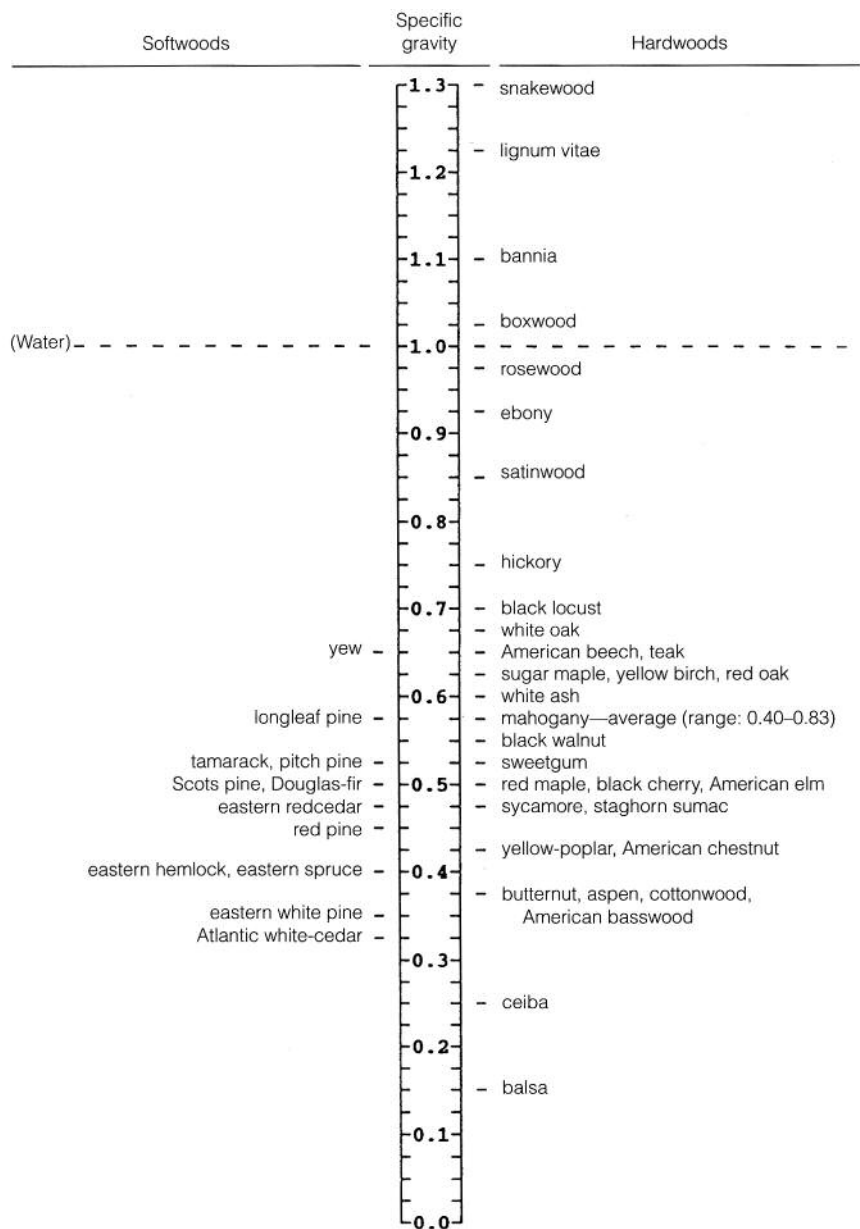
hardwood have no literal accuracy and should therefore be interpreted as designations for botanical groups rather than density groups.

The complex of cellulose and lignin forming the walls of wood cells has a specific gravity of approximately 1.5. The average specific gravity should therefore suggest something of the nature of cell types to be found in a wood. For example, in a wood such as lignum vitae (*Guaiacum* spp.) with a specific gravity of about 1.2, one might expect to find cells with very thick walls and relatively small cell cavities. A wood as light as balsa (*Ochroma pyramidale*) will have relatively thin walls and large cell cavities.

Cell structure

The most obvious differences between hardwoods and softwoods are apparent when the cell structure of the two groups is compared. Within either group, analysis of cell structure accounts for the extent of earlywood-latewood variation within a single growth ring. Figure 5a–d shows examples of the cell structure of representative softwoods and hardwoods.

Softwood cell structure

Among the softwoods, the bulk of the wood tissue (approximately 90% by volume) consists of longitudinal tracheids. These cells are conspicuously elongated, with lengths of up to one hundred times their diameters, the lengths averaging from 2 to 7 mm among the various conifers. Transverse sections (Fig. 5a–d, left-hand column) reveal that the tracheids occur in rather uniform radial rows, and that they are quite uniform in tangential diameter. Among the conifers, the diameters of the tracheids are used as a relative measure of the texture of the woods. Tracheid diameters range from an average of 60–70 μm in the coarsest textured softwoods, such as baldcypress (*Taxodium distichum*) and redwood (*Sequoia sempervirens*), to an average of only 15–20 μm in fine-textured softwoods, such as yew (*Taxus* spp.) and eastern redcedar (*Juniperus virginiana*). Many softwoods, such as eastern white pine (*Pinus strobus*) and spruce (*Picea* spp.), have average tracheid diameters in the medium texture range of 30–40 μm. It is apparent that the average diameter and cell-wall thickness of the earlywood tracheids will determine the physical surface configuration on machined wood surfaces and will thereby be related to the ability of a surface coating to fill or penetrate the wood surface.

Tracheids are largest in radial diameter in the earlywood. Radial diameter decreases and cell walls become thicker toward the latewood portion of the growth rings, resulting in greater density and darker appearance of the latewood. The extent of variation of radial diameter and cell-wall thickness determines the overall contrast in density between earlywood and latewood. The lower density softwoods, such as eastern white pine and northern white cedar (*Thuja occidentalis*), have minimal change of density from earlywood to latewood. These woods tend to have fairly uniform working properties, as well. The higher density softwoods, such as larch, Douglas-fir (*Pseudotsuga menziesii*), or southern yellow pine (*Pinus* spp., southern group), have thin-walled earlywood but strikingly thicker latewood. The southern yellow pines, for example, typically average 0.5–0.6 specific gravity overall. However, these values represent the average of earlywood of 0.3 specific gravity and latewood of up to 0.95 specific gravity. This variation renders drastic differences in radial and tangential surfaces and the tissue exposed, and to paint applied to them.

Figure 5a–d
Transverse surfaces (*left-hand column*) (×4.08) and stained sections (*right-hand column*) (×40.8) of representative softwoods and hardwoods: (a-1, a-2) longleaf pine (*Pinus palustris*), an uneven-grained softwood; (b-1, b-2) eastern white pine (*Pinus strobus*), an even-grained softwood; (c-1, c-2) northern red oak (*Quercus rubra*), a ring-porous hardwood; and (d-1, d-2) American basswood (*Tilia americana*), a diffuse-porous hardwood.
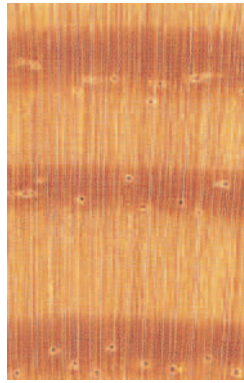
a-1
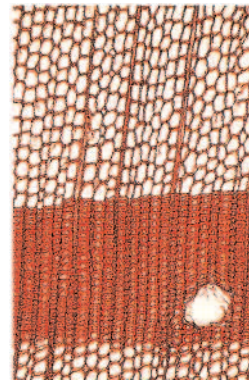
a-2

b-1
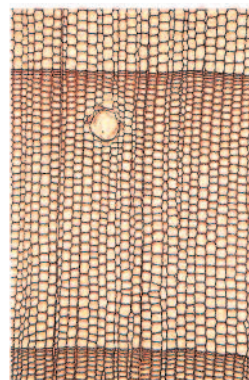
b-2
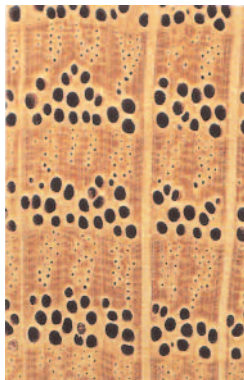
c-1

c-2
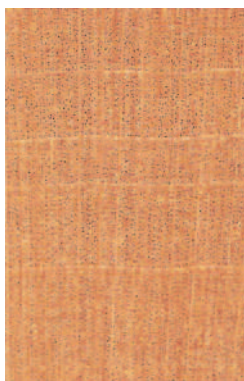
d-1
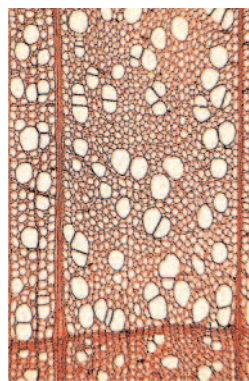
d-2

Certain softwoods—such as pines (*Pinus*), spruces, larches, and Douglas-fir—have *resin canals* (tubular passageways that occur randomly through the wood) both longitudinally and radially. Epithelial cells line the resin canals and exude resin, or "pitch," into them. The contents of the resin canals may emerge on wood surfaces, interfering with the bonding of paint films or bleeding through painted surfaces.

Some of the conifers, such as cedars, redwood, and baldcypress, have a cell type known as *longitudinal parenchyma*. These are short cells that occur in vertical strands, a given strand occupying the analogous position of a single longitudinal tracheid. Although few in number, these cells commonly have colored contents in their cell cavities. The materials of these inclusions may bleed through to the surfaces of paint layers and cause resulting discoloration of painted surfaces.

Softwoods have relatively small rays, usually only one cell wide (as viewed tangentially). The rays have an insignificant effect on wood surfaces relative to paint films.

Hardwood cell structure

Compared to softwoods, hardwoods exhibit several major differences in cell structure. First, hardwoods have many more specialized types of longitudinal cells, representing a wider range of dimensions and relative cell-wall thickness. Because of the variety of cell sizes, arrangement of cells is typically irregular, compared to the orderly radial rows of tracheids that characterize softwood structure. Second, where earlywood-latewood variation occurs, it results from the sorting of different cell types across the growth ring. Third, ray size among hardwood species varies from invisibly small rays (as routinely found in the softwoods) to very large, visually conspicuous rays.

Longitudinal cell types in hardwoods are specialized according to function and vary from the large diameter and thin-walled *vessel cells,* specialized for conduction, to the smallest diameter and sometimes very thick-walled *fiber cells,* obviously specialized to contribute strength to the tree. There are intermediate cell types, as well.

The most conspicuous cell types in hardwoods are the vessel cells. These cells, also referred to as *vessel elements,* form in the tree in an end-to-end arrangement; because they no longer have end walls, these cells form continuous conductive pipelines. In comparing hardwood species, the average diameter of the largest vessels serves as a relative measure of texture. The coarsest textured woods—such as oak, chestnut, ash, and mahogany—have vessel diameters of up to 300–350+ μm. Vessels of this size are easily seen with the unaided eye on cleanly cut surfaces. At the other extreme, vessel diameters average only 40–60 μm in holly and 50–80 μm in sweetgum. The vessel elements in such fine-textured hardwood are invisibly small and can scarcely be discerned with a 10× hand lens. In medium-textured woods, such as birch or cottonwood, the larger vessels average 130–150 μm in diameter and are barely visible.

When vessels are cut transversely, the exposed open ends on a cross-sectional surface are referred to as *pores*. Evenness of grain in hardwoods is largely determined by the distribution of vessels and fibers and can be assessed by noting the arrangement of pores on a transverse surface. If the largest pores are concentrated in the earlywood, the wood is said to be *ring-porous*. In a typical ring-porous wood (Fig. 5c-1, c-2), it is

the zone of large pores that defines the earlywood portion of the growth ring. Latewood pores are much smaller. Oak and ash are examples of ring-porous woods. In these woods, the thin-walled earlywood vessels are surrounded by other cell types—parenchyma cells and tracheids, which are much smaller in diameter and also thin walled. Collectively, therefore, the earlywood is a weaker, softer layer than the latewood—which is dominated by fibers of small diameter and very thick walls, resulting in relatively dense tissue. Most ring-porous woods are, therefore, inherently uneven-grained. In the highest density ring-porous woods, such as black locust (*Robinia pseudoacacia*) or hickory (*Carya* spp.), the earlywood zone of large pores is narrow, and the latewood is characterized by fewer, smaller pores and fibers with extremely thick walls. In lower density ring-porous woods, such as chestnut and catalpa (*Catalpa* spp.), the latewood is characterized by greater numbers of latewood pores or masses of thinner walled fibers.

If the pores are uniform in size, and evenly distributed throughout the growth ring, the wood is said to be *diffuse-porous* (Fig. 5d-1, d-2). Woods in this category include maple (*Acer* spp.) and basswood (*Tilia* spp.). Although most diffuse-porous woods of the temperate regions are rather fine textured, many diffuse-porous tropical woods, such as mahogany, are coarse textured. Ring-porous tropical species, such as teak (*Tectona grandis*), are least common. Ideally, diffuse-porous woods such as maple and sweetgum are so even-grained that there may be little or no indication of earlywood and latewood; the growth-ring boundary may be delineated only by a slightly darker coloration in the most recently formed fibers.

Some woods, such as butternut (*Juglans cinerea*) and black walnut (*Juglans nigra*), are *semi-ring-porous*. Large pores are found at the earlywood edge of the growth ring, but pore diameter decreases gradually across the growth ring to a small diameter in the outer latewood, with no apparent delineation of earlywood and latewood. Some woods, such as cottonwood (*Populus* spp.) and willow (*Salix* spp.), have medium to medium-small pores that gradually diminish in diameter to smaller and fewer pores in the latewood. These woods are called *semi-diffuse*.

The size of rays varies widely among hardwood species. In only a few hardwoods, such as chestnut, aspen (*Populus* spp.), and willow, the rays are exclusively uniseriate (that is, only one cell in width as viewed tangentially), as is found in most softwoods. In many hardwoods—such as ash, basswood, and birch (*Betula* spp.)—the rays range from two to several cells in width (multiseriate) but are still inconspicuous. In some woods—such as maple, cherry (*Prunus* spp.), or yellow-poplar (*Liriodendron tulipifera*)—the multiseriate rays may be imperceptible on tangential surfaces but may display a conspicuous pattern, known as *ray fleck,* on a radial surface. In beech and sycamore (*Platanus occidentalis*), the multiseriate rays are easily seen on tangential surfaces and appear as pronounced ray fleck on radial surfaces. Oaks have rays of two distinct sizes; most are uniseriate and invisibly small, but some are very large. These multiseriate rays are up to thirty to forty seriate, and measure up to an inch in height in the red oaks (*Quercus* spp., subgenus *Erythrobalanus*) and up to several inches in height among the white oaks (*Quercus* spp., subgenus *Leucobalanus*). Radial surfaces of oak may display a dominant ray fleck figure, with large patches of ray tissue exposed.

Wood-Moisture Relationships

No discussion of wood properties and performance can be complete without consideration of moisture and its relationship to dimensional change. It is customary to think of the moisture content of wood as that which can be driven off by heating the wood to 100–105 °C. Moisture content of wood is measured quantitatively as the ratio of water weight in a sample of wood to the oven-dry weight of the wood, expressed as a percentage. For example, if a stick of wood originally weighed 112 g but weighed only 100 g after oven drying, the 12 g weight loss divided by the oven-dry weight of 100 g would indicate a moisture content of 0.12, or 12%.

Trees contain a liquid referred to as sap, which is mostly water with dissolved trace minerals and nutrients. In considering the properties and behavior of wood, it is appropriate to think of the moisture in wood simply as water, whether it is the original sap leaving the wood or other water reentering the wood.

Water exists in two forms in wood tissue—as bound water and as free water. In the "green" wood of living trees, the cell walls are saturated and fully swollen with molecular water held by chemical attraction within the fibrillar structure. This water is called *bound water*. The moisture content at which all cells are saturated with bound water is the fiber saturation point, which represents a moisture content of about 28–30%.

Water in the tree in excess of the fiber saturation point exists simply as liquid water in the cell cavities and is called *free water*. When wood is dried, the free water is the first moisture to be lost from wood tissue. Only when all free water has evaporated and diffused out of the wood tissue will the bound water begin to leave, thus affecting the cell walls. Loss of free water has little effect on wood properties other than weight, but as bound water leaves the cell walls, the wood increases in strength and shrinks in dimension.

Hygroscopicity

When wood is initially dried or "seasoned" for use, all of the free water is removed, plus some of the bound water. The amount of water remaining is determined by the relative humidity of the surrounding atmosphere. Because the humidity usually varies, the bound water content of wood varies also, losing or desorbing moisture when the humidity is low, gaining or adsorbing moisture when the surrounding air is humid. The term *equilibrium moisture content* indicates the level of bound water moisture content that a piece of wood will eventually attain when exposed to a given level of relative humidity. The relationship between relative humidity and equilibrium moisture content is shown in Figure 6 for a typical species, white spruce (*Picea glauca*). An important factor not indicated in this illustration is time; obviously, thicker pieces of wood will take longer periods of time to reach a new equilibrium in a new environment. The cell walls at the surface will respond almost instantaneously; thin veneers may take only a matter of hours; and thick planks may take weeks or months to reach equilibrium, depending on other factors, such as density.

Dimensional response

Dimensional change is perhaps the most telling consequence of bound water sorption. As bound water is adsorbed into the cell walls, the fibrils

Figure 6
Relationship between equilibrium moisture content and relative humidity for white spruce, subject to normally variable atmospheric conditions.
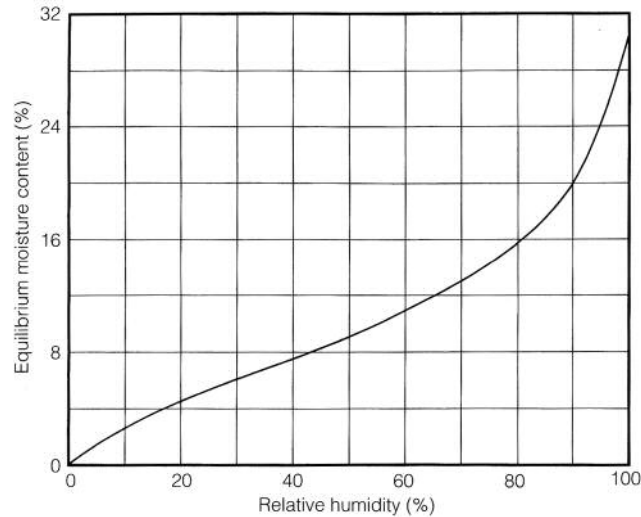
expand laterally, and collectively the wood cells swell, principally across the grain. Conversely, as wood loses moisture, the wood shrinks.

Shrinkage and swelling of wood is approximately proportional to moisture content change over the range of moisture content between the fiber saturation point and the oven-dry condition. However, dimensional change is dramatically different according to the anatomical direction in the wood, and varies among species, so shrinkage is determined separately in the tangential, radial, and longitudinal directions for each species. It is common to express dimensional change in wood as a total shrinkage percentage, which is determined by measuring a fully swollen piece before and after drying and dividing the loss of dimension by the original dimension. For example, if a flatsawn board measured 25.40 cm across its tangential width when green but only 23.36 cm when oven-dried, the loss of 2.04 cm divided by the original 25.40 cm would indicate a shrinkage of 8%.

Longitudinal shrinkage for normal wood of all species averages only 0.1–0.2%. Fractional amounts due to humidity-induced moisture content changes are insignificantly small and are usually ignored. It is usually assumed that wood is dimensionally stable in the grain direction; transverse dimensional change is both significant and troublesome; tangential shrinkage among species varies from 4% to 12%, but the average is about 8%; and radial shrinkage is only about half this magnitude, typically about 4%, but ranging from 2% to 8% among various species. Boards or panels cut from the wood with growth-ring placement that is intermediate between flatsawn and quartersawn will understandably have intermediate dimensional properties. Table 1 lists values of tangential and radial shrinkage for a number of representative woods.

The approximate amount of shrinkage or swelling to be expected in a piece of wood can be estimated on the basis of anticipated variation in relative humidity, as illustrated in Figure 7. This diagram can also be used in conjunction with the values in Table 1 for making comparisons between alternatives, such as between species or between radial and tangential cuts of the same species.

Warp in boards or panels is the result of uneven dimensional change, and can take such forms as *cup* (distortion across the width of a board), *bow* (end-to-end distortion along the flat surface of a board), *crook* (end-to-end deformation along the edge of a board), or *twist* (four corners

Table 1 Shrinkage percentages for common woods (Hoadley 1980:74)

Species	Tangential shrinkage (%)	Radial shrinkage (%)
Softwoods		
baldcypress (*Taxodium distichum*)	6.2	3.8
Douglas-fir (coastal) (*Pseudotsuga menziesii*)	7.8	5.0
fir, balsam (*Abies balsamea*)	6.9	2.9
hemlock, eastern (*Tsuga canadensis*)	6.8	3.0
pine, eastern white (*Pinus strobus*)	6.1	2.1
pine, longleaf (*Pinus palustris*)	7.5	5.1
pine, red (*Pinus resinosa*)	7.2	3.8
redcedar, eastern (*Juniperus virginiana*)	4.7	3.1
redwood (old growth) (*Sequoia sempervirens*)	4.4	2.6
spruce, red (*Picea rubens*)	7.8	3.8
tamarack (*Larix laricina*)	7.4	3.7
white cedar, northern (*Thuja occidentalis*)	4.9	2.2
Hardwoods		
ash, white (*Fraxinus americana*)	7.8	4.9
aspen, quaking (*Populus tremuloides*)	6.7	3.5
basswood, American (*Tilia americana*)	9.3	6.6
beech, American (*Fagus grandifolia*)	11.9	5.5
birch, yellow (*Betula alleghaniensis*)	9.2	7.2
butternut (*Juglans cinerea*)	6.4	3.4
cherry, black (*Prunus serotina*)	7.1	3.7
chestnut, American (*Castanea dentata*)	6.7	3.4
cottonwood, eastern (*Populus deltoides*)	9.2	3.9
elm, American (*Ulmus americana*)	9.5	4.2
hickory, shagbark (*Carya ovata*)	10.5	7.0
mahogany (*Swietenia* spp.)	5.1	3.7
maple, sugar (*Acer saccharum*)	9.9	4.8
oak, northern red (*Quercus rubra*)	8.6	4.0
sweetgum (*Liquidambar styraciflua*)	10.2	5.3
sycamore (*Platanus occidentalis*)	8.4	5.0
teak (*Tectona grandis*)	4.0	2.2
walnut, black (*Juglans nigra*)	7.8	5.5
willow, black (*Salix nigra*)	8.7	3.3
yellow-poplar (*Liriodendron tulipifera*)	8.2	4.6

For each species listed, the average values for total linear shrinkage in the tangential and radial directions are given. Each value is the ratio of total dimensional change (shrinkage) to the original green dimension, expressed as a percentage.

of a board that do not lie in a plane). Cup is perhaps the most familiar and usually is seen in flatsawn boards, due to the difference between radial and tangential shrinkage. In a flatsawn board, the surface layer nearest the pith is more nearly radial than the opposite surface that was nearer to the bark. The pith side will therefore shrink or swell less, the bark side

Figure 7

Chart for the estimation of shrinkage or swelling of wood. For example, longleaf pine (*Pinus palustris*) has a tangential shrinkage percentage of 7.5% (from Table 1). As shown by the dashed lines on the chart, a moisture content change (ΔMC) from 14% to 7% would produce a dimensional change (ΔD) of approximately 1.75% across the face of a flatsawn (tangentially cut) board.
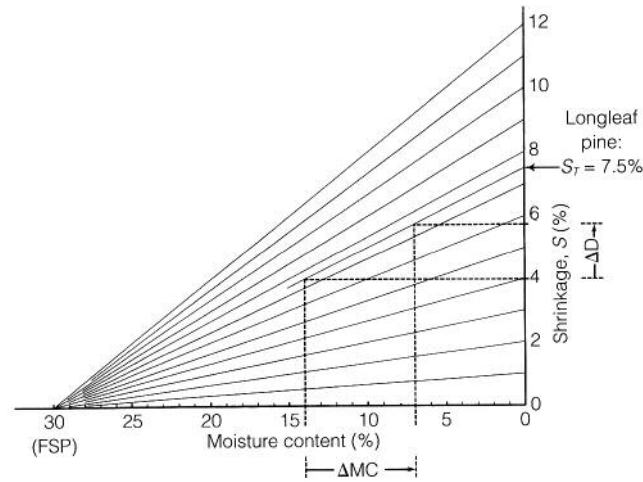
more, and the board will cup—concave to the bark side as it dries or concave to the pith side as it gains moisture.

A noteworthy effect of dimensional behavior is known as *compression shrinkage*. This occurs when a relatively dry piece of wood is restrained from normal perpendicular-to-grain swelling as its moisture content increases. This has the effect of crushing the wood. Wood has the ability of deforming elastically less than 1%, and any additional crushing will cause permanent set. If the now-crushed wood is returned to its original moisture content, it will shrink to a smaller dimension than it had originally. This apparent loss of dimension is compression shrinkage.

Compression shrinkage is well known as the cause of loose tool handles and wobbly furniture. It is also the major cause of surface checking in unprotected board surfaces. When a relatively dry wood surface is exposed to extremely high humidity or is directly wetted, the surface layer of wood cells quickly adsorbs moisture to fiber saturation. The wet surface-wood cells attempt to swell but are held in place by the restraint of the substrate of dry, unswollen wood beneath. The restrained surface layers take on compression set. When eventually redried to the original moisture content, the stress-set surface will shrink excessively (compression shrinkage) and may cause the board to cup or develop surface checks. Each time the cycle is repeated, wetting occurs in the previously opened checks, damaging and deepening each one a little more. This is a primary mechanism in the surface weathering of unprotected wood. It also explains why weathered boards are usually cupped to the weathered side, regardless of the placement of growth rings.

Dimensional change in wood shows significant correlation with specific gravity. With some exceptions, the higher the specific gravity, the greater the shrinkage percentage. It follows that dimensional change is variable in woods with variable density tissue. In southern yellow pine, for example, the latewood will swell and shrink more than earlywood.

Summary

In the overview of anatomical features and properties presented here, the objective is to characterize the physical nature of wood as a potential surface for paint application. This also provides a basis for summarizing some of the specific points of interest relative to interaction with a coating of paint (see also Mecklenberg, Tumosa, and Erhardt, herein). A paint layer

interacts with the wood physically to the extent that it flows into the depressions created by the cell cavities at the surface, and to some extent even deeper, according to its ability to penetrate additional cells through pits and perforations of the cell walls. Paint also interacts chemically, by bonding to chemically reactive sites exposed at the surfaces of any cells contacted. Once the paint layer has set, it must then survive the mechanical stresses of dimensional change in the wood substrate, as well as the chemical degradation of the adhesive bonding with the wood.

The wood and the paint film share an interesting symbiotic relationship. For its survival, the paint film depends on the stability and bonding sites of the wood surface; at the same time, the wood surface relies on the paint film to mitigate the sorption of moisture that changes its dimensional status and competes for bonding sites, and to shield the chemical bonds between wood and paint from the degradation of ultraviolet light.

In reviewing the features of wood relative to the paint layer, the three-dimensional structure of wood is of primary importance, since it results in such a contrast in surfaces depending on the plane of cut. The greatest contrast is between end-grain (that is, transverse or cross-sectional) surfaces and side-grain (that is, tangential, radial, or any intermediate longitudinal) surfaces. The end grain is in many respects more "open" to surface penetration as it is generally found that wood is approximately ten to fifteen times more permeable to liquids in the direction of the longitudinal cells than perpendicular to them. However, the end-grain surface presents reduced exposure of chemical bonding sites and is subject to major dimensional change in every direction. The greater longitudinal permeability of wood exacerbates the consequence of dimensional response near end-grain surfaces. Compression shrinkage and resulting radial checks into the ends of boards are therefore more severe than into side-grain surfaces.

The exposure of cell cavities along side-grain surfaces presents relatively shallow depressions for the paint layer interface, depending on the texture of the species, whereas a maximum of chemical bonding may be available. Along longitudinal surfaces the wood is quite stable in the grain direction, but unstable perpendicular to the grain. Here the importance of growth-ring placement becomes apparent, given that wood is approximately twice as unstable tangentially as radially.

The average specific gravity of wood tissue is related to the integrity of paint films in two important ways. First, lower density generally reflects thinner cell walls and relatively greater cell-cavity volume open to the surface, with resulting greater intervention of the paint film into the wood surface. Second, greater specific gravity not only predicts greater dimensional change across the surface, but also means that the paint layer has less ability to restrain the dimensional change of the surface. Among even-grained woods—that is, woods with uniform distribution of cell size—lower density and coarser textured woods therefore provide an excellent surface for establishing a paint layer with the best chance of survival under varying conditions of moisture. Conversely, dense woods with fine texture and maximum dimensional response would present a most difficult surface for paint-layer survival.

Variation of wood structure, as found in some species, presents additional complications. In uneven-grained woods, for example, the difference between earlywood and latewood is a crucial element, especially as related to orientation of growth-ring emergence at the surface. In

even-grained conifers such as southern yellow pine or redwood, the poorer adhesion and survival of paint on latewood results in dramatic surface effects of paint failure. On flatsawn surfaces, denser and stronger latewood emerges at the surface in relatively wide and irregular bands, presenting larger continuous areas of exposed tissue surface, which is most unstable. By contrast, quartersawn surfaces are dimensionally more stable, and the latewood is exposed in narrow bands of tissue limited in width to the thickness of the latewood, and regularly interspersed with earlywood. Paint films with greater adherence to earlywood bands are better able to maintain integrity across the narrow strips of latewood and thereby survive more successfully on radial surfaces. This is dramatically apparent in woods with characteristically narrow latewood, such as western redcedar (*Thuja plicata*).

Among hardwoods, a somewhat opposite pattern of behavior results in higher density ring-porous species that have particularly uneven grain (oak or ash, for example). As such wood picks up moisture, the denser, more unstable latewood swells at will, expanding into the earlywood and crushing the weaker earlywood vessels. The effect is especially apparent in relatively fast-grown wood with fairly wide bands of latewood. In thicker material where moisture variation is concentrated at surfaces and the surface response is restrained by the unaffected wood below the surface, compression shrinkage manifests itself as concentrated damage to earlywood layers. On surfaces of painted ring-porous wood, the failed bands of earlywood are a common sight. In sharp contrast, ring-porous woods that have not been subject to extreme moisture variation may show greatest wear and failure of paint on latewood surfaces, with the greatest survival of paint where there was greater volume retention originally in the earlywood.

Some species have chemical compounds that may have an effect upon painted surfaces. Conifers in certain genera of the pine family (Pinaceae—e.g., pines, spruces, larches, and Douglas-fir) have resin canals. The resin or pitch contained in these resin canals may bleed through certain paints, possibly resulting in darkened or yellowish dots or spots in the paint layer. In these same woods, excessive resin may be produced, which saturates surrounding cells and results in areas called *pitch streaks*. When such areas of wood with excessive pitch are painted over, the paint may be discolored by bleed-through of the pitch. Excessive pitch routinely occurs in the area of tree-branch bases, so knots in exposed wood surfaces are characteristically the source of discoloration of paint if not primed with a sealer. The contents of parenchyma cells and other heartwood extractive materials may be the source of paint discoloration, such as the dark, blotchy discoloration that can emerge on painted cedar or redwood. The extractives of cell content of some woods—such as teak, rosewood (*Dalbergia* spp.), or lignum vitae—may be oily in nature, and surfaces of such woods may be self-contaminated and resist proper bonding of paint films.

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Paints Based on Drying-Oil Media

David Erhardt

THAT CERTAIN PLANT AND SEED OILS harden to form solid, transparent films has been known for well over a thousand years. The earliest uses of these drying oils seem to have been as varnishes or coatings, but the incorporation of inorganic pigment or filler to form an opaque layer of paint must have followed soon after. Early examples of oil painting have been found, for example, in tenth-century objects from Japan (Uemura et al. 1954; Hirokazu 1961) and twelfth-century Norwegian altar frontals and polychromy (Plahter 1983, 1984), although these methods were relatively isolated until oil painting techniques were adopted throughout Europe in the fifteenth century.

History of Oil Processing

Used from earliest times as sources of heat, food, and illumination, oils were expressed from crushed seeds or plant material by various methods. The bag press, in which a bag of crushed seeds was twisted to force out oil, was developed five thousand years ago in Egypt. The beam press, screw press, and wedge press followed. Each involved the use of leverage to compress bags of seeds.

Though the early extraction processes were inefficient, the cold-pressed oils they produced were relatively pure. Processing of the oil for use in a varnish or paint might consist of washing with water or allowing the oil to sit (often in the sun) so that extraneous material, such as protein or mucilage, could settle out. This *tanking* or sun refining also bleached and thickened the oil, and the resulting *sun-thickened* oil was regarded as the best quality material for artists' use. Oil also could be thickened by heating, often in lead pots. Direct heating at high temperatures (up to 260 °C) produced a thickened, partially polymerized, and darker oil. The formation and dissolution of lead salts during heating in lead pots (or the simple addition of lead compounds or pigments) resulted in an oil that dried quickly to a hard film, although it was darker and tended to yellow more than oil without such *driers*.

The craft of producing and painting in oil was well developed in Europe by the mid–sixteenth century, and few changes occurred during the following two hundred years. Almost the entire process of producing paint (grinding pigments, mixing paint) was conducted in the artist's studio. Raw materials (oil, bulk pigments) were purchased individually, and the quality of each could be assessed before the paint was produced. The

entire process of producing paint, and indeed the production of paintings, was often conducted according to a formalized routine.

References to heating the seeds before or during crushing appeared in the eighteenth century. References to the refining of the oil also became more common during this period. Heating increases the efficiency of oil extraction—raising the yield from approximately 20% to 28%, in the case of linseed oil—but also removes more extraneous material from the seeds. The resulting oil contains a larger proportion of contaminants and is inferior to cold-pressed oil unless refined to remove the impurities. The impetus for more efficient extraction methods coincided with the industrial and scientific revolutions. Growth in the manufacture of machines, vehicles, and metalwork requiring protective coatings necessitated a large increase in the amount of paint produced. To meet this need, efficient, large-scale methods for preparing painting materials were developed.

Hydraulic presses were introduced in the late eighteenth century. While more efficient in expressing oil from seeds, they tended to heat up during use. The first pressings of the day were considered the best quality and often were reserved for the highest grade paint. Later pressings, including repressings of the combined seedcakes, yielded oil that was of lower quality but still satisfactory for commercial quality paint after refining. Acid refining was introduced in 1792, possibly in response to the increase in hot pressing.

The introduction of premixed paste colors in 1793 represented a significant change. Prior to this time, artisans mixed their own paints, using dry pigments and oil, a task requiring considerable time and training. The new paste colors, however, consisted of pigments wetted with a minimum of oil. These colors could be brought quickly to the proper consistency simply by adding more oil. Painting became more portable than before, and more accessible to those who had not learned the craft of paint making. Most important, paint now became a commercial product. Control of the product shifted to industry, as the artist or artisan no longer selected or mixed the raw materials. Manufacturers developed formulations amenable to large-scale production and mechanical mixing. Considerations other than those of the artist or craftsperson—such as shelf life, packaging, and production efficiency—were now taken into account.

Developments in drying-oil production and paint manufacture continued through the nineteenth century and into the twentieth. Heating prior to or during pressing became common. Syringe tubes containing premixed paints were introduced in 1840. This was followed in 1845 by tin tubes, a packaging form still standard today. Solvent extraction, first proposed in the 1840s, was not immediately adopted as a production method because of problems with the process and the lack of a source of cheap, suitable solvents. This method became more practical in the twentieth century with the development of the petroleum industry as a range of cheaper, more highly refined solvents became available (including nonflammable chlorinated solvents) and as problems of residual solvent remaining in the oil were solved. The screw expeller, introduced in 1903, was able to extract oil in a continuous process, but produced so much heat during use that no oil produced by it could be considered "cold-pressed." Steam jacket heating replaced fire boiling or direct heating, so that lower controlled temperatures (less than 100 °C) could be used for postextraction processing to produce a thickened *stand* oil.

Alkali refining was introduced in 1923. This produced a very clean oil, but one that did not wet pigments well, and therefore often required the use of additives for the satisfactory preparation of paint. Currently, virtually all oil is obtained from heated seed using solvent or expeller extraction followed by alkali refining.

Differences in the physical, mechanical, optical, and chemical properties of dried oil-paint films often result from variations in the methods of pressing, processing, and refining oils, as well as the formulation and preparation of the paints. Many of these differences can be explained in terms of the chemistry of drying oils, the topic of the following section.

Molecular Structure and Chemistry of Drying Oils

Triglycerides

Oils and fats are both chiefly composed of chemicals known as triglycerides. Triglycerides are esters, compounds that result from the chemical combination of an alcohol and an organic acid, with the loss of water. In a triglyceride, the alcohol component is glycerol (also called glycerin), which has a molecular structure with three alcohol functional groups. This polyfunctional nature allows glycerol to combine with three fatty acid molecules, hence the name *triglyceride* (Fig. 1). Mono- and diglycerides are also possible, in which glycerol combines with only one or two fatty acids, leaving two or one of the alcohol groups unreacted.

Although chemically similar, the various oils and fats differ considerably in their properties. Melting point is a primary physical distinction: at room temperature, oils are liquid, and fats are solid. Oils also differ in their ability to "dry" and form solid films, a measure of their suitability as paint binders.

These and other differences result from the facts that (1) there are several fatty acids that can react with glycerol to form triglycerides;

Figure 1

Molecular composition of a triglyceride formed from glycerol. Glycerol, a trifunctional alcohol, can react to form ester linkages with up to three fatty acids. The properties of the resulting triglyceride are determined by the specific combination of fatty acids it contains.
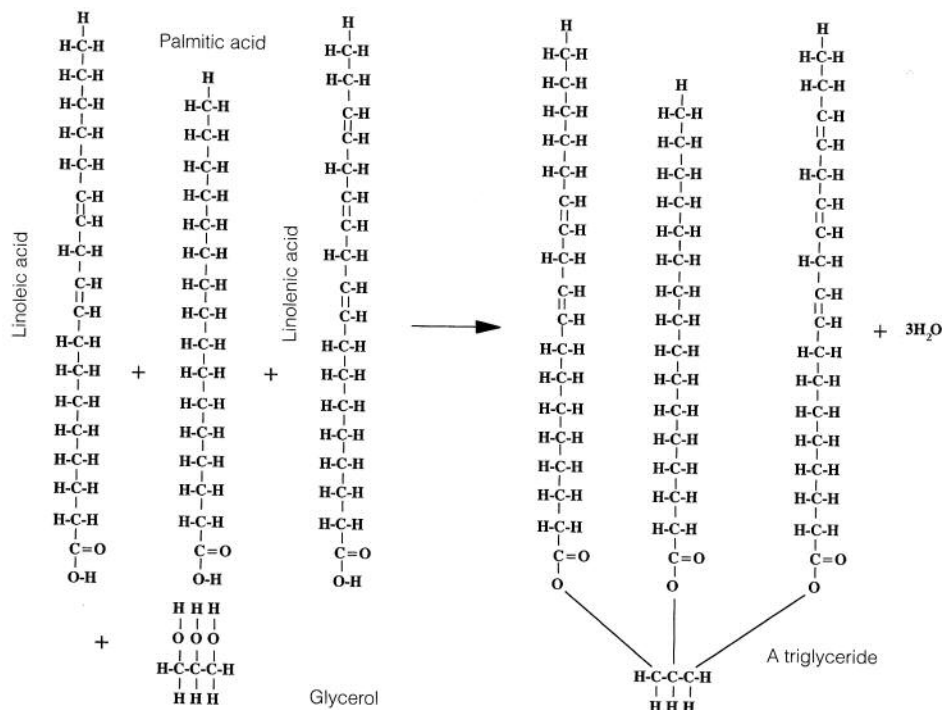
(2) there are even more ways to combine one, two, or three of these fatty acids within a triglyceride; and (3) each oil or fat may consist of several different triglycerides, with the types and distribution determining the overall characteristics of the mixture.

Fatty acids

Fatty acids consist of a carboxylic acid group ($-COOH$) at the end of a long carbon atom chain (usually of the straight-chain hydrocarbon type, although some contain branches or functional groups such as alcohols). In general, fatty acids differ in two basic ways: the total number of carbon atoms in the molecule, and the number (and position) of carbon-carbon double bonds ($C=C$). Most fatty acids contain an even number of carbon atoms between twelve and eighteen, with eighteen being the most common. If all of the carbon-carbon bonds in the chain are single bonds, the fatty acid is referred to as *saturated*. *Unsaturated* fatty acids have one (monounsaturated) or more (polyunsaturated) carbon-carbon double bonds. The carbon atoms in the chain are numbered consecutively, starting with the carboxyl carbon atom. The locations of double bonds are indicated by the lower number of the two carbon atoms of the double bond. Most unsaturated fatty acids have the first double bond at carbon 9 (C9), with succeeding double bonds at C12 and C15. Fatty acids in this regular series are designated by the number of carbon atoms followed by the number of double bonds. The sixteen- and eighteen-carbon saturated fatty acids are palmitic acid and stearic acid, denoted by the figures 16:0 and 18:0, respectively. Oleic, linoleic, and linolenic acids are the eighteen-carbon acids with one, two, and three double bonds, respectively (18:1, 18:2, and 18:3). The reaction of three of these acids with the alcohol groups ($-OH$) of glycerol to form ester groups ($-COOC-$) is illustrated in Figure 1. The resulting compound is a triglyceride.

The composition of oils

Each oil is composed of a mixture of triglycerides, as well as small amounts of mono- and diglycerides, free fatty acids, and other compounds. While it is fairly difficult to identify and quantify the individual triglycerides present, it is relatively easy to convert triglycerides to their component fatty acids and then identify and quantify them. Although factors such as climate, soil composition, and variations within plant species can affect the distribution of fatty acids, oil composition is often relatively consistent for oil from a particular source, such as linseed or walnut. Thus, differentiation of many oils by their fatty acid composition is possible, although less so for aged oil films. Tables of the composition of oils known to have been used in artists' materials have been published (Mills and White 1994; Erhardt et al. 1988). The composition of an oil determines whether it is a liquid or a solid (i.e., a *fat*) at room temperature. High proportions of the longer (sixteen carbon atoms or more), saturated fatty acids result in a melting point above 25 °C (a solid). The shorter fatty acids (fourteen carbon atoms or fewer), and the longer unsaturated ones with bends in the carbon atom chain produced by the rigid double bonds, do not pack and interact as well and remain liquid at room temperature. In general, fats contain high percentages of longer,

saturated fatty acids, while oils are more unsaturated and/or contain larger proportions of shorter fatty acids.

Chemistry of the Drying Process

The primary sites of reaction in triglycerides are the ester linkages and double bonds. Reaction of the ester linkages is generally slow, except under acid or alkaline conditions or in the presence of certain enzymes (lipases), and is discussed in the section on degradation that follows. The double bonds can undergo a number of reactions that result in the formation of bonds connecting the glyceride molecules (cross-linking). This thickens and eventually hardens the oil. The same type of reaction, or further reaction of the products initially produced, can result in the chemical breakdown of the polymeric matrix of the dried oil and the eventual deterioration of the paint film.

Polymerization reactions

Polymerization of an oil involves reactions resulting in chemical bonds linking many oil molecules together. This converts an oil from a liquid consisting of individual triglycerides into a more or less rubbery solid in which the oil molecules have combined to form an interconnected three-dimensional lattice. Such reactions occur primarily between the most reactive fatty acid groups at their double bonds, specifically those with two or three double bonds (most commonly linoleic and linolenic acids). If at least two such cross-links form per triglyceride molecule, the reactions lead to a fully cross-linked network; thus, drying oils are those in which at least two-thirds of the fatty acids are polyunsaturated. Non- and semidrying oils consist of more than one-third saturated and monounsaturated fatty acids. The reactions that constitute the drying process can be separated into two basic types—oxidative and thermal (or nonoxidative).

Oxidative polymerization

When a drying oil is laid out as a thin film, oxidation of the polyunsaturated fatty acids begins to occur. This oxidation leads to reactive products that then react with the double bonds of unsaturated fatty acids in other triglyceride molecules, forming chemical bonds that link the triglycerides together. This can occur via a free-radical chain-reaction mechanism in which an initial oxidative step leads to the linking (polymerization) of a number of triglyceride molecules. Reactions of this kind also lead to the formation of cross-links between triglyceride polymer chains. The process is not a simple one, and a number of different reactions are possible. The reader is referred to Mills and White (1994) and Wexler (1964) for a more detailed discussion of the mechanism and reactions. Oxidative cross-linking results in an uptake of oxygen by the oil film (around 10% or so, by weight) and a corresponding increase in volume (and possible wrinkling). The dried oil film contains a number of carbon-oxygen-carbon cross-links, as well as other oxygen-containing functional groups. The oxygenated sites are prone to further oxidation, discussed later under degradation processes. It should be noted that not all of the oxidative reactions lead to polymerization or the formation of cross-links; scission reactions can occur, breaking the fatty acid chain and yielding reaction products smaller than the original

fatty acid. The exact size of the products depends on the position at which the scission occurs. The major product is azelaic acid, a nine-carbon dicarboxylic acid (diacid), that results from oxidation of a double bond at C9, which is the double bond closest to the carboxyl carbon in most unsaturated fatty acids of glycerides. Most of the azelaic acid is still attached to the oil matrix through the original ester linkage of the glyceride, and is found during analysis only if this linkage is broken by hydrolysis, a reaction that is the reverse of the ester formation (esterification) reaction shown in Figure 1. Other products include the eight- and ten-carbon diacids, as well as even smaller amounts of monocarboxylic acids. Some of these compounds can also be produced by oxidation of the oil film that occurs after the drying process is complete.

Thermal polymerization

Polymerization reactions can also be initiated thermally, and oils often are prethickened by heating. If oxygen is present, the reactions are probably much the same as for unheated oils. Blowing oxygen through an oil during heating thickens it and reduces the subsequent drying time. "Blowing" can force the drying of oils that would otherwise be only marginal drying oils.

If oxygen is not present, however, a very different set of reactions takes place (see Mills and White 1994 or Wexler 1964 for more details). One type of reaction involves the rearrangement of the position of double bonds to more reactive configurations (such configurations occur naturally in tung oil, one of the better and faster drying oils). The fatty acid groups with these more reactive double-bond positions can undergo direct addition to unsaturated fatty acids of other triglyceride molecules in the absence of oxygen. The resulting *stand* oils contain primarily carbon-carbon crosslinks. While these thickened oils take up some oxygen in the final phases of drying after they are spread out, the amount of oxygen (about 3% by weight) and increase in volume are less than for oxidatively dried films. Fewer oxygenated sites in the resulting film means fewer sites prone to further oxidation. This resistance to oxidation causes stand oil films to be more durable and less prone to yellowing.

Effects of additives on the drying process

The drying process can be affected by substances added to the oil. Some materials, such as lead and cobalt driers, are added specifically for their effect on the drying process. Substances added for other reasons, such as pigments, can also affect the drying of oils. The effect is usually due to a modification of the oxidation process. Some compounds speed up (catalyze) the oxidation process, while others inhibit it or interrupt the chain reactions that produce drying.

Oxidation catalysts

Some materials, especially compounds containing metals that can exist in more than one oxidation state, tend to catalyze the oxidation process. Lead, manganese, and cobalt—in that order—show an increasing ability to speed up the drying rate of oils. Some compounds of such metals have been commonly used as pigments, but could also be added specifically for their effect on the drying process. Only small amounts are required. Heating oil in a lead pot results in enough dissolution of lead to have the

desired effect (presumably by reaction with free fatty acids to form lead soaps that can dissolve in the oil). Alternatively, oil-soluble metal salts of organic compounds (resinates, naphthenates, fatty acid soaps) can be added directly to the oil.

Oxidation inhibitors

A number of naturally occurring organic compounds can function as antioxidants or inhibit oxidation reactions. These function either by reacting preferentially with oxygen initially or by reacting with the intermediates formed during the drying process and interrupting the free-radical chain reaction. Phenols are such a class of compounds and are found in a number of pigments, such as bitumen, carbon black, and Vandyke brown. Oils containing such pigments may dry very slowly or only after a significant delay, when most of the inhibitor present has reacted, or not at all. Larger than usual amounts of oxygen may be taken up, resulting in greater expansion and wrinkling. Drying oils themselves contain small amounts of phenolic compounds that may be responsible for an initial delay in the drying process.

Rate of the drying process

The drying process of oil paints runs to completion fairly quickly (with the exception of those containing inhibitors). Oil films gel and become dry to the touch usually within days, and they are reasonably hard and can be varnished within a matter of months. Essentially, all of the polyunsaturated fatty acid groups in the triglycerides disappear within a few years. Their reaction (usually to form bonds with other triglycerides) means that all of the triglycerides become bound up in the polymeric matrix. Indeed, the author found that exhaustive extraction of a three-year-old linseed-oil film yielded no di- or triglycerides and only hints of monoglycerides, possibly of the unreactive saturated fatty acids. Physical data also suggest similar time periods for the completion of the drying process. Oil films of different thicknesses prepared from the same paint differed in their mechanical properties after four years, suggesting that the rate of drying is slower at greater depths within the films. The differences between films of varying thickness (up to 0.38 mm) had disappeared after thirteen years (Mecklenberg and Tumosa 1991). Other reactions, however, can continue to occur. These reactions result in relative, rather than fundamental, changes in the physical and chemical properties of dried oil films.

Degradation of the Dried Oil Medium

The ester linkages and now-reacted double bonds remain reactive sites in a dried oil matrix. Consequently, an oil-paint film is subject to continuing changes and eventual degradation caused by further oxidation, hydrolysis, or external effects (i.e., cleaning, varnishing, or environmental factors). These changes can affect both the appearance of the film and its sensitivity to solvents and other cleaning agents. In general, older oil films tend to be darker (as discussed above) and more resistant to solvents, and to increase in hardness and refractive index. Extremely degraded oil films, though, can soften and become sensitive to solvents because low molecular weight components, present in increasing amounts, function as plasticizers and are sensitive to leaching by cleaning. Loss of these low-molecular-weight

components through volatilization, blooming, or solvent leaching may cause the paint layer to become stiffer and matte (dull or less shiny) and ultimately less coherent.

Effects of continued oxidative reactions

The major class of continuing reaction in dried oil films is oxidation. The products resulting from initial oxidative cross-linking are prone to further oxidation, especially at the carbon atoms attached to oxygen. Certain pigments, chemical driers (metallic salts), and other paint additives may also contribute to further oxidation of the oil film. Continued oxidative reactions can result in an increase in weight because of the addition of oxygen, but they can also cause the eventual loss of weight. The breakage of cross-links and fatty acid chains yields the same types of smaller molecules that are produced during the drying process (e.g., azelaic acid can be found immediately after drying, and further aging produces increasing amounts). Weight loss occurs when these smaller molecules migrate to the surface and volatilize, are removed during cleaning, or are extracted into applied varnish films (Tsang and Erhardt 1992). Continued oxidation can eventually lead to softening and weakening of the oil film.

Solvent sensitivity

Oxidation of a dried oil film results in an increase in the number of chemically reactive polar functional groups—such as the hydroxyl groups of alcohols and carboxyl groups of carboxylic acids—as well as the production of smaller molecules. These functional groups are more polar than the original hydrocarbon chains of the fatty acid groups because of partial charge separations in the carbon-oxygen bonds. The increase in polar groups should result in stronger interactions within the oil film due to the attractive forces between the partially charged polar groups. The presence of more polar groups also might be expected to shift the sensitivity of the oil film to more polar solvents. A study has shown, however, that while comparable oil-paint films containing lead white and raw sienna differed in their absolute sensitivity to a given solvent, the change in sensitivity with change in solvent polarity was similar for both films (Tsang and Erhardt 1992). Both the lead white and raw sienna films were most sensitive to the same solvents, but the lead white film, which should have been more oxidized, was less sensitive to all solvents, as shown in Figure 2. The practical effect was that the range of solvents with a significant effect on the lead white film was narrower. Nonpolar (low Hansen's solubility parameter) solvents that affected the raw sienna film had little effect on the lead white film, which required solvents closer to the center of its solubility range to achieve any significant effect. Some of the resistance of lead white films is probably due to the formation of insoluble lead salts, but these results indicated that oxidation will result, at least initially, in an oil film that is generally more resistant to solvents rather than in a film whose solvent sensitivity has shifted to more polar (higher Hansen's solubility parameter) solvents. To produce a significant shift in the center of the solubility range, therefore, may require more severe oxidation than that which occurs during normal aging.

Density and refractive index

The increase in number of functional groups should have other effects. As a general—though not strict—rule, oxidation and an increase in the num-

a

b
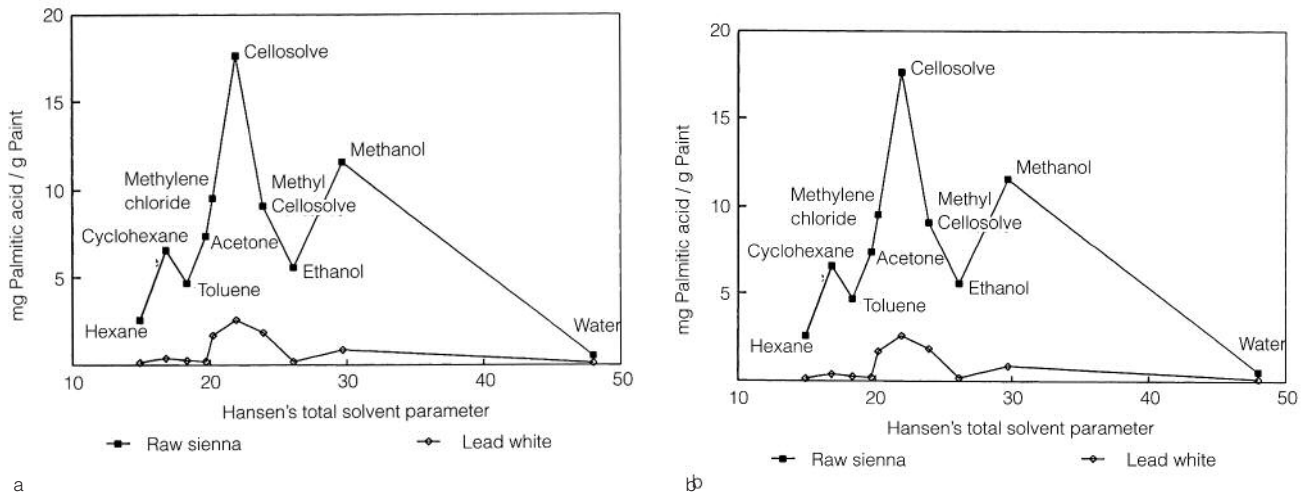
Figure 2a, b
Plots of the amount of palmitic acid extracted in six hours from oil paint samples versus Hansen's total solvent parameter for the solvent. One plot (a) shows that the overall solvent sensitivity of lead white is much less than that of raw sienna; and the second (b), in which the scale of the lead white plot is expanded, shows that the solvent sensitivity is not shifted, but simply reduced (from Tsang and Erhardt 1992:88).

ber of functional groups should result in a greater density and a higher index of refraction. The index of refraction of linseed oil is about 1.48 (Gettens and Stout 1966) but rises during the drying and aging processes to values as high as 1.57 for aged films (Feller 1957). The increase in index of refraction reduces reflection at oil-pigment interfaces and allows light to penetrate paint films more deeply (de la Rie 1987). This helps to explain the phenomenon of pentimento, in which underdrawing or overpainted design becomes visible as the covering layer grows increasingly transparent. At the same time, the presence of more functional groups (along with increased density) should result in a harder film.

Yellowing of dried oil media
Yellowing of oil-paint films is also related to the oxidative process, although the exact mechanisms are still not clear (see Mills and White 1994 for a discussion of proposed mechanisms). Highly unsaturated drying oils (those with the most linolenic and related acids) are particularly prone to yellowing. Thus, oils that dry best (the most highly unsaturated ones) also tend to yellow the most. Linseed oil is more unsaturated and dries better than either poppy-seed or walnut oil, but it yellows more. This is one reason that poppy-seed and walnut oils often were used to formulate lighter colored paints. There are numerous examples of paintings on which walnut oil was used in lighter colored areas, and linseed oil in areas with darker pigments, where yellowing of the medium has less effect on the appearance.

Proposed mechanisms for yellowing include *condensation reactions* (the formation of bonds between molecules with the loss of small molecules, such as water) of fatty acids oxidized at more than one position to yield quinone-type structures. Condensation reactions with nitrogen-containing compounds (amines)—either ammonia in the atmosphere or amines present in the oil (proteins, for example)—could also produce chromophoric groups, which are chemical structures associated with color.

Yellowing occurs more readily in the dark, and can be at least partially reversed by exposure to light. This yellowing–light-bleaching cycle can be repeated, although the bleaching probably is not a true reversal of the yellowing process. More likely, exposure to light promotes oxidation of

double bonds in the chromophores that are responsible for the color. The oxidation may initially yield compounds that are colorless, but such compounds may be capable of producing more colored compounds through further oxidation or condensation.

Low-molecular-weight degradation products

Continued oxidation may break the initial oxidative cross-links and fatty acid chains, resulting in the presence of smaller, mobile molecules in an aged oil film. These smaller molecules can act as plasticizers that tend to produce a softer film. These small components can be extracted from the oil film, however; thus, their presence tends to make the film more sensitive to solvents or other cleaning agents (Erhardt and Tsang 1990; Feller, Stolow, and Jones 1985; Erhardt and Bischoff 1994). Small molecules can migrate through the oil film and may appear as a bloom on the surface or, ultimately, volatilize. The loss of extractable material—either quickly, through cleaning, or slowly, through evaporation—can result in shrinkage and a stiffer and stronger film (see Mecklenburg, Tumosa, and Erhardt, herein).

The loss of material from a film often results in lighter color and a more matte surface. Voids in an oil film increase the scattering of light and reduce light-pigment interactions. If too much of the organic binder is lost and the pigment particles are no longer bound by the oil matrix, the surface becomes chalky and friable.

Effects of continued hydrolysis

Hydrolysis of ester linkages of glycerides in a dried oil is the reverse of the reaction presented in Figure 1. Water reacts with a glyceride to split the ester into its acid and alcohol components. Hydrolysis cleaves the ester group into the two functional groups (hydroxyl and carboxyl) from which it was formed, yielding an alcohol and a carboxylic acid, respectively. The alcohol (glycerin) is likely to remain attached to other fatty acid groups through ester linkages, thus persisting as part of the polymer matrix of the dried oil. Depending on its structure, the carboxylic acid may react to form bonds with other triglycerides, in which case it also remains part of the dried oil matrix. However, if the fatty acid is saturated and has not reacted with other triglycerides, or was unsaturated but has undergone a scission reaction, hydrolysis yields either the original saturated free fatty acid or scission products such as diacids, hydroxy acids, or short-chain fatty acids. These are no longer attached to the polymer matrix. Thus, hydrolysis produces effects similar to oxidation, increasing the number of functional groups, causing breaks in the polymer matrix, and producing low-molecular-weight degradation products.

Effects of pigments, chemical driers, and other additives

Pigments and other additives affect the degradation process in much the same way that they affect the drying process. Their main effect is to influence the process of oxidation, either catalyzing it or hindering it. Some pigments may catalyze photooxidation, speeding up the degradation of oil films exposed to light. Rasti and Scott (1980) examined the effects of a number of pigments on the photodegradation of oil films. Chemical driers (lead, manganese, or cobalt salts) continue to catalyze oxidative reactions in a dried oil film. Consequently, paints containing such driers are prone to yellowing and to hastened deterioration.

However, pigments and other additives may contribute to the degradation of oil paints through other mechanisms. Reactions with environmental pollutants may occur. For example, paint films containing lead white will darken when the pigment reacts with hydrogen sulfide to form black lead sulfide.

Interactions between the components of the oil and the pigments or other materials in the paint film may also take place. Oils generally contain up to a few percent by weight of free carboxylic acids, which can form salts with the metal ions of some pigments. These carboxylic acid salts are soaps, and their surfactant effect initially helps the oil to wet, disperse, and bind to the pigment.

The presence of these salts may contribute to the durability and the solvent resistance of some oil paints. Such is the case with lead white films, where the formation of lead salts of fatty acids (which tend to be insoluble in most aqueous and nonaqueous solvents) yields solvent-resistant oil-pigment bonds, and helps to immobilize otherwise mobile or volatile free fatty acids. Solvents cause less swelling and extract less material from lead white pigmented oil films than those containing, for example, raw sienna or vermilion.

By contrast, some pigments or other additives may lower the resistance of paints to solvents. Certain pigments are soluble or sensitive to water or other polar solvents. Consequently, oil paints containing such pigments (e.g., zinc oxide) will exhibit increased sensitivity to polar solvents. Incorporating soluble organic materials, such as resins or waxes, into an oil medium also greatly increases the solvent sensitivity of the resulting film.

Modern paints may contain other additives used to produce the properties required of industrial products. For instance, alkali-refined oils have low amounts of free fatty acids and may require added surfactants to wet pigments well and to keep oil and pigments from separating during the periods between manufacture, sale, and use. The long-term effects of these and other additives vary considerably.

Environmental effects

Environmental factors, such as changes in relative humidity (RH), also affect oil films. For example, high RH can essentially "reset" some of the hardening of oil films. Absorbed water causes swelling, which may disrupt the oil-pigment interactions or the ordering of the oil matrix that occurs over time. The disruption of oil-pigment bonds and the voids produced by loss of material can give the paint a matte appearance and lighter color as mentioned in the discussion of blanching.

Effects of oil processing

Modifications in oil processing affect the chemistry and composition of oils, which in turn influence the drying properties, durability, and degradation of paints. Table 1 summarizes these effects.

Cold pressing, a technique rarely used today, results in a clean, high-quality oil that produces very durable paint films. The more common practice of heating before or during oil extraction results in an impure oil requiring additional refining. Heating may also alter the oil chemistry, especially if oxygen is present or the temperature is too high, resulting in a less durable oil film.

Table 1   The chemical and practical effects of oil processing and treatment

Effects of oil refining and treatment

Type of treatment	Chemical effect	Practical effect
Cold pressing	Removes oil and little else, without altering the oil	Clean, high-quality oil
Heating before or during oil extraction (includes most modern processes)	Increased amounts of protein, mucilage, etc., extracted compared to cold pressing	Postextraction refining is required
Addition of chemical driers (lead, manganese, cobalt salts)	Catalyzes oxidative processes (drying and deterioration)	Fast drying on exposure to air; less durable film; lead salts may darken on exposure to pollutants
Acid refining	Increased amounts of free fatty acids	Wets pigments well
Alkali refining	Reduced amounts of free fatty acids	May require addition of surfactant (such as aluminum stearate) to wet pigments
Heating after oil extraction in absence of oxygen (*stand oil*)	Nonoxidative prepolymerization of oil, some precipitation of impurities; low temperatures (up to 100 °C) yield best quality; high temperatures (up to 260 °C) yield darkened oils	Hard, tough film that is less prone to oxidation; heated oil can be thick and difficult to work with; may require thinning with solvent before use
Heating after oil extraction with air blown through (*blown oil*)	Oxidative prepolymerization of oil	Faster drying than unblown oil, but with similar chemistry; marginal drying oils can be used

Alkali refining, the method most often used to refine oils obtained using heat-extraction techniques, reduces the amount of free fatty acids in the oil, thereby decreasing the ability of the oil to wet pigments. To counteract this, soaps such as aluminum stearate are added to improve wetting and prevent the separation of oil and pigment.

Heating after the extraction process tends to cause impurities to coagulate and settle out. If oil is heated at moderate temperatures (up to 100 °C) in the absence of air, a nonoxidative prepolymerization takes place that results in a thickened *stand oil* that will form a hard, tough film resistant to oxidation.

More intense heat, however, can lead to darkening and decomposition. At high temperatures, bubbles form in the oil. While the oil appears to boil, the bubbles actually indicate the evolution of gases generated by decomposition. Such treatment is now rarely used, and "boiled" oil generally refers to oil with chemical driers added. These chemical driers, as stated previously, continue to catalyze oxidation even after initial drying, resulting in less durable films that are prone to yellowing. The lead from a drier present in an oil film can also react with pollutants to cause darkening.

Heating oil in the presence of oxygen (*blown oil*) results in much the same chemical processes as occur during air drying of oil films, but the resulting oxidatively prepolymerized oil dries quickly. This technique, however, does not produce an oil resistant to yellowing and further oxidation.

Effects of Conservation Treatments

Cleaning

The cleaning of oil-paint films can have several negative effects if it is not carefully carried out (see Mills and Smith 1990 for a number of articles on cleaning). Soluble material can be removed from the film, resulting in changes in both the optical and mechanical properties. The low-molecular-weight materials that are most easily extracted function as plasticizers, and their loss results in a stiffer film with a higher modulus of elasticity (see Mecklenburg, Tumosa, and Erhardt, herein). Loss of material also results in a blanched or matte appearance. Though a slight swelling of an oil film due to exposure to solvents is largely reversible, excessive swelling results in an irreversible disruption of the oil matrix and oil-pigment bonds. Resulting voids and disorder of the film can also produce a matte appearance even if no material is extracted. Such effects can sometimes be partially reversed by careful application of a solvent to achieve partial dissolution and reforming of the film.

Cleaning agents that affect pigments or oil-pigment bonds can have similar effects. This is especially true for polar solvent or aqueous mixtures. Partial dissolution of pigments (of zinc oxide by water, for example) also disrupts the oil film.

Cleaning agents that include nonvolatile solvents or reagents, such as soaps formulated from resin acids, may leave residues. Such cleaning agents may also extract material or disrupt an oil film but may not have the visible effects of volatile solvents, since the residues serve to fill in voids and darken the oil film, providing a saturated rather than matte appearance. A number of effects were studied as a function of the presence or absence of individual components of typical resin soap formulations (Erhardt and Bischoff 1994), however the long-term effects of such residues have not been studied.

Varnishing

Varnishing serves two primary purposes: to improve the appearance of the paint film and to protect it. A varnish layer serves to fill in surface voids and defects, thereby reducing the scattering of light and increasing light-pigment interaction (De la Rie 1987). This is especially true of deteriorated or damaged paint films in which the surface is no longer smooth or uniform. The resulting darker, saturated appearance is more typical of a fresh, intact film. Matting agents such as wax or fumed silica may be added to varnishes to make them less shiny or reflective, depending on the final effect desired.

Varnishes protect paint films physically from dust and abrasion. They absorb little visible light (unless quite thick and yellowed) and may absorb some incident ultraviolet (UV) light, but they cannot provide substantial protection against UV light unless a UV absorber is present in the varnish. Varnishes may not prevent oxidation directly since the diffusion of oxygen through a varnish film is still faster than any oxidation reactions that might consume it. Instead, they inhibit the reaction indirectly by reducing the amount of photooxidation that takes place.

As noted above, the removal of varnishes, as well as other non-original layers and accretions, has the potential of significantly altering the paint film. The application of a new layer of varnish also must be performed carefully since the solvents used in the application can affect the paint film, as well. Solvent in the applied varnish can diffuse into and swell

the paint layer, dissolve soluble material, and transport this material into the varnish layer as the solvent eventually diffuses to the surface of the varnish and evaporates (Tsang and Erhardt 1992). The presence of oil components in the varnish layer may cause confusion if the varnish layer is subsequently analyzed, possibly causing a pure resin to be identified as an oil-resin varnish. Mixing of material and blurring of the paint-varnish interface during varnish application can complicate determination of the proper extent of subsequent varnish removal.

Analysis of Aged Drying-Oil Films

Analysis of aged drying-oil films depends on a knowledge of their original composition and on the chemical changes that occur during processing, drying, and aging. Because aged drying-oil films are polymeric, they generally are hydrolyzed as the first step in analysis. The hydrolyzed film contains three important classes of materials: (1) unreacted fatty acids (predominantly the saturated ones); (2) degradation products; and (3) higher-molecular-weight components resulting from the cross-linking of the unsaturated fatty acids. At present, constituents of the first two groups are readily identified and quantified (Mills and White 1994; Erhardt et al. 1988) and yield information about the original oil and its processing. Gas chromatography (sometimes combined with mass spectrometry) is the optimal method for the analysis of fatty acids and their degradation products, and of many common paint additives, such as waxes and resins.

Because the saturated fatty acids are essentially unreactive, they are present in the dried film in the same ratios as in the original oil. Although analysis of the saturated fatty acids alone provides less information than could be obtained from the original oil, it is still sufficient to identify a number of important oils. The three important drying oils of Western European oil painting (linseed, walnut, and poppy seed) differ, with little overlap, in their ranges of the ratio of palmitic to stearic acid (Mills and White 1994; Mills 1966). Even in more obscure cases, an oil may be identified if possible sources are known and samples of the oil or results of previous analyses are available (Erhardt and Firnhaber 1987).

The degradation products provide information about the processing and aging of the oil, as well as its identity. The amount of azelaic acid (the C9 diacid) in drying-oil films increases slightly as they age. Films more than about a hundred years old tend to contain amounts of azelaic acid equal to or greater than the amounts of the unsaturated fatty acids. This is in contrast to nondrying oils, such as egg, that tend to contain smaller amounts of azelaic acid even when very old. Egg contains fewer unsaturated fatty acids that can degrade to azelaic acid; thus, egg can be differentiated from a drying oil such as walnut, even though their palmitate-to-stearate ratios overlap in range, by the lower amount of azelaic acid in egg. (Other methods of analysis can also be used since egg yolk, even without albumen, is about one-third protein.)

Azelaic acid is the predominant degradation product. It results from oxidation at the C9 double bond of unsaturated fatty acids, which is the most common position of the initial double bond. Less common acids or reactions can produce other diacids, such as the C8 and C10 compounds. Thermal rearrangement of double bonds of drying oils before oxidative polymerization increases the proportion of the C8 and C10

diacids relative to azelaic acid. Thus, larger than normal amounts of the C8 and C10 diacids are indicative of a heated, or *stand,* oil. Additives or processes that catalyze oxidation will increase the rate of degradation processes leading to diacids but should have little effect on the relative amounts of the different diacids. Thus, blown oil or oil with added driers cannot necessarily be differentiated from unprocessed oil by comparing the relative amounts of the diacids. Driers such as metal salts can be detected by other methods of analysis.

Conclusion

Many of the physical, chemical, and optical properties of oils, and the oil paints prepared from them, are affected by the processing and treatment of the oil. Historically, the processing of oil has been determined by the increasing importance of industrial concerns: speed, efficiency, and marketing and commercial factors. Many of the changes have adversely affected the qualities of oils that are important to artists or have resulted in the need for further refining or the use of additives in an attempt to regain some of the properties of cold-pressed, high-quality oil. The effects of the differences in oil-processing methods can be described in terms of their effects on the chemistry of the oil, which in turn affect the drying properties, strength, durability, optics, and permanence of the resulting oil film. Aging of oil films tends to produce contradictory effects. While oxidation is initially responsible for the drying of oils, continued oxidation results in degradation. Reactions that initially cause hardening may eventually soften the film if they continue. Differences in the composition of oils, as well as differences due to processing and aging, can be useful in the analysis and identification of oils.

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Tempera and Other Nondrying-Oil Media

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ALTHOUGH DRYING OILS are the major binding medium on many of the painted wooden artifacts discussed in this book, numerous other natural binding media are of historical importance. This article provides an introduction to animal and fish glues, egg white and yolk, casein, plant gums, plant resins and shellac, and waxes. Lacquer, a natural material widely utilized in China, Japan, and surrounding countries, has been discussed in a recent publication (Brommelle and Smith 1988). Other materials have been used by various cultures but cannot be discussed here due to space limitations; a recent bibliography can be consulted for references to some of these (Hansen, Walston, and Bishop 1994).

Binders are discussed here according to general composition, beginning with those made up entirely of proteins (animal and fish glues, egg white) or containing substantial amounts of proteins (egg yolk, casein); followed by those made up of carbohydrates (plant gums), natural resins and shellac (quite variable in composition, although most contain related groups of compounds), and waxes (also quite variable in composition, but containing some similar compounds). The section on each binder gives examples of its use, descriptions of sources, chemical composition, analysis, and degradation.

Comments on degradation focus mainly on chemical changes. Because paints are mixtures of pigments and binders, degradation is only partially determined by the nature of the binder. Many paints based on the binders discussed in this chapter are very fragile; consequently, their susceptibility to physical or mechanical damage is generally a more important cause of conservation problems than chemical changes in the binders themselves.

The appendix at the end of this chapter introduces the binding media identification techniques referred to here, discussing their individual strengths and limitations. Table 1, in the appendix, summarizes the applications of specific techniques to individual media and particular types of samples. Abbreviations for instrumental techniques given in that table are used throughout the chapter.

Protein-Containing Media

Proteins are an important constituent of four common media: animal and fish glues, egg white, egg yolk, and casein. Because their sources and behavior as paint media are quite different, each is discussed separately. However, since they all contain proteins, this section begins with a review

of the chemistry of proteins, aspects of degradation common to all proteins, and identification methods for proteins that can be applied equally well to all of the binders.

Chemical composition of proteins

All living organisms contain proteins, which are polymers of amino acids. The structures of some common amino acids are shown in Figure 1. Peptides are polymers of as few as two amino acid molecules (dipeptides) or as many as several dozen (oligopeptides). By convention, peptides have molecular weights of 10,000 daltons (atomic mass units) or less; amino acid polymers of higher molecular weights are proteins. In proteins, individual amino acid molecules are usually chemically bonded to only two other amino acid molecules. Certain amino acids can form more than two bonds, and in some proteins these are bonded to more than two other amino acid molecules. The types and relative amounts of amino acids present in proteins differ widely, as does the molecular weight.

Some proteins are water soluble; in their natural state, they are highly folded structures that can be nearly spheroidal in shape (globular proteins). The proteins in egg white, egg yolk, and casein are of this general type. Other proteins occur in long, threadlike strands and are not water soluble. Examples are keratin (hair, wool, and feathers) and fibroin, which occurs in silk. One fibrous protein that has the unusual property of breaking down to form a solution when heated in hot water is collagen. It is found in tendons and connective tissues of animals and some fish, and it is the major component of animal and fish glue binders.

Animal and fish glues and egg white contain only traces of compounds other than proteins. Egg yolk and casein contain some proteins that are chemically bonded to carbohydrates or lipids, as well as substantial amounts of other compounds.
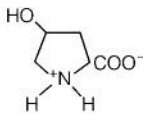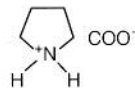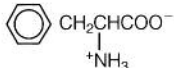
Aging and degradation of proteins

Many proteins exist in very complex structures that can be affected, often in irreversible ways, by changing the acidity or alkalinity, by heating or other changes in their environment, or simply by evaporation of water. Changes in the original structure are called denaturation; if irreversible, these can greatly affect solubility. Some changes are physical, involving the physical structure; others involve weak (noncovalent) bonds. Thus, a protein that exists in its native state in a water solution may be totally insoluble after drying.

Proteins readily react with acidic solutions (hydrolysis). A small amount of hydrolysis rapidly reduces the molecular weight of a protein, weakening its binding abilities. Microorganisms, or even enzymes found naturally in some of the binders, can rapidly hydrolyze proteins; and individual amino acids may also undergo chemical reactions. The stability of amino acids varies considerably: some are stable indefinitely; others rapidly degrade under the same conditions. Egg white, egg yolk, and casein all contain relatively high levels of more readily oxidized amino acids than does animal glue (Karpowicz 1981)—although the by-products of oxidation of amino acids are not well known. To date, no studies have been done on whether chemical changes in particular amino acids are significant in the degradation of protein-bound paint.

Figure 1
Structures of some of the amino acids found in protein-containing media.

Amino acids can undergo *racemization,* a structural rather than a chemical change that takes place both in proteins and in the free amino acids. This is the basis for an archaeological dating technique applied mainly to bone and teeth (Aitken 1990:204–13); while racemization undoubtedly takes place in protein-bound paints, it is not known whether this produces any noticeable effect on the properties of a paint.

The simultaneous presence of proteins and carbohydrates in a paint or varnish can cause a type of deterioration reaction known as the *Maillard reaction* (Horie 1992). This reaction produces a volatile polymeric by-product that is brownish in color. One possible example of this has been cited (Stoner 1990).

Some interactions may occur between a protein binder and pigments. Acidic pigments in the presence of water, for example, may cause hydrolysis of the binder and/or may form salts of the breakdown fragments.

Analysis of protein-containing binders

Most analytical schemes for protein-containing binders focus on the protein components. Stulik and Florsheim (1992) outline a general microchemical test for proteins. Another long-applied microchemical test involves detection
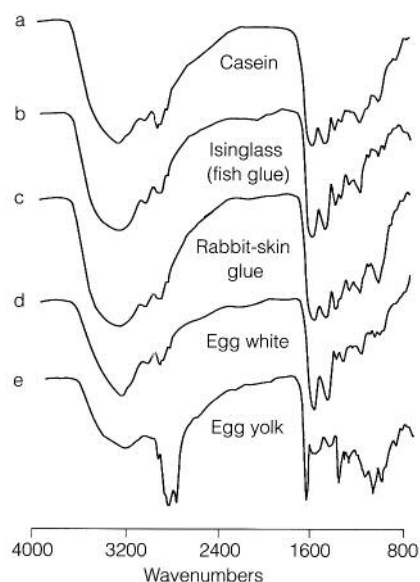
Figure 2
Infrared transmittance spectra of some protein-containing materials. Note that the spectra are quite similar, with the exception of egg yolk, which contains a substantial amount of oil in addition to protein.

with ninhydrin (Feigl 1960:293–94). Proteins have been identified in paint cross sections by staining reactions: common visible-light stains are described by Martin (1977) and Johnson and Packard (1971); and fluorescent stains by Wolbers and Landrey (1987). While a method to distinguish between some of the different proteins with visible-light staining has been published (Martin), the primary use of the staining reactions is simply to indicate presence or absence of proteins.

A general instrumental analysis technique for proteins is infrared (IR) spectrometry (Fig. 2). Pyrolysis–gas chromatrography (Py-GC) can verify the presence of proteins (Chiavari et al. 1993). Although it cannot always provide a positive identification of the protein present, Py-GC may help narrow down the possibilities. To date, amino acid analysis is most often used to identify specific proteins in binders (Halpine 1992a, 1995; Schilling, Khanjian, and Souza 1996; Schilling and Khanjian 1996). Thin-layer chromatography (TLC) has been frequently applied, but gas chromatography (GC) and high-performance liquid chromatography (HPLC) are better suited to quantitative analysis, which is necessary for definitive identifications. Egg white and egg yolk can be difficult to distinguish even by quantitative amino acid analysis, but all of the other protein binders are readily distinguished from one another because of substantial variations in relative amounts of the different amino acids (Fig. 3). Through the use of HPLC for the analysis of amino acids, the binder of the paint on a large group of wooden figures from the Middle Kingdom in Egypt (Fig. 4) was found to be bound with glue (Fig. 5). The amino acid profile of the nearly four-thousand-year-old binder did not differ substantially from that of modern collagen. Other tests that have been applied to distinguish particular protein binders from one another are noted in the following.

Animal and fish glues

Probably the most widely utilized binders historically are glues derived from animals. For example, animal glues were probably the main paint binder in the paintings of China and most other East Asian countries (Winter 1984). An early manuscript from India describes the use of buffalo-skin glue in wall paintings (Coomaraswamy 1934). Glue has long been assumed to have been a major binder in ancient Egyptian painting, and recent analyses have confirmed that this was quite common (Newman and Halpine 1994). Glue also was used for medieval illuminations and early European fabric paintings (Roy 1988).

Research from recent years suggests that mixtures of animal glue and other binders may have been used occasionally on panel paintings. Kockaert (1973–74) has postulated that an oil–animal-glue emulsion was utilized by late medieval Flemish painters, a medium with useful handling properties for the intricately detailed paintings for which these artists are known. In addition to its use as a paint binder, another common use on European and American painted objects was in gesso or ground layers.

Chemical composition. Animal glues are based on the protein collagen, the most common protein in animals, and are derived from white connective tissue in skin, bones, and tendons. Five distinct variants of collagen have been identified in vertebrates, although their overall amino acid compositions are quite similar (Lollar 1984). Collagen occurs in the skins of fish and is virtually the only component of the swim bladder of the sturgeon. In its native state, it is virtually insoluble. It exists in the form of a triple helix of three protein strands. Each strand, which contains
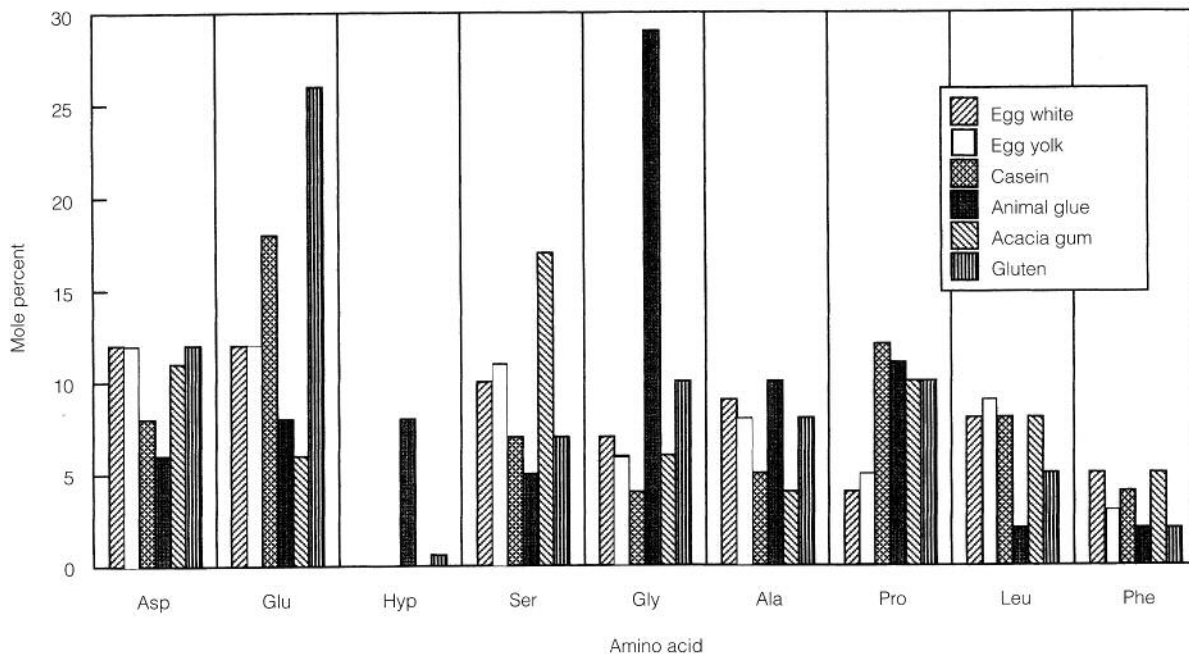
Figure 3
Amounts of some amino acids in a number of protein-containing binders and other non-proteinaceous materials. Asp, aspartic acid; Glu, glutamic acid; Hyp, hydroxyproline; Ser, serine; Gly, glycine; Ala, alanine; Pro, proline; Leu, leucine; Phe, phenylalanine. The first four materials contain substantial amounts of proteins, the last two only very small amounts of amino acids. (Sources of data: acacia gum, from *Acacia campylacantha,* Anderson, Hendrie, and Munro 1972:734; gluten from durum wheat, and all others from Halpine 1992b)

more than one thousand amino acid units, has a molecular weight of about 100,000 daltons. The strands are held together by hydrogen bonding and by some covalent bonds, the latter increasing with the age of the collagen. Collagen also contains a minor, chemically bound carbohydrate component (Traub and Piez 1971:272–73).

The unusual property of collagen that makes it useful as a binder is that it can be solubilized by heating in water. Current commercial preparation of collagen-based glues usually involves treatment with acid or alkali, which degrades the collagen rather than simply solubilizing it (Von Endt 1984). Thus, the molecular weights of the strands in a glue are often much lower than those of the strands in their native state; in fact, most commercial glues contain molecules with a wide range of molecular weights. Gelatin is quite similar to glue but is a purer material since it is manufactured under more stringent processing conditions and control than glues.

Figure 4
Painted wood model of a procession, Egypt, Deir el-Bersha tomb 10A, Middle Kingdom, Dynasty 11 (2061–1991 B.C.E.). Museum of Fine Arts, Boston (accession no. 21.326).
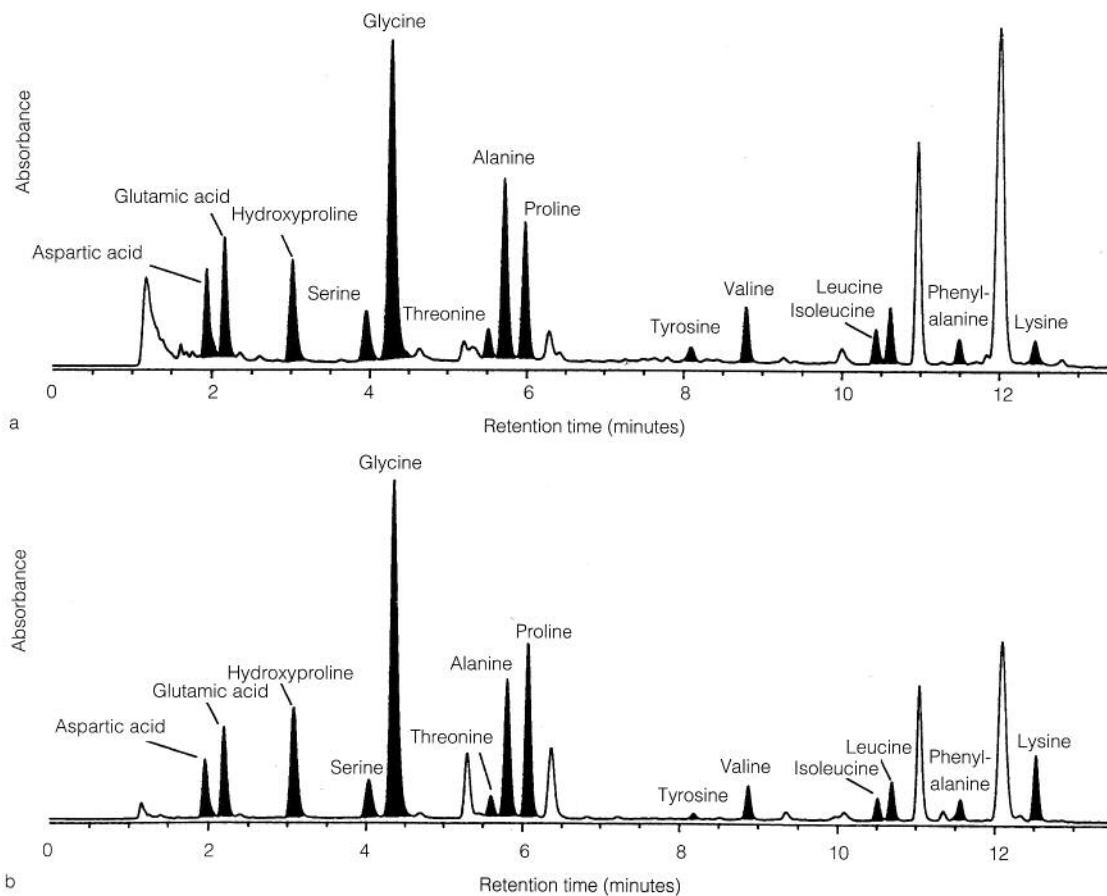
If a collagen solution is allowed to cool to around 30 °C, it will gel. As water evaporates, the gel forms a solid, which can be ground and readily dissolved by warming in water. The inconvenience of working with a warm solution of the binder can be overcome by allowing the solution to sit for a time and partially decompose. As an early medieval treatise stated, "after a few days it will stay liquid without heating. It may smell bad, but it will be very good" (Thompson and Hamilton 1993:13). The decomposition mainly results in further breakdown of the protein strands into smaller fragments that no longer gel at room temperatures. A dried gelatin film consists of collagen strands arranged in at least a somewhat orderly fashion, partly duplicating the original stucture of the native collagen. The film readily absorbs water and loses strength in the process. Glue-bound paints are lean (i.e., the amount of binder is low relative to pigment), so the paint tends to be porous and matte. The ability of the three-stranded collagen molecules to stretch gives glue-bound paints a flexibility that egg-white paint (containing globular proteins) does not have.

Analysis. The ability of glue-bound paints to be solubilized in hot water sets them apart from most other protein-bound paints. Solubility, coupled with a positive result for protein, strongly suggests the presence of glue.

Hydroxyproline, which makes up around 10% of the overall amino acid units in collagen, is absent from the other common protein-containing binders, although it can be found in some other nonproteinaceous binders at low levels. A microchemical test for this amino acid has been described in the conservation literature, but the sample size is larger

than would typically be available (Collings and Young 1976). The amino acid composition of different genetic varieties of collagen varies somewhat. It has been claimed in one recent paper that fish and animal glues can be distinguished by quantitative amino acid analysis (Sinkai et al. 1992); but this should be more thoroughly investigated, since the variations are rather subtle.

Modern gelatins and glues are more highly processed than older glues. It has been noted that old glues contain small amounts of fatty acids (lipids), which are amenable to analysis by the same procedures as are applied to oil paints (Skans and Michelsen 1986; Mills and White 1987). This is a possible criterion for distinguishing between older and more modern glues.

Egg white
The best documented use of egg white as a binder is in European manuscript illuminations (Thompson 1956:50–55). Several medieval treatises discuss the preparation and use of egg white as a binder, the preparation being carried out either by whipping or by taking up the white in a sponge and squeezing it out repeatedly until no froth forms.

There are no documented uses of egg white as a binder on painted wood artifacts. However, it has been suggested, although not proved by modern analyses, that egg white was utilized as a paint binder in ancient Egypt (Lucas and Harris 1962:1–2). Egg white appears to have been used in varnishes on paintings in the medieval period, a practice that continued into the twentieth century (Stringari 1990; Peres 1990; Woudhuysen-Keller and Woudhuysen-Keller 1994); the practice may also have been carried out on painted wood artifacts. Documentary sources suggest that egg white probably served as a temporary varnish; ordinarily, as much of it as possible would have been removed before a final varnish was applied. The fourteenth-century *De Arte Illuminandi* mentions a combination of egg white and plant gum or cane sugar in varnish (Thompson and Hamilton 1993:22).

Chemical composition. Egg white is a viscous material that consists of about 10–12% solids suspended in water. The solids are about 90% protein, of which there are several types. Egg white also contains a small amount of sugars (about 4%)—some bound to proteins (glycoproteins)— and salts (about 4%). The stringy property of egg white is due to one of the minor proteins (ovomucin). To make a useful binding medium, the white is beaten. The froth formed by beating is discarded, while the remaining solution, no longer viscous, can be further thinned and mixed with pigments. The binder contains many of the original components of the egg white, of which the major one is the protein ovalbumin. Egg white dries by evaporation of water to form a weak, brittle film.

Aged egg white can be highly insoluble. This suggests that changes in some of the proteins during drying and aging are not reversible; however, under controlled laboratory conditions, egg white can be resolubilized after complete drying.

Analysis. Because of the similarity of the amino acid profiles for egg white and yolk, a further test for lipids (as discussed in the section on egg yolk that follows) would be prudent in order to eliminate the possibility that yolk is present. The most conclusive evidence for egg white comes from identification of specific biological marker compounds unique to egg white. Ovalbumin, which makes up nearly 60% of the white's protein, can be

identified in paint cross sections by reaction with its antibody (Kockaert, Gausset, and Dubi-Rucquoy 1989). The overall reliability of this type of test is not yet certain.

It is also possible to use microscopic examination to identify avidin, a very minor component of egg white. Avidin, a glycoprotein, makes up about 0.05% of solid egg white (Wolbers 1988). The procedure can be applied on cross sections, but again, its reliability needs to be more thoroughly studied.

Egg yolk

The principal documented use of egg yolk as a paint medium is in Italian medieval and Early Renaissance paintings. This technique was described by Cennino Cennini (1954) and has been thoroughly discussed in a recent exhibition catalogue (Bomford et al. 1989:26–29). The use of the medium may date back to a considerably earlier time, but firm analytical identifications in earlier paintings are rare. One Egyptian mummy portrait from the Roman period was determined to have been painted in an egg medium (Ramer 1979), either yolk (as indicated by its lipid content) or whole egg. While *tempera* is a general term for water-based paint media, it most often refers to paint bound with egg yolk (egg tempera). There are indications that during the later medieval period in Europe, egg-oil emulsions were sometimes used on panel paintings (Kockaert, Gausset, and Dubi-Rucquoy 1989; Kockaert 1984). Such mixtures have also been identified on later paintings (Plesters 1987; Mills 1987).

Chemical composition. The solids of egg yolk, which make up a little over half the fresh yolk by weight, consist of about one-third protein and two-thirds lipids. Very small amounts of natural colorants produce its characteristic yellow color. As with egg white, the yolk contains numerous proteins, some of which contain chemically bound phosphorus. Some also contain chemically bound carbohydrate. By definition, lipids are a broad group of heterogeneous natural products that are soluble in organic solvents but not in water. The lipids in egg yolk seem mostly to be intimately associated with some of the protein(s), perhaps buried within the approximately globular form of the proteins in their native states.

The lipid content of yolk can be divided into two major categories, phospholipids (about one-third) and triglycerides (about two-thirds). For a discussion on the structures of triglycerides—the compounds that make up natural oils—see the chapter by Erhardt on drying-oil media in this volume. The fatty acids in the triglycerides (oil) of fresh yolk consist of about one-third saturated acids and two-thirds unsaturated acids. Oleic acid accounts for about 60% of the unsaturated fatty acid, and linoleic about 25%, giving egg yolk oil a partially "drying" nature. The saturated fatty acids are mainly stearic and palmitic, in a ratio of about 2:1.

Like triglycerides, phospholipids consist of a backbone of glycerol, which is bonded to three other molecules, one of which is a phosphate. The major phospholipid in yolk is lecithin, a natural emulsifier that allows intimate mixing of the water-soluble components (proteins) and the water-insoluble components (triglycerides) of the yolk. The other major component of egg yolk is cholesterol, which makes up around 3.5% of the dry weight of the yolk.

In order to be used as a binder, egg yolk is simply diluted with water and mixed with pigments. An egg yolk film initially dries by evaporation of water. As water evaporates, the protein complexes become irre-

versibly denatured. The oil component undergoes similar reactions to those of drying oils in oil-paint films, eventually becoming somewhat polymerized. The lipid components, since they are only partially drying in nature, undoubtedly contribute some flexibility to egg yolk, which the other strictly protein-based binders do not have once they dry. Therefore, egg yolk films do not exhibit the typical stress patterns shown by films of water-soluble media that dry simply by water evaporation, such as gums, egg white, and glues (Keck 1969).

Analysis. The oil component provides one means of distinguishing yolk from other protein binders. The fatty acids of dried yolk films can be analyzed in the same manner as the fatty acids of drying-oil films, whether by microchemical testing or instrumental analysis. One current standard instrumental technique is GC. An aged egg yolk film contains substantial amounts of palmitic and stearic acids, and typically only a small amount of azelaic acid, a by-product of the drying process. For some years, the National Gallery in London, which pioneered the application of GC to analysis of binding media, has used analysis of the lipid component for identification of egg yolk.

An example of the possibilities of instrumental analysis and the difficulties in interpretation is the original tinted coating on an eighteenth-century commode in the Museum of Fine Arts, Boston (Newman 1994). Amino acid analysis by HPLC gave a profile similar to that of egg, while analysis of a separate scraping by gas chromatography–mass spectrometry (GC-MS) indicated the presence of drying oil with a small amount of pine resin. Cross sections showed the presence of a single red paint layer, which stained rather evenly for oil. From examination of cross sections and the instrumental analyses, it seemed most likely that the original tinted finish contained both egg and drying oil.

Infrared spectrometry of egg yolk paint films detects the lipid and protein components of the media simultaneously. If it is assumed that the lipid could not have come from another source (such as drying oil), the combination of protein and oil implies egg yolk as a binder. Py-GC also can be used to identify the presence of lipid and protein components in the same mixture (Chiavari et al. 1993).

One unique component of egg yolk not found in other common binders is cholesterol. Cholesterol is not highly stable, and to date it has not been proved that it can be easily identified in aged egg yolk paint films (Mills and White 1982); in fact, the compound may have undergone chemical alteration in many old paints. The specific pigments present in an egg yolk film can also have a major influence on the stability of cholesterol.

Degradation. Medieval paintings carried out with egg yolk often remain in good condition, indicating that the medium is among the most stable of the natural binders. The oil component, however, undergoes the same types of autoxidation and polymerization as drying oils. Ultimately, these produce a mixture of low-molecular-weight polymers or breakdown products that may be susceptible to leaching by various solvents. Polymerized proteins are one possible by-product of such reactions, as are brownish condensation products (Horie 1992). There have been no published studies that focus on the degradation of egg yolk films over time, although one recent publication points to the complex nature of the medium's behavior (Khandekar, Phenix, and Sharp 1994). As mentioned in association with egg white, pigments that are acidic in nature may cause partial hydrolysis of the proteins in the binder and form inorganic salts

with liberated amino acids or fragments of the proteins. Infrared studies of old paint samples suggest that this occurs.

Casein

The early history of casein in paints is sketchy. Ancient Hebrew documents reportedly mention its use (Gettens and Stout 1966:8). Cennini's *The Craftsman's Handbook* (1954:68) mentions the use of casein glue but does not mention casein paints. Lime casein was reported to have been the medium of some late-twelfth-century wooden panels from the ceiling of a church (Denninger 1969). Casein paints, which were produced in the United States on a commercial scale beginning in the late nineteenth century, were apparently very popular in interior and exterior house painting throughout the nineteenth century, probably popularized by a late-eighteenth-century French book that appeared in translation just after 1800 (Phillips 1994:253). How extensively casein paints were used, and what the specific formulations were, can be understood only by analysis of paint samples. Virtually no detailed examinations of these paints have been published to date.

   Chemical composition. By definition, casein refers to a group of several proteins that are found in milk. Casein proteins are usually divided into four major fractions, but each fraction may contain more than one specific protein. With reference to paint, the term *casein* usually indicates any paint with a binder derived from milk, although such binders may contain significant amounts of compounds (lipids and/or carbohydrates) other than the casein proteins themselves (Phillips 1994).

   The solids of milk, which make up about 13% by weight of the natural material, are complex in composition. About 24% is made up of proteins, 31% of lipids (fats), 38% of lactose (milk sugar), and the remainder (7%) mainly of various ions. About 80% of the protein is casein. In raw milk, the several individual casein proteins combine to form roughly globular micelles suspended in water. The casein proteins contain phosphorus (about 1% by weight overall). One of the casein proteins also contains some carbohydrate as part of its structure. Most of the carbohydrate content of raw milk, however, is in the form of lactose, a disaccharide (formed from the simple sugars galactose and glucose). The lipids in raw milk are present in the form of triglycerides, the same type of compounds found in drying oils. A typical distribution of the fatty acids in cow milk fat is around two-thirds saturated fatty acids and one-third unsaturated. The major saturated fatty acids are palmitic, stearic, and myristic, in a ratio of approximately 2:1:0.8. Oleic makes up most of the unsaturated fatty acid. Because of the low unsaturated fatty acid content, this oil is essentially nondrying in nature.

   Casein paint can be quite variable in composition and properties, depending on how it is prepared. Whatever the formulation, casein paint films are brittle, porous, and matte. The simplest "casein paint" would simply involve mixing milk with pigments. If whole milk were used, the dried paint would contain all of the components of the original milk. Drying simply involves evaporation of water. As the water evaporates, the protein micelles become denatured. This is an irreversible change, meaning the protein micelles are no longer soluble in water after drying. However, the milk sugar component remains readily soluble in water; thus, such a milk paint would probably be easily damaged by water.

A purer casein paint could be produced by beginning with curds, which are precipitated from soured milk and are rich in casein (the casein micelles become unstable under acidic conditions). Washed, dried, and ground curds are largely insoluble in water but can be solubilized by the addition of a base. Drying of such a casein paint involves evaporation of water; if a volatile base (such as ammonia) has been used, the protein will precipitate as the water and the base evaporate. If a nonvolatile base is used (such as lime), the cation of the base (calcium, in the case of lime) reacts with the protein molecules during drying to form highly insoluble calcium-protein complexes; reaction occurs at the phosphate groups on the protein. Depending on formulation, a casein paint could remain readily soluble in alkaline water or could be virtually insoluble after drying. If skim milk were used for the curds, the resulting paint would contain little if any of the original oil or fat component but could still contain some milk sugar. For example, a canvas painting by William Morris Hunt recently analyzed at the Museum of Fine Arts in Boston was done in casein paint (Newman 1991). Analyses showed that the fat content was minimal, but appreciable lactose was present in the paint, which was sensitive to water.

Analysis. Analysis for phosphorus has been an additional test used to distinguish caseins from other protein binders (Stulik and Florsheim 1992; Martin 1977). The phosphorus content of the casein proteins is much higher than that of the proteins in the other common protein-rich binders; thus, a positive result for protein and phosphorus in a paint sample suggests casein, but it would not be positive proof. Analyses for sugar content could be useful since many older caseins may contain milk sugar. Identification of equal amounts of glucose and galactose, the two simple sugars that make up lactose, would be very suggestive. Since the solubility properties of casein paints can vary considerably, sensitivity to water is not a very useful criterion in itself.

Degradation. While the other common protein-containing binders show little compositional variation from one sample to another, caseins can show a quite considerable variation depending on method of preparation. For this reason, degradative reactions could vary considerably from one casein to another. For example, reactions between the sugar and protein components, as well as between the lipid and protein components (discussed earlier with reference to other proteins), would be potentially more important in less purified caseins.

Carbohydrate-Containing Media

The only common carbohydrate-containing binding media are plant gums. Other carbohydrates much more rarely used as binders include honey and starch.

Chemical composition of carbohydrates

Carbohydrates consist of monosaccharides (simple sugars) or compounds that can be broken down into monosaccharides by hydrolysis. Monosaccharides are small molecules that occur in many living organisms (Fig. 6). Polymers that are formed from two monosaccharide molecules are disaccharides; common examples are lactose (milk sugar) and sucrose (cane or beet sugar). Polysaccharides are polymers formed from hundreds or

a   Arabinose
b   Xylose
c   Rhamnose
d   Glucose
e   Galactose
f   Galacturonic acid
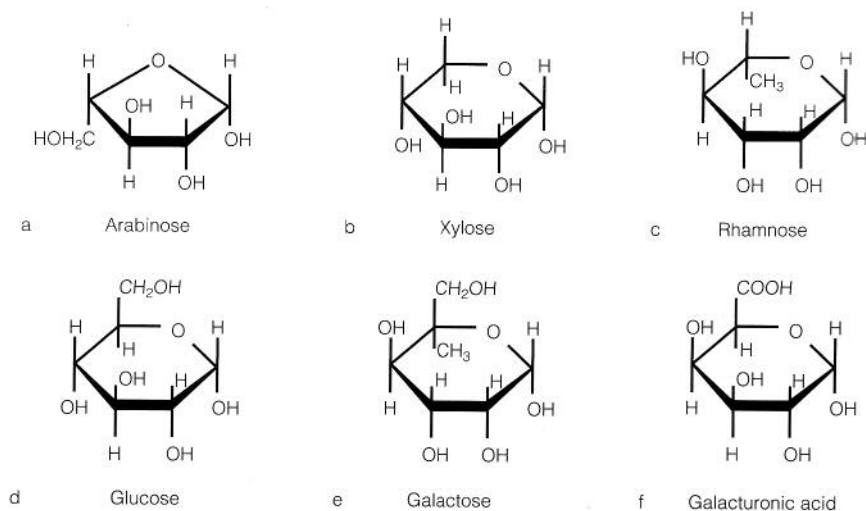
even thousands of monosaccharide molecules. Some have a linear structure
(each sugar bonded at each end to another sugar molecule); cellulose (the
structural material of plants) is an example of this type of polysaccharide.
Cellulose is formed from only one type of monosaccharide (glucose).
Starch—chiefly found in plant seeds, roots, bulbs, and tubers—consists of
two different carbohydrates. One of these (amylose) is a linear carbohy-
drate similar to cellulose but much smaller in size; it is water soluble. The
other carbohydrate in starch (amylopectin) has a highly branched structure,
in which many sugar molecules are bonded to more than two other sugar
molecules; this fraction is not water soluble. As with cellulose, the only
monosaccharide in both of the carbohydrate fractions of starch is glucose.

Many plants produce polysaccharides known as gums, in which
the simple sugars are bonded together to form large, branched molecules
that are soluble (or dispersible) in water. Gums typically are formed from
more than one type of monosaccharide.

Plant gums

The major applications of gum-bound paints have been in manuscript illu-
minations and watercolor paintings on paper. Plant gums were probably
one of the major painting media in ancient Egypt (Newman and Halpine
1994); however, few identifications of gum binders on wooden artifacts
have been published. Plant gum as a varnish or coating was found to be
applied locally to gilding on some Gothic polychrome sculptures, includ-
ing a 1466 altarpiece by Friedrich Herlin (Broekman-Bokstijn, van Asperen
de Boer, and Serck-Dewaide 1970). The carbohydrate-containing medium
may have been mixed with a protein and was probably applied to attenu-
ate the brilliance of the leaf.

One of the most common of the gums is gum arabic, the most
common source of which is the bushlike tree, *Acacia senegal,* which grows in
central and northern Africa, extending east to the Sind region of India. The
gum molecules are made up of well over one thousand individual sugar
units (Anderson, Hirst, and Stoddart 1966). As with most polymers, mole-
cules of gum arabic display a range of molecular weights. Another gum
that has been used in artifacts is gum tragacanth, an exudate from various
species of *Astragalus* (Twilley 1984). This gum, which is only partially solu-

ble in cold water, consists of at least two rather different polysaccharides (Aspinall and Baillie 1963). Other gums—including fruit-tree gums such as apricot, peach, and cherry—have been identified in artifacts (Birstein 1975). Other types of *Acacia* gums besides *Acacia senegal* may have been utilized in artifacts. One has been suggested as a binding medium for the wall paintings in Nefertari's tomb in Egypt (Stulik, Porta, and Palet 1993).

Chemical composition. Plant gums consist almost entirely of polysaccharides. They also contain small amounts of amino acids (Anderson, Hendrie, and Munro 1972). Specific gums contain two or more different monosaccharides, the identity and relative amounts of which often vary from one plant source to another. In addition, gums usually contain one or two different types of uronic acids, which are compounds derived from monosaccharides (for example, the one shown in Fig. 6f).

Plant gums are simple to collect; tears of solidified gum can be broken off branches of the plant or allowed to collect around a cut. Gum-bound paints dry by evaporation of water without any significant change in the shape or composition of the molecules. They tend to be brittle and remain sensitive to water but can become less soluble with age (Daniels and Shashoua 1993).

Analysis. The common microchemical tests detect simple (reducing) sugars (Stulik and Florsheim 1992; Feigl 1960:426), which are easily liberated from gums by hydrolysis; many carbohydrate-containing binders would respond positively to these tests. In ultraviolet light, plant gums fluoresce bright bluish white. In some instances it may be possible to detect gum in paint cross sections or chips of paint under an ultraviolet fluorescence microscope by using a reagent that chemically alters sugars, destroying the fluorescence (Wolbers 1990:30–33). Infrared spectra of different plant gums show some variations, but usually this technique is useful only for general identification (Fig. 7). More specific information is obtainable through the use of Py-GC, which can distinguish some gums from others in paint samples (Derrick and Stulik 1990).

Specific attempts at identification usually involve breaking down the gum into its constituent monosaccharides and uronic acids, and then separating these. To date, most analyses of this type have been carried out by TLC or GC. Some sample preparation and analytical procedures (typically TLC) can characterize both the neutral monosaccharides and uronic acids, and this would be desirable if the identification of a specific gum type is required (Masschelein-Kleiner 1986). Other sample preparation methods (typically those used for GC) readily characterize only the neutral monosaccharides (Twilley 1984; Erhardt et al. 1988); but this information, too, can be useful, since types and relative amounts of such sugars often vary from one type of gum (or other carbohydrate-containing material) to another, as shown in Figure 8. The red paint on a Ptolemaic period Egyptian canopic container (Fig. 9) was determined to have a gum binder on the basis of GC analysis of its simple sugar content (Fig. 10a). The gum was clearly not *Acacia senegal* (gum arabic), a chromatogram of which is also shown (Fig. 10b), but it could have been another species of *Acacia*.

Since plant gums contain small amounts of amino acids (usually less than 1% by weight), it is also possible to partially characterize them on the basis of analysis of their amino acid profiles. The amino acid profiles of plant products such as gums are quite distinct from the amino acid profiles of the common protein-containing paint binders (Anderson, Hendrie, and Munro 1972) discussed previously.
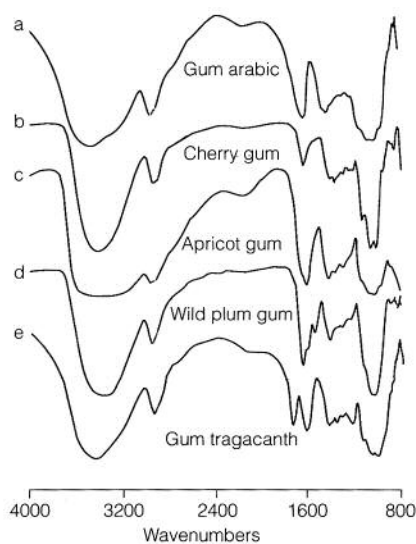
Figure 7
Infrared transmittance spectra of some plant gums. Note that the spectra are quite similar, with the exception of gum tragacanth.
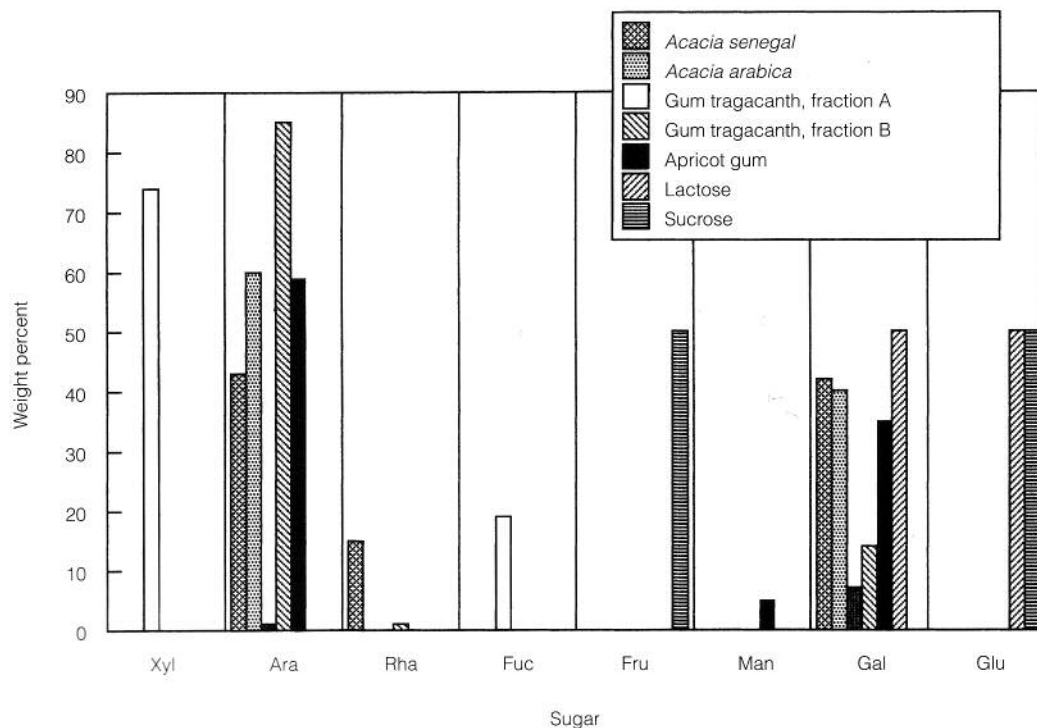
Figure 8

Monosaccharides in some gums and other carbohydrate-containing materials. The first two materials are varieties of gum arabic. Gum tragacanth contains two water-soluble fractions (A and B), which differ in composition. Lactose (milk sugar) is found in unpurified caseins. Sucrose (table sugar) is a major component of honey. Xyl, xylose; Ara, arabinose; Rha, rhamnose; Fuc, fucose; Fru, fructose; Man, mannose; Gal, galactose; Glu, glucose. (Sources of data: *Acacia* gums: Anderson and Karamalla 1966; gum tragacanth: Aspinall and Baillie 1963:1704; Twilley 1984:381).

Degradation. Little is known about the degradation of plant gums over long periods of time. Some portions of gum molecules are readily hydrolyzable under acidic conditions, so it is likely that gum-containing paints that have been buried or stored in a humid environment may have broken down to some extent. As with other natural polymers, limited hydrolysis greatly reduces the size of the molecules and probably weakens the paint without any chemical changes in the constituent mono-saccharides. While it is not clear whether chemical changes figure prominently in the aging of gum-bound paints, oxidation and other reactions that occur during the aging of cellulose and other complex carbohydrates found in wood and paper (Hon 1981) may also take place in gums.

Other Carbohydrates

Honey has been identified as a binder in a single ancient Egyptian paint sample (Masschelein-Kleiner, Heylen, and Tricot-Marckx 1968). In more recent times, starch or dextrin (produced by partial hydrolysis of starch) might be encountered. Starch was utilized in East Asian painting from an early period, although usually as an adhesive rather than a paint binder (Winter 1984). Dextrin is an ingredient in many modern commercial artists' watercolor paints. Plant juices, which contain simple sugars, were sometimes used in manuscript illuminations, according to documentary sources (Thompson 1956:61).

The analytical procedures already described can be applied to identification of these other carbohydrate-based binders. In addition, there is a specific microchemical test for starch that can be used (Stulik and Florsheim 1992).

Plant Resins and Shellac

There are numerous natural resins. With the exception of shellac (which is of insect origin), all are sticky, water-insoluble materials that exude from

Figure 9
Painted wood canopic chest, Egypt, Ptolemaic period (332–331 B.C.E.). Museum of Fine Arts, Boston (accession no. 98.1128).

Figure 10a, b
Chromatograms (a) of a sample of red paint from the canopic chest shown in Figure 9; and (b) of *Acacia senegal* (gum arabic). Analyses carried out by gas chromatography–mass spectrometry. The paint and gum samples were hydrolyzed, and monosaccharides were analyzed as trimethylsilyl oxime derivatives (each sugar gives rise to two major peaks). Note that the paint sample differs from gum arabic in that it contains virtually no rhamnose; the paint binder also has a greater arabinose : galactose ratio than gum arabic.
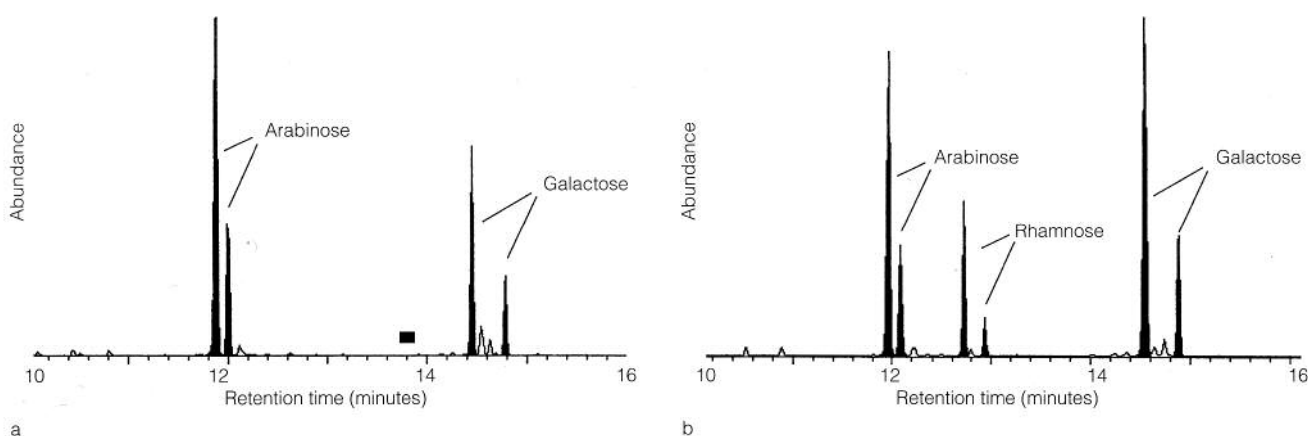
many kinds of trees and plants. Probably the earliest uses of natural resins on wooden artifacts were as varnishes, coatings, and adhesives. In ancient Egypt, for example, resin varnishes were used on some artifacts beginning in the Middle Kingdom (Lucas and Harris 1962). These varnishes, which appear to have been applied in very viscous forms, could have been simply the natural solvent-containing resins extracted from their source trees. Medieval European varnishes were probably solutions of one or more resins in drying oils (Barry 1932:2–8); residues of such varnishes have been identified on medieval Italian egg tempera paintings (Dunkerton, Kirby, and White 1990). Resin solutions in solvents (spirit varnishes) were probably not common until after the medieval period. Particularly in the context of furniture, varnishes may have been made from mixtures of several different natural resins. A popular eighteenth-century European treatise, for example, described over a dozen individual resins for use in furniture varnishes (Mussey 1982). The preparation of a varnish depends on the resin or resins involved in the recipe. Some resins are quite readily soluble, while some of the less soluble resins were often heated or "run" as part of the preparation, a process that can cause partial decomposition.

Small amounts of natural resin may have been incorporated in some oil paints from the earliest periods from which oil paintings are known. A particularly common example is copper resinate glazes, fairly transparent solutions of the pigment verdigris in resin and oil. Such solutions have been found in panel paintings and were also used in early English and American architectural (house) paints (Welsh 1994). Resin-rich oil paint media have been popular in certain periods and places, some of the best known being megilp and *gumtion* of nineteenth-century England and America. Both contained linseed oil and mastic resin (Carlyle 1990).

Natural resins can occur in other contexts on wooden artifacts. For example, brocades on some medieval European polychromed sculptures were underlaid by mixtures of wax and natural resin(s). Tinted glazes, probably bound by natural resins, were also used on metal leaf—for example, to make tin leaf appear to be gold.

In contrast to the plant resins, the use of shellac on painted wooden artifacts is mostly restricted to varnishes and coatings. The secretion from the lac insect was also the source of a red colorant (commonly known as *lac*), first mentioned about 250 C.E. (Barry 1932:237). The use of the secretion in varnish is first mentioned in an Indian text of 1590, and around the same time the resin apparently became known in Europe.

Shellac was a component of some European varnish recipes by the seventeenth century (Bristow 1994). The resin was also used to seal knots and absorbent wood surfaces before painting.

Chemical composition of plant resins

When freshly collected, plant resins contain varying amounts of natural solvents, up to about 30% by weight in some cases. Most resins are marketed in the form of the solid material left behind after evaporation of the volatile constituents. The solubilities of resins vary considerably: some are completely soluble in several organic solvents (alcohols, turpentine, methylene chloride, etc.), others only partially soluble. As with solubility, the melting ranges of resins vary considerably, from slightly under 100 °C to around 300 °C. Thin, dried films of the soluble natural resins are brittle; they remain soluble in organic solvents, although in most cases their solubility changes substantially with aging as a result of chemical reactions.

Most plant resins contain many different compounds, most of which fall into two general chemical categories: diterpenoids and triterpenoids. These two classes of material never occur together in a single resin. Examples of resins that contain diterpenoids are pine, larch (commonly known as Venice turpentine), sandarac, copals (of which there are many varieties), and copaiba balsams. Triterpenoid resins include mastic, damar, and elemi. The chemical compositions of the natural resins are discussed in detail in several publications (Mills and White 1977; Mills and White 1987). The structures of a few specific compounds found in plant resins are shown in Figure 11. Plant resins that contain substantial amounts of involatile compounds other than diterpenoids and triterpenoids include benzoin, myrrh, and frankincense (olibanum). Some resins are collected from the ground, rather than taken from living trees, and may be a few thousand years of age (for example, kauri copal). Amber is a true fossil resin of much greater age.

Unlike the resins just mentioned, shellac is of insect origin and has a composition quite different from those of the plant resins. It is made from the secretion of an insect, with shellac making up about 80% of the secretion (Barry 1932:248). Shellac appears to consist of small polymers of sesquiterpene acids (which contain 15 carbons) and hydroxycarboxylic acid.

Analysis of plant resins

The best approaches to detection and identification of natural resins depend on the nature of the sample, of which there are two categories: (1) a varnish or slightly tinted coating in which natural resin is the only major component; and (2) a paint film, consisting of pigments and binders, of which resin is one component but typically not the major one.

In a varnish, even relatively thin layers of natural resin can be detected in cross sections by their milky green fluorescence, utilizing ultraviolet fluorescence microscopes; shellac can usually be distinguished by its orange-tinted fluorescence. A reactive reagent (antimony pentachloride in chloroform) has been used as a further confirmation for plant resins in varnish layers in cross sections (Wolbers and Landrey 1987). Analysis of thin cross sections by infrared (IR) microspectrometry can provide more specific information, even permitting some identifications of specific resins (Derrick et al. 1992). This technique can be particularly useful in the case of objects such as furniture, which may have multiple coating layers of

Figure 11

Structures of some diterpenoids (top six com-
pounds) and triterpenoids (bottom two com-
pounds) found in plant resins. Abietic acid is
an important constituent of pine resins and
some other conifer resins, and is also found in
kauri copal. Dehydroabietic acid is a major
constituent of aged pine and conifer resins.
Sandaracopimaric acid, a component of pine
and other conifer resins, is also a major com-
ponent of sandarac resin. Larixol is a compo-
nent of Venice turpentine and is not found
in any other major resin. Agathic acid is
found in a number of copal resins, eperuic
acid in a number of African copal resins.
Dammaradienol is found in damar resins,
masticadienonic acid in mastic resins.

Abietic acid

Dehydroabietic acid

Sandaracopimaric acid

Larixol

Agathic acid

Eperuic acid

Dammaradienol

Masticadienonic acid
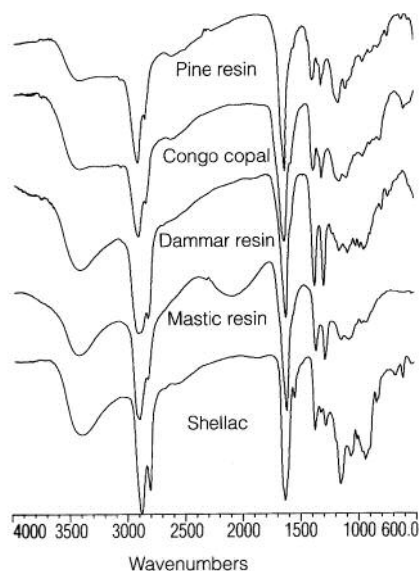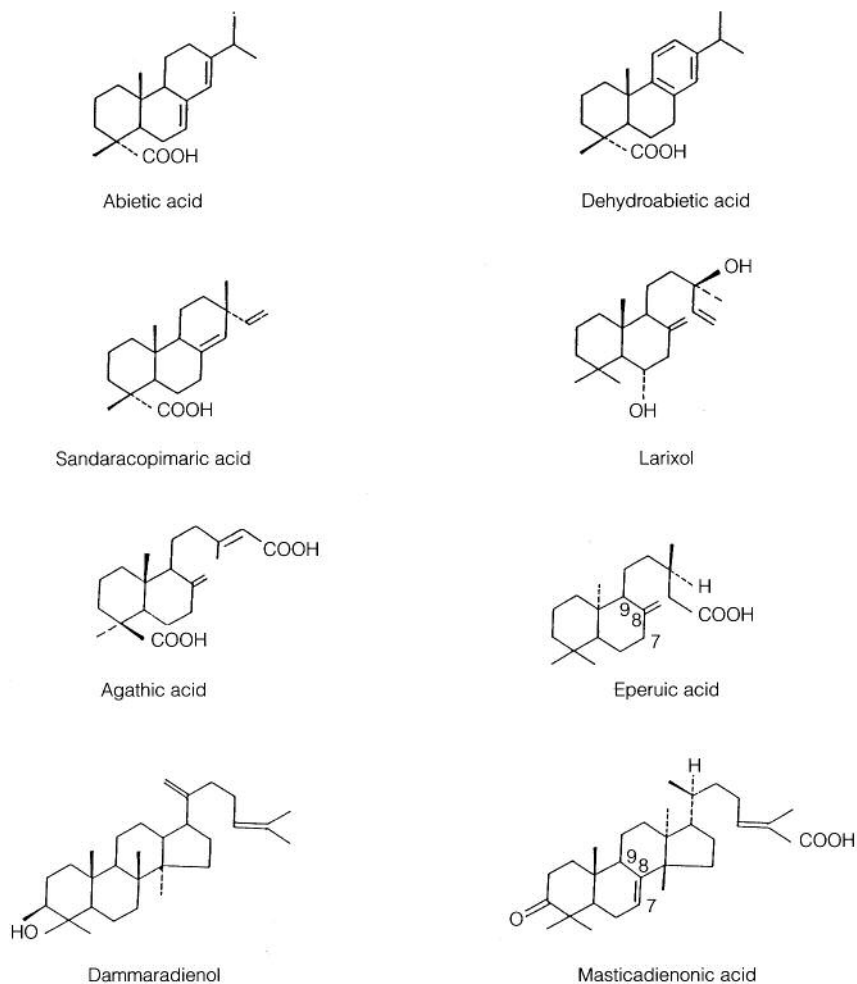
Figure 12

Infrared transmittance spectra of some resins.
While all these spectra of fresh, unaged resins
are generally similar, there are distinctive
differences that permit specific identifications,
particularly in the region below about 1800
wave numbers. Aged resins are more difficult
to identify.

differing compositions. Small amounts of resins in paint films (for example, oil-resin binders) generally cannot be detected in cross sections by any currently utilized technique, including IR microspectrometry.

With bulk samples that consist mainly (or entirely) of resin, most of the instrumental techniques listed in Table 1 (see appendix in this article) have been applied. Infrared spectrometry of varnishes can in some cases provide specific identifications and possibly even identify the individual components of mixtures (Derrick 1989), although the latter is probably an area where the technique would not be highly useful. Figure 12 shows representative IR spectra of a number of resins. Py-GC can distinguish individual resins from one another (Shedrinsky, Wampler, and Baer 1988); its application to samples containing several different resins, as could occur in old varnishes, has not been studied in any detail.

Of the current techniques, gas chromatography is the most useful for specific identifications of individual resins and mixtures of resins (Mills and White 1987:149–52; Koller and Baumer 1993). Because of the complexity of resins, GC-MS is more definitive than GC alone. GC-MS can also be successfully applied to identification of small amounts of resins in paint films (for example, Mills and White 1982; White and Kirby 1994). Aged resins are often very different in composition from fresh samples of the same resins, but enough work has been published on numerous natural resins that characteristic compounds detectable in older samples are

known. An example of GC-MS analysis of a complex paint sample is shown in Figure 13. While not all of the compounds detected in the sample could be identified, the presence of linseed oil, pine resin, mastic resin, and probably an African variety of copal resin was confirmed.

Degradation of plant resins

Many of the compounds in natural resins are relatively unstable. Loss of solubility and increasing yellowness with aging are two well-known problems with natural resin films. While the rate of degradation varies from one resin to another, most undergo oxidation and photochemical reactions of various types (e.g., see De la Rie 1988). The nature and extent of degradation depends on environmental conditions (e.g., access of light and oxygen to the resin) and the type of resin. For example, Bronze Age samples of mastic resin excavated from shipwrecks contain many of the characteristic compounds of freshly tapped mastic (Hairfield and Hairfield 1990), whereas excavated samples of pine resin from the same period consist almost exclusively of oxidation products not present in fresh pine resins (Beck, Smart, and Ossenkop 1989). Changes in the solubility of resins with aging may be partly due to some polymerization in certain instances. Heating during preparation of a resin can alter the chemistry of some resins; undoubtedly, changes occur during the "running" process that was

Figure 13a, b

Chromatogram of green paint sample from *Beach Scene at Concorneau* (n.d.), a painting by Robert Henri (1865–1929). The sample was saponified, extracted, and methylated for GC-MS analysis. Top (a): full chromatogram, showing that the major peaks are due to azelaic, palmitic, and stearic acids. These show that the major component of the sample is drying oil, probably linseed. Bottom (b): detail of the later part of the chromatogram, showing a number of smaller peaks. Small amounts of some fatty acids (labeled A20 and A22) and some hydrocarbons (labeled H24 and H26) were detected, probably trace components of the oil. Two compounds characteristic of aged pine resins have been detected: P1, dehydroabietic acid; P2, 7-oxodehydroabietic acid. Four other peaks are characteristic of copal resins: C1, eperuic acid; C2, probably communic acid; C4, agathic acid. C3 is a compound whose identification has not been determined, but it is found in some Congo copals. While the specific type of copal cannot be identified, it is probably an African variety since eperuic acid seems to be restricted to these copals. Later in the chromatogram (retention times from 27 to 32 minutes), some triterpenoid compounds were detected that match those of reference mastic resins.
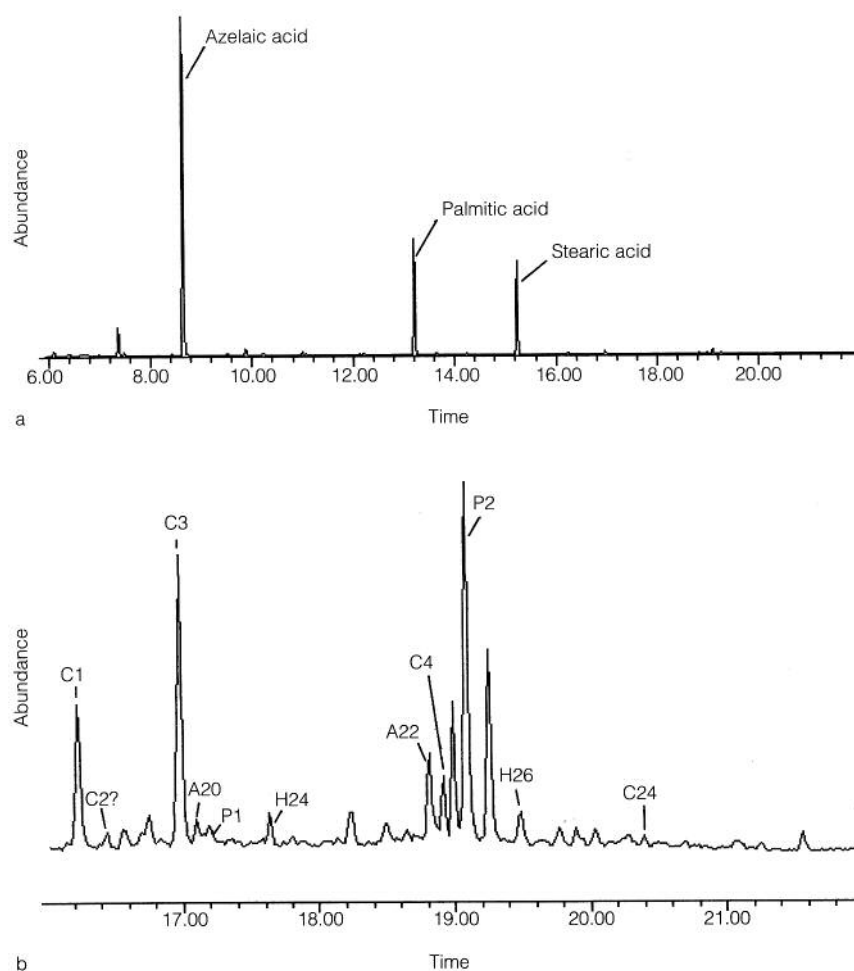
used to put some of the harder resins into solution during the manufacture of varnishes, although the nature of these changes has not been studied to any great extent.

Resins can undergo reactions with other media and with certain pigments. Many contain substantial amounts of acidic compounds, which can form salts with some pigments. It is likely that chemical reactions occur between natural resins and drying oils in oil-resin varnishes or paints that contain both types of materials.

Waxes

Waxes are a loosely defined group of materials of plant, animal, and mineral origin. While rather diverse in composition, they are all translucent solids with low melting points and a "waxy" feel. Beeswax, from beehives, is probably the first natural wax to have been utilized in painting. It was reportedly used as a binding medium in ancient Egypt, although there are very few reliable identifications of use before Roman times (Lucas and Harris 1962:352–53). It has been identified on some wall paintings, but most likely it served as a varnish or coating rather than as a paint medium. Documentary sources indicate that wax painting was a popular technique in Greek and Roman times. The earliest surviving wax paintings are the well-known Fayum portraits (so-called mummy portraits) found in tombs in the al-Fayyūm region of ancient Egypt. The binding medium in these paintings may actually be Punic wax. Pliny the Elder described the preparation of Punic wax (Kühn 1960), which involved heating beeswax in alkaline salt water three times, a procedure that would have led to partial saponification. Because the alkali contained nonvolatile metallic ions (sodium, potassium, or calcium), the final product contained salts of the fatty acids liberated by saponification. The Fayum portraits seem to have been executed with melted wax, applied with metal implements or with brushes.

One other common use of beeswax was in pastes associated with appliqué relief brocades on European medieval polychromed objects (Serck-Dewaide 1990). Several identifications have been reported, usually of wax mixed with natural resin(s), perhaps also with oil or honey. Beeswax has been a common polishing or coating material on furniture.

There are many natural waxes of plant origin, including carnauba (from the carnauba, or fan palm—*Copernicia cerifera*—which mostly grows in Brazil) and esparto (from esparto grass, of Spanish and Algerian origin). A recent analysis indicated the use of esparto wax as the binding medium in paints applied on planks from a Phoenician ship of about 400 B.C.E. (Glastrup 1995).

Chemical composition of waxes

Straight-chain saturated hydrocarbons with the general formula $CH_3-(CH_2)_n-CH_3$ are found in a number of waxes. Ozokerite—found associated with some lignite coal beds—and ceresin—refined from ozokerite—consist almost entirely of hydrocarbons; typically, these contain between about 20 and 32 carbon atoms, with the most abundant hydrocarbons falling in the range between about 23 and 29 (Mills and White 1987). Hydrocarbons make up about 14% of beeswax by weight; they contain only odd numbers of carbon atoms in the range 25–35, with the most abundant being the 27-carbon compound. Esparto and other waxes also contain hydrocarbons (Tulloch 1973).

Other important components of many waxes include fatty acids, long-chain alcohols, or esters derived from the acids and alcohols. Beeswax, in addition to hydrocarbons (14%), contains about 12% by weight free fatty acids (the major one contains 24 carbons) and 65% esters (Tulloch 1972). The majority of these esters are monoesters; that is, esters formed from a fatty acid and an alcohol that has one alcohol functional group (mono-alcohol). The most abundant fatty acid found in these esters is palmitic acid. Mills and White (1987) review the compositions of waxes and include references to analytical studies.

Because of its heterogeneous composition, beeswax melts within a temperature range of about 60–65 °C. Reaction with alkali (saponification) breaks down the beeswax esters, liberating fatty acids and alcohols. A partially saponified beeswax (of which Punic wax may have been an example) melts within a range extending somewhat higher than that of pure beeswax. Extensive enough saponification can result in a material that may be emulsified in water. As a binder, pure beeswax can be used in two basic ways: either as a solution in an appropriate organic solvent (such as turpentine) or melted. If sufficiently saponified, the wax could be used as an emulsion in water. Most other waxes could also be applied by melting or in solutions.

Analysis of waxes

Since wax-bound paint samples usually soften and melt at much lower temperatures than paints in the other common media, melting point measurements have often been applied to establish the presence of wax in paint samples. Many waxes are fairly readily soluble in weak organic solvents such as petroleum benzine, another property that can be useful in tentatively identifying waxes, as virtually no other common medium is substantially affected by such solvents. Infrared spectrometry has been widely utilized for identifying beeswax and other waxes, although specific identification is not always possible (Kühn 1960); to aid in an IR identification, the medium can be extracted with a solvent to eliminate most of the interference from pigments. Some representative IR spectra are shown in Figure 14. Although

Figure 14
Infrared transmittance spectra of some waxes. Ceresin wax consists entirely of hydrocarbons. The characteristic pairs of sharp peaks due to these compounds are indicated by the letter H; hydrocarbons are also found in the other three waxes shown. Candelilla (from a species of plant that grows in the southern United States and Mexico), beeswax, and carnauba (from a type of palm that grows mostly in Brazil) contain esters (characteristic peaks marked E). Carnauba also contains other types of compounds. The IR spectrum of a wax can sometimes provide specific identification, while in other cases it may only narrow down the possibilities.
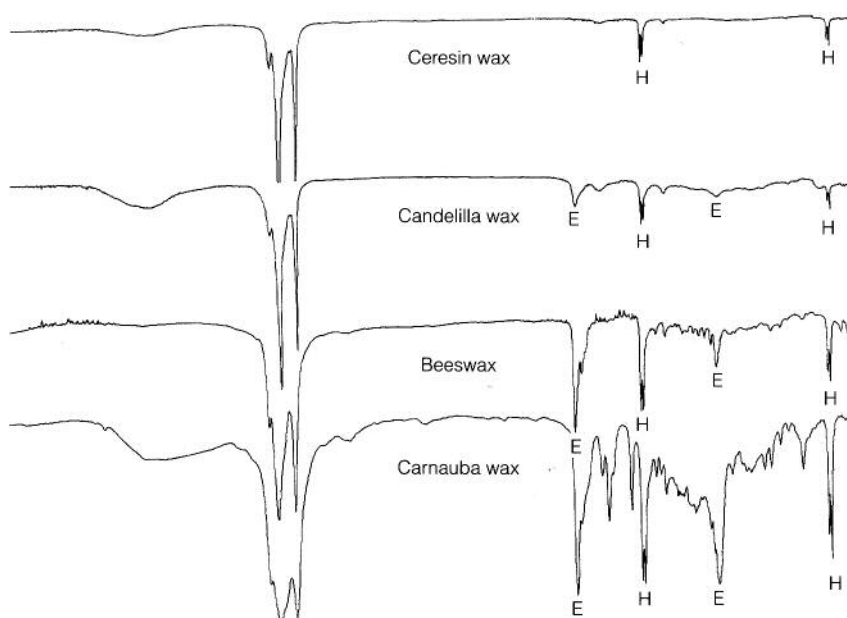
not widely used for identification purposes, thin-layer chromatography has recently been shown to be useful (Striegel and Hill 1997).

      Specific identification of waxes can be carried out by gas chromatography. It is possible to directly analyze solutions of waxes (White 1978). All of the hydrocarbons found in waxes are readily identified by GC. The monoesters in beeswax and other waxes are also sufficiently volatile for direct GC analysis, although the higher-molecular-weight esters and some other compounds in many waxes are not. Another common approach to analyzing ester-containing waxes involves saponifying the sample, which liberates fatty acids from the esters (Mills and White 1987:146–47). GC analysis of a saponified sample of beeswax, for example, shows the hydrocarbons (which are not affected by the chemical treatment), the free fatty acids of the original wax (also not affected by saponification), and the fatty acids derived from the esters. Altogether these compounds make up only a small fraction of beeswax, but their pattern is sufficiently distinctive to permit positive identification of the wax. An example is shown in Figure 15, which compares a chromatogram from

Figure 15a, b

Chromatograms (a) of a reference beeswax sample; and (b) of a paint sample from an Egyptian Fayum portrait (Museum of Fine Arts, Boston). Both samples were saponified and methylated for GC-MS analysis. Hydrocarbons are labeled H, followed by the number of carbon atoms; fatty acids are labeled A, followed by the number of carbon atoms (for example, A16, palmatic acid; A18:1, oleic acid; A18, stearic acid). The patterns of even-numbered fatty acids and odd-numbered hydrocarbons charactistic of beeswax can be seen in the Fayum portrait sample, although in the portrait the overall level of hydrocarbons is distinctly lower.
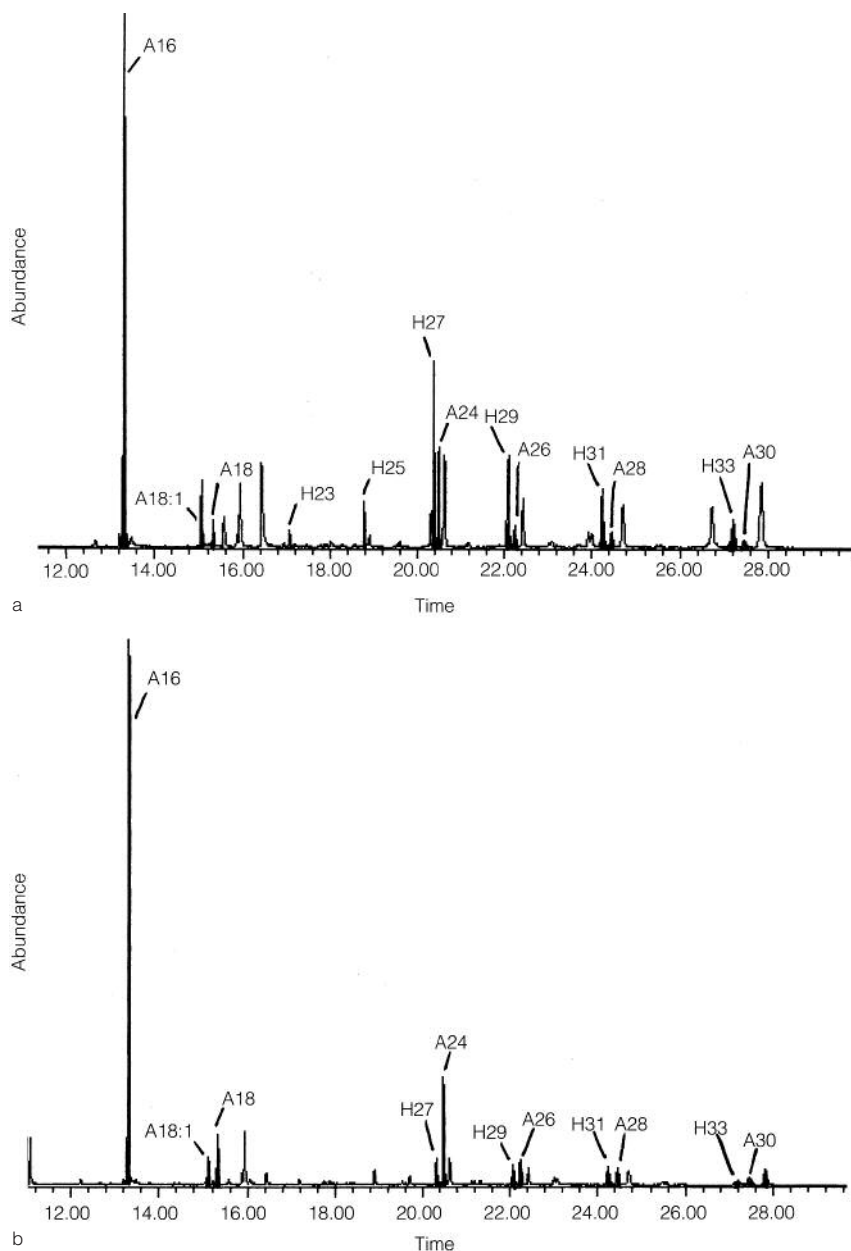
a Fayum portrait paint sample and a beeswax standard. Direct analysis of a solution of a beeswax-containing paint sample by GC could probably distinguish a partially saponified wax on the basis of the profile of esters and free fatty acids, but this has not been systematically investigated.

Wax can be an additive to other types of paints, such as oil paints. Small quantities of admixed wax can usually be readily detected by GC, but it would be difficult to detect by any other of the commonly used identification procedures.

Degradation of waxes

The hydrocarbon components of beeswax and other waxes are chemically very stable. Like other esters, the esters in beeswax can be broken down by saponification. Beeswax contains virtually no unsaturated fatty acids; thus, little oxidative degradation would be expected. A two-thousand-year-old sample from a Fayum portrait showed virtually no azelaic acid, confirming that oxidative degradation of the fatty acids in the esters had not taken place. Interaction with certain pigments may occur, resulting in the formation of fatty acid soaps, which are salts of inorganic ions. These interactions would be virtually the same as those that could occur in oil-paint films.

Appendix

Identification of Binding Media in Paint Samples

While documentary sources provide crucial information on media used by particular cultures or artists, expansion of current knowledge is dependent on analysis of paint from artifacts. A basic understanding of media identification is important because the use of appropriate techniques is critical to the technical study of painted artifacts. Table 1 summarizes the most widely used current techniques. While many procedures can be applied to identification of any particular medium, each procedure has unique capabilities and limitations. The following comments provide an overview.

General considerations

In approaching medium analysis, a first consideration is desired *specificity* of identification. Some methods determine the general chemical class of binders (for example, protein) but cannot distinguish between specific varieties within that class (glue, egg, casein, etc.); others can provide more specific information. A second consideration is *scale* of analysis, which depends on both the amount of paint sample available and the structure of the sample. Some analytical procedures require larger samples than others. If only a very small sample were available, it would not be worthwhile to apply certain techniques because the amount of binder could well be below the levels detectable by the technique. The structure of the paint sample also must be considered. For a single paint layer, a scraping of paint could be used for the analysis; any results could be reasonably concluded to indicate the nature of binder in that layer. However, where multilayer paint structures are found, different binders could have been used in various parts of the structure. In such cases, it would be best to apply a technique that would work directly on a cross section of the paint structure, unless individual layers can be mechanically isolated for separate analysis.

Some analytical procedures are more universal in nature than others. A truly universal procedure, of which there are few, would simultane-

Table 1   Common analytical procedures for binding media identification

Procedure	Sample type	Proteins	Carbohydrates	Plant resins and shellac	Waxes	Drying oils
Microchemistry	B	G	G	G?		G
Infrared (IR) spectrometry	B	G	G	G, S?	G, S?	G
Pyrolysis–gas chromatography (Py-GC)	B	S?	S	S		S
Thin-layer chromatography (TLC)	B	S	S		S	
Gas chromatography (GC) and GC–mass spectrometry (GC-MS)	B	S	S	S	S	S
High-performance liquid chromatography (HPLC)	B	S				
Visible-light staining of cross sections	CS	G, S?				G
Fluorescent staining of cross sections	CS	G, S?	G?	G?		G
Infrared (IR) microspectrometry of thin cross sections	CS	G		G, S?		G

B   =   bulk sample (scraping, chip, etc.)

CS   =   cross section

G   =   procedure that is usually used only to identify the general class of material indicated in the column heading

G?   =   procedure that can sometimes determine the presence of the general class of material, but not always

S?   =   procedure that can sometimes determine specific varieties within the general class

S   =   procedure that can often determine specific varieties within the general class

ously identify many different types of binders during a single analysis. Since most tests or analyses will not simultaneously detect all the types of compounds found in organic binders, a full characterization typically requires more than one procedure or one series of analyses. Confirmation of the presence of some materials and lack of detection of others provides a more certain identification than simple confirmation of one material, and ultimately the identification will be more useful for future researchers if a systematic series of tests is carried out.

Current analytical procedures

The conservation literature on media identification is quite extensive. Masschelein-Kleiner (1986) provides a useful summary of the major literature on analytical procedures up to 1986. A systematic series of microchemical procedures was recently described by Stulik and Florsheim (1992). Microchemical tests are the most affordable approach but require somewhat larger samples than might be available from many artifacts. Thin-layer chromatography, a comparatively inexpensive specific analysis procedure, has recently been reviewed (Striegel and Hill 1997). Erhardt and coworkers (1988) very briefly described a systematic instrumental analytical procedure that encompasses nearly all of the instrumental techniques currently widely utilized for binder identification. Microchemical tests and the major instrumental procedures all require scrapings (bulk samples) and cannot be utilized directly on cross sections.

Infrared spectrometry is a universal instrumental technique. Pigments, however, frequently interfere with results, and for the most part the technique is useful for general rather than specific identification in paint samples. Fourier-transform infrared (FT-IR) microscope systems, which are becoming increasingly common, can provide information on extremely small samples (Derrick, Landry, and Stulik 1991), generally

much smaller than those that can be analyzed by the other common instrumental techniques.

Another universal instrumental approach couples pyrolysis, a sample preparation technique, with gas chromatography (Py-GC). Pyrolysis involves heating a paint sample to a high temperature, causing the organic binder to break down into smaller volatile fragments. The pyrolytic products are then separated in a gas chromatograph. Pigments do not seem to interfere with the results, and, to some extent, specific media identifications can be carried out by this technique. Shedrinsky and coworkers (1989) recently reviewed applications of pyrolysis–gas chromatography to art and archaeological materials.

Plant gums and proteinaceous media are natural polymers that can be chemically broken down into their fundamental building blocks (monomers). In the case of gums, the monomers are monosaccharides and acids derived from some of these monosaccharides (uronic acids); in the case of proteins, the monomers are amino acids. Separation of these monomers along with at least some quantitation of the different types of monomers can provide very specific information on binder type. Analysis is usually carried out by a chromatography technique: these range from thin-layer chromatography, already mentioned, to the more expensive instrumental procedures, such as gas chromatography, high-performance liquid chromatography (HPLC), and tandem techniques such as gas chromatography–mass spectrometry. Chromatography procedures are not universal but can provide the most specific identifications of any of the routinely applied binder identification techniques.

Aged drying-oil films are also polymeric in nature (see Erhardt, herein). Unlike the gums and proteins, dried oil films cannot be broken down into their original monomeric units, but they can be at least partially broken down into smaller fragments that are useful for identification purposes. GC and GC-MS are the standard techniques for the analysis of these fragments. This type of analysis is the only current method by which specific identifications of different types of drying oils is possible.

Gas chromatography and, better yet, GC-MS are also the current techniques of choice for specific identification of plant resins, which typically consist of mixtures of a number of different compounds. In many instances, these compounds differ enough from one resin to another to allow for separation and specific identification of resin types.

The most widely utilized procedure for identification of binders in cross sections is biological staining. Applications, for the most part, focus on determination of the presence of proteins and lipids (drying or other oils, fats, etc.), although some specific identification is possible. Some stains can be viewed under visible light (Johnson and Packard 1971; Martin 1977); others need to be viewed with a microscope that has an epifluorescence attachment (Wolbers and Landrey 1987). Stains can also be applied in certain cases for the confirmation of the presence of other materials, such as carbohydrates and resins.

Fourier-transform infrared microspectrometry, already mentioned as a technique that can be applied to scrapings of paint (or bulk samples), can also be applied on cross sections (Derrick, Landry, and Stulik 1991). The least ambiguous results, using both staining and infrared analysis, are obtained on thin sections, which are sliced from cross sections with a microtome.

Cautions on identifications

Modern analytical techniques in some cases are so sensitive that it is now possible to identify small amounts of organic residues in samples taken from artifacts. This makes possible a wealth of information that was not previously obtainable, but it also may open the door to misinterpretation. Of particular concern in the study of samples from artifacts are previous restorations or treatments. Consolidation of paint or repeated cleanings and applications of varnishes can introduce many types of organic materials into paint films while potentially removing some of the original organic components or accelerating their deterioration. Obviously, if added components are of an altogether different chemical nature than the original components, careful analysis could distinguish original material from these additions. However, many materials used, particularly in past decades, were of natural origin and include many of the materials discussed in this chapter. Treatment with a gelatin solution of an artifact painted with glue-bound paints would make analysis of the original binder impossible—even with current instrumental analytical procedures—because an old glue cannot be distinguished from a glue of recent origin. Treatment of a polychromed wooden object with wax would preclude any possibility of identifying wax as an original component of the binding medium, unless the wax were of a modern type with a different chemical structure than the type or types that would have been available when the object was painted.

Codes of ethics of modern art conservation usually state that any organic material introduced onto an old painted surface should be of an altogether different composition than that of the original organic components, so as not to make future analysis problematic. However, even some widely utilized modern synthetic materials could potentially cause problems. For example, cellulose ethers are currently used to consolidate fragile paint. Hydrolysis of such a material would yield glucose. While it is not a component of plant gums, glucose can occur in some carbohydrate-containing binders, and the introduction of this carbohydrate by a treatment would make the original presence of glucose impossible to ascertain. Many such scenarios could be given; the important point is that results of analyses must be interpreted with caution.

The ideal approach would be to characterize the original materials as completely as possible before treatment. It is also advised that one take into account the binders most likely to be present in the paint film when choosing a consolidation material and adhesives for a given treatment.

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Microscopic Examination and Analysis of the Structure and Composition of Paint and Varnish Layers

James S. Martin

Paint and varnish often are applied individually or together to create decorative and protective coatings on wood surfaces. Paint consists of a film-forming component called a *binder* and one or more organic or inorganic colorants called *pigment.* Varnish is an organic protective coating that does not contain a colorant. Paint binders and varnishes are often composed of similar materials, such as drying oils, proteins, natural and synthetic resins, gums, or waxes. The composition and purity of paints and varnishes have varied through history as commerce, trade, and technology have provided artists and artisans with new materials. The composition of these materials, their manner of application, and the ways in which they have altered and degraded have a very practical bearing on the conservation, interpretation, and authentication of historic and artistic works of which they are a part.

Microscopy permits one to observe the structure of layers (stratigraphic analysis) and the solubility and melting point of specific layers. Microscopy also allows one to determine the elemental composition of microscopic samples (elemental analysis) and to identify the chemical groups formed by these elements (chemical analysis). Elemental and chemical analysis may involve microchemical reactions between a sample and a reagent (chemical microscopy) or use of an instrument to detect the absorption or emission of electromagnetic radiation by a sample (spectroscopy).

Samples

Samples from painted and varnished wood may take different forms—flakes, particles, or scrapings. To facilitate discussion, samples used for microscopic analysis can be divided into two general categories: layered samples and particle samples (Fig. 1). Layered samples contain one or more complete layers, while particle samples contain only a portion of a particular layer. Layered samples are used to study the number, sequence, condition, and interaction of layers. Both layered and particle samples are used to study the solubility, melting point, or composition of specific layers.

Samples are taken with the expectation that the information derived from analysis will be representative of the area sampled, if not the object itself. This is a rather tall order for microscopic samples. Reedy and Reedy (1988:14–16) describe theoretical approaches to sampling that have a statistical bearing on the likelihood of obtaining samples that are representative. A review of documentary records, thorough surface examination,

Figure 1
Idealized schematic representation of a
painted and varnished surface (A); B = a lay-
ered sample, C = thin-section samples, and
D = particle samples.
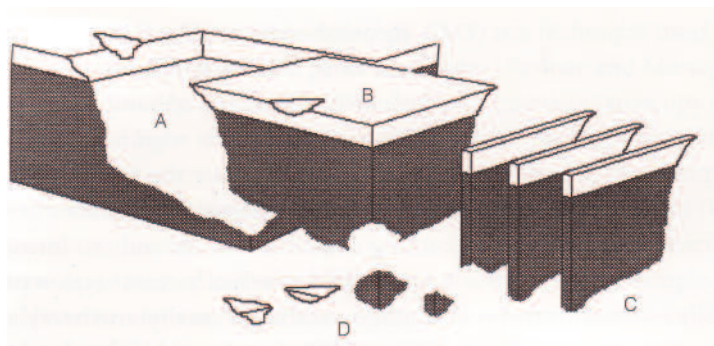
and a detailed sample record are helpful in obtaining representative sam-
ples, and in interpreting the results.

So-called surface examination techniques are used to determine
the areal distribution of materials, and the characteristics that may help to
narrow the initial investigation and confirm or support analytical results.
Color, opacity, discoloration, fading, surface reflectance, texture, and layer
continuity each reflect the ability of a paint or varnish to form and main-
tain a continuous film or to resist environment-induced alteration.
Fluorescence under ultraviolet light is characteristic for a small number of
pigments, including cadmium colors, Indian yellow, natural madder, and
zinc white (De la Rie 1986). While visual inspection of binder and varnish
fluorescence is not indicative of particular materials, surface fluorescence
may reveal the distribution of paints, varnishes, restoration, and grime.
Infrared vidicon systems (van Asperen de Boer 1986) and infrared photog-
raphy (Hoeniger 1991) are commonly used to study infrared-absorbing
underdrawing, and some researchers have reported success in differentiating
between similarly colored paint films that are composed of different pig-
ments. X-radiography (Van Schoute and Verougstraete-Marcq 1986) is
used to study the composite structure of objects and the distribution of
X-ray-absorbing materials, such as heavy metal pigments, metals, fabrics,
and wood supports. X-ray fluorescence spectrometry (XRF) is an instru-
mental technique for noninvasive point analysis of elemental composition
(Hanson 1970); however, instrumentation is very costly and the technique
is not widely available.

The amount of sample required for microscopic analysis is very
small. The literature commonly reports sizes in the range of 0.1–0.5 mm^3
for layered samples, while particle samples rarely exceed 0.1 mm^3 and fre-
quently are much smaller. In practice, sample sizes are governed less by
arbitrary measurement than by more practical constraints imposed by
the object's size and condition, the location of sample sites, and whether
samples might be returned following analysis. A variety of tools may be
used to remove layered samples—for example, pointed scalpel blades,
tungsten probes, forceps, and hypodermic needles. Particle samples,
being much smaller, may be scraped from the surface of an exposed layer
using a scalpel or probe, or collected as fragments from thin sections.
Contamination and alteration may interfere with analysis or render sam-
ples unusable; therefore, they should be handled only with clean tools,
stored in inert containers, and protected from extreme heat and light.

Sample preparation is an integral part of the analytical process
and is tailored to the sample and the microscopic technique used. Particle
samples are usually crushed and separated for analysis of component par-
ticles, and are often called *dispersed samples*. Layered samples are often cut

or polished to reveal a flat, planar cross section for examination and analysis; thus, layered samples are frequently called *cross sections* or *cross-section samples.* Most layered samples are so small or fragile that mounting in or to a solid matrix is required so they may be handled for sectioning and examination. Since the 1950s, layered samples typically have been prepared by placing a sample on a platform of hardened polyester resin and covering it with additional resin to form a solid block that is then ground and polished to reveal a cross-section plane (Plesters 1956); earlier techniques used paraffin or methyl methacrylate resin (Laurie 1914:18–24; Gettens 1940). The sectioned block is leveled on a piece of wax or clay and examined using reflected visible and epifluorescence illumination. Derrick and coworkers (1994) describe a wider range of embedding media used in conservation and in forensic and biomedical applications (polyester, epoxy, acrylics, cyanoacrylates, gelatin, wax, hot-melt adhesives, and silicones), and Pilc and White (1995) describe the use of silver chloride for embedding samples prior to thin-sectioning for infrared microscopy. Cross-section samples may be cut by microtome to yield numerous thin sections (Martin 1991; Gettens 1936; Tsang and Cunningham 1991; Malis and Steele 1990), or they may be polished on opposite sides to yield a single thin section (Garrido and Cabrera 1986). A thickness of 5–50 μm is commonly reported for thin sections in the conservation literature. A nontraditional approach to the preparation and examination of layered samples is presented in the appendix to this chapter.

Microscopic Techniques

The human eye has an average resolving power of about 0.1 mm, and thus is incapable of distinguishing most paint and varnish layers, let alone individual pigment particles. Light (photon) microscopes and electron microscopes provide the magnification and resolution required to inspect and analyze samples.

Compound light microscopes are one of several light microscopes that form enlarged color images using glass or reflecting lenses and the near ultraviolet or visible regions of the electromagnetic spectrum. The maximum useful magnification obtained with compound light microscopes is about ×1000 with a resolution of approximately 0.2 μm (0.0002 mm). Compound light microscopes can be equipped with a wide variety of reflected and transmitted illumination sources, objectives, and filters. These variations permit examination of individual layers and their component particles, determination of solubility and melting point, and analysis of optical properties and elemental and chemical composition. Compound light microscopes are used for two techniques that are fundamental to the microscopic analysis of paint and varnish: polarized light microscopy (PLM) and fluorescence microscopy (FM). Polarized light microscopy is used to characterize and identify particle samples (Fig. 2) and fiber samples, based on their absorption or refraction of polarized light (Slayter and Slayter 1992; McCrone and Delly 1978). Fluorescence microscopy is used to differentiate materials based on their primary fluorescence, or on the secondary fluorescence of fluorochromes used to mark them (Birk 1984). Other techniques use special optics to enhance contrast in samples (Hemsley 1989; Hoffman 1989) or use spectrophotometers to measure visible reflectance and fluorescence (Larson, Shin, and Zink 1991); these techniques are not used commonly in the art conservation field and will not be described in this chapter.
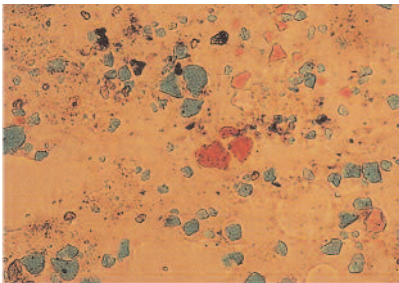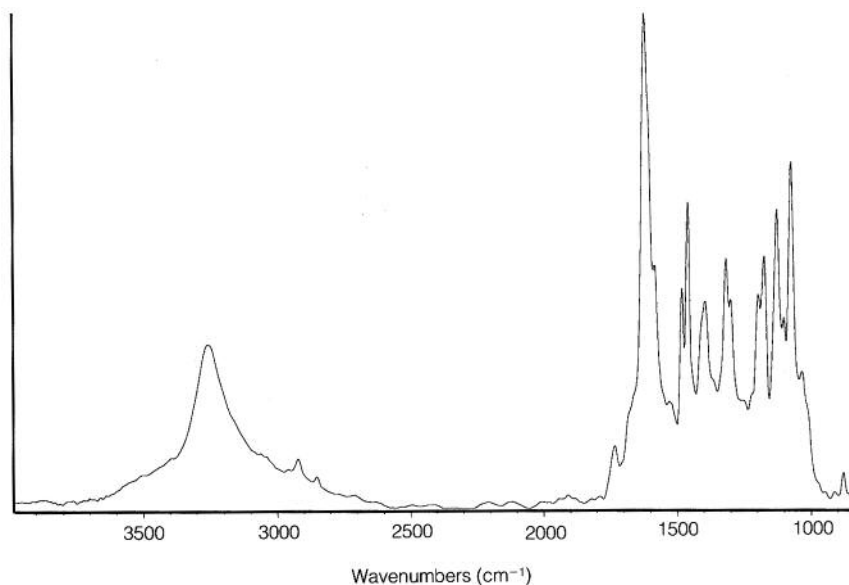

Figure 2
Photomicrograph of a particle sample of paint dispersed in Cargille meltmount 1.662. The sample consists of viridian, red iron oxide, madder lake, yellow ochre, and lead white. The sample was photographed using transmitted plane-polarized illumination and a ×40 objective.

Infrared microspectroscopy (IMS) is a technique used for molecular analysis of layered and particle samples (Reffner and Martoglio 1995; Derrick, Landry, and Stulik 1991). Infrared microspectroscopy couples a compound light microscope with an infrared spectrometer. The compound light microscope is used to position a portion of a sample in an infrared beam that originates in a Fourier-transform infrared (FT-IR) spectrometer; hence, the technique is sometimes called FT-IR microspectroscopy. Infrared radiation that is not absorbed by the sample is passed to a detector and converted into a graphical representation—called a spectrum—of the sample's absorbance (Fig. 3). The spectrum may be used to determine the purity, degradation, and composition of the sample. When two or more materials are present in a sample—for example, pigments and a binder, or a varnish mixture—the spectrum represents data for all materials combined, complicating interpretation. Mixtures may be separated before analysis using chromatography or extraction, and spectra may be processed by computers to subtract the absorbance of one or more materials. Little or no sample preparation is required for infrared microspectroscopy, and the sample is neither consumed nor chemically altered in analysis; thus, it can be used for further analysis. Depending on opacity and layer thickness, samples may be analyzed in transmittance or reflectance modes. Transmittance spectroscopy is the method used most commonly for particle and thin-section samples. Transparent coatings on reflective surfaces, such as metal or metal leaf, might be analyzed using reflection/absorption spectroscopy. Opaque samples and surface layers may be analyzed using one of several reflectance techniques, including attenuated total internal reflection (ATR) (Harrick 1967).

Scanning electron microscopy (SEM) is a technique used for topographical examination and analysis of elemental surface composition (Slayter and Slayter 1992). The scanning electron microscope uses a beam of electrons and electromagnetic lenses to form enlarged, monochromatic images of specimens. The maximum useful magnification of these images is around ×20,000 with a resolution of about 10 nm (0.01 μm)—a significant increase over compound light microscopes. So-called backscatter images are formed by electrons that are reflected, or backscattered, from the sample surface. Secondary electron images are formed by electrons

Figure 3
Infrared absorbance spectrum of the organic pigment indigo. The frequency (X axis) and intensity (Y axis) of absorption peaks are characteristic of the molecular structure of the material and are used to study changes in composition, purity, and degradation.
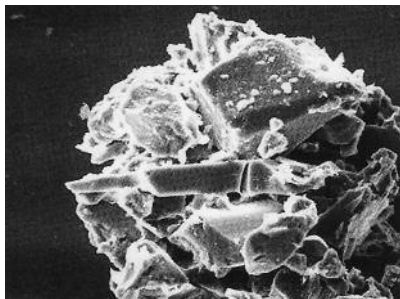
Figure 4
A scanning electron micrograph of the pigment smalt, imaged using secondary electrons. The sample is from an eighteenth-century polychrome sculpture. Smalt was made by adding cobalt oxide to molten glass, which was cooled and ground into fine particles. The micrograph reveals a cluster of these particles and associated paint binder. X rays emitted from the sample indicate that the pigment is composed of silicon, potassium, and cobalt.

that are emitted from the sample following an inelastic collision with the electron beam. Both types of images convey surface topography (Fig. 4). Backscatter images may also convey compositional differences within samples. Most scanning electron microscopes are equipped with one or more X-ray spectrometers that detect X rays emitted when the electron beam interacts with a sample's surface. The frequencies of these X rays are characteristic of the elements composing the area of interaction. Thus, SEMs equipped with X-ray spectrometers may be used for analysis of the elemental composition of layers or specific particles within layers. Two types of X-ray spectrometers are used: energy-dispersive spectrometers (EDS) and wavelength-dispersive spectrometers (WDS). Each technique provides a spectrum of X-ray frequencies that is used to identify constituent elements; the WDS detector also provides a map of the distribution of single elements. In a related technique called electron microprobe analysis (EMPA), an X-ray spectrometer is coupled with a compound light microscope. Both layered and particle samples may be analyzed using SEM. Samples generally are made conductive by mounting them to a support made of aluminum, carbon, or beryllium and coating them with a thin layer of carbon, gold, gold-palladium, aluminum, or chromium (new high-pressure environmental SEMs do not require this sample preparation). Some thermal decomposition may result from interaction with the electron beam, but samples can often be retrieved for further analysis.

Applications

Many applications arise from simple microscopic inspection of layers and individual particles: stratigraphic analysis, study of finish history, evaluation of the progress of surface-related treatments, and determination of solubility and melting point. Microchemical and microspectroscopic techniques may be used to characterize sample composition. These applications are often complementary and interdependent. For example, stratigraphic analysis aids in identifying a particular layer within a layered structure for analysis, while composition study aids in comparing two or more layers from the same or different samples.

Stratigraphic analysis

Layered samples are used most commonly for stratigraphic analysis and for three practical applications: (1) study of finish history, (2) evaluation of the progress of surface-related treatments, and (3) determination of solubility and melting point. The compound light microscope is the primary tool for stratigraphic analysis. Comparative examination of two or more samples, and multiple sectional planes within a single sample, helps to ensure that anomalies in a single sample do not result in erroneous conclusions. Individual layers may be differentiated by their color, fluorescence, reflectance, texture, opacity, pigmentation, and evidence of prolonged exposure and physical alteration (Fig. 5). Observations made on multiple samples, or on successively exposed cross sections of single samples, may be used collectively to sort out the number and sequence of layers, their thickness and continuity, their condition, how they have physically interacted and altered, and the distribution of particles such as pigments and grime. Layers may be further distinguished by their optical properties, solubility, melting point, and composition.
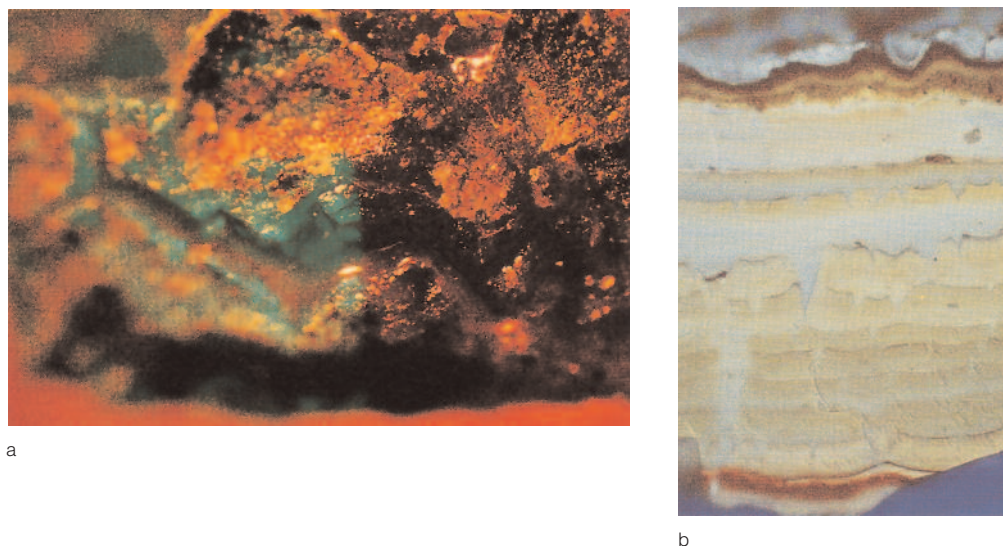
a

b

Figure 5a, b
Photomicrographs of a layered sample from a painted and varnished Concord coach. The top surface of the sample (a) is photographed in simultaneous oblique visible illumination and epifluorescence illumination (left half) and oblique visible illumination (right half), using a ×4 objective; and a cross section of the sample (b) is photographed in epifluorescence illumination, using a ×10 objective. Discolored varnish layers that are indistinguishable in visible illumination are readily distinguished in epifluorescence illumination, permitting study of layer thickness and weathering, and deposition of grime.

Conservators, curators, and art historians often want to know what the original appearance of an object was, or how many times it has been painted or varnished. Paint and varnish layers are often applied in sets of multiple layers, so each layer observed in a cross-section sample is not necessarily a separate finish. Knowledge of how finishes were created and evidence of surface exposure can help in distinguishing the layers that compose separate finishes. So-called presentation surfaces often, but not always, exhibit surface weathering, fluorescence, deposition of debris or grime, fading of pigments, and infiltration by later layers. Stratigraphic and composition analyses might suggest or confirm the presence of an original finish, but a definitive determination requires thorough surface examination and an unequivocal finding that finishes have not been completely removed.

Examination of layered samples taken before and during treatment provides a means of evaluating the progress of surface-related treatments, such as the removal of degraded varnish or overpaint. Wolbers, Sterman, and Stavroudis (1990) describe the use of a compound light microscope and layered samples to monitor the selective removal of degraded surface varnishes on a fire-damaged, tall case clock. Carlyle, Townsend, and Hackney (1990) used a scanning electron microscope to study the effects of chelating agents on the surfaces of paint films in layered samples. Numerous other applications may be imagined in which layer-specific examination and elemental or molecular analysis would be useful—for example, evaluating the penetration of cleaning systems, varnishes, and consolidants.

Knowing how an object will react to solvent and heat is beneficial when planning and implementing a treatment procedure. When surface tests are ambiguous or fail to account for the behavior of subsurface layers, solubility of layered and particle samples may be tested using liquid solvent (or other cleaning systems) or solvent vapors. Tests on layered samples permit observation of the dissolution, swelling, and undercutting of layers, and quantification of this behavior as a function of time and dimensional change. Stolow (1957–58) describes a microscopic apparatus for measuring the dimensional change associated with swelling and dissolution. A particularly interesting application of solubility testing was described by Makes (1987), who determined the rate of enzymatic hydrolysis of coating layers

in cross-section samples. Melting point may be determined on thin sections and particle samples using a melting point apparatus, a microscope hot stage, or epifluorescence illumination (Martin 1992), the last of which can induce sample-plane temperatures above 49 °C.

Composition study

Composition studies involve the characterization or identification of a material such as a pigment, binder, or varnish. The characterization process may involve examination of visual features, as well as analysis of optical and physical properties, elemental and molecular composition, and atomic structure. Identification is made by comparing features or properties of a sample with those of known materials. Identification may be complicated or even prevented by the presence of complex mixtures or by contamination from restoration or conservation treatments. Some studies are focused only on the primary components of a sample, while others may involve analysis of trace components.

Pigments

The conservation literature pertaining to the microscopic identification of pigments commonly used in artists' paints is expansive. Feller (1985) and Roy (1993) provide in-depth descriptions of the composition of many important traditional artists' pigments and their identification using microscopic and instrumental techniques. Definitive identification of pigments principally involves the use of polarized light microscopy; one or more additional techniques are often used for confirmation. Sometimes analysis of atomic structure using X-ray diffraction spectrometry (XRD), a nonmicroscopic technique, is used for confirmation. One sample of approximately 0.1 mm³, or 1 μg of paint, is more than sufficient for analysis of pigments using polarized light microscopy, fluorescence microscopy, infrared microspectroscopy, scanning electron microscopy, and X-ray diffraction spectrometry.

Many traditional artists' pigments may be identified, or eliminated from consideration, through the use of polarized light microscopy. Particle samples usually are dispersed on a glass slide in a medium that reduces light scatter and that has a known refractive index, thus providing a reference for measurement of the refractive index. After visually distinguishing particles by color, particles can be characterized based on physical properties, such as size and shape, and on optical properties, including refractive index, pleochroism, birefringence, and extinction. Fluorescence illumination is useful for distinguishing the presence of occasional fluorescent pigments and flakes of binder and varnish in samples. Most traditional artists' pigments exhibit a unique set of optical properties, permitting their identification using only polarized light microscopy. When unique optical properties are not observed, particular elements or chemical groups of which the pigment is composed can be identified using microchemical tests and the compound light microscope. Microchemical tests are very sensitive and may be applied to single particles, small clusters of particles, or layered samples. McCrone (1982) describes a broad range of optical, microchemical, and instrumental techniques for identification of traditional artists' pigments, including the use of a hot stage. Gettens and Stout (1936), Plesters (1956), and Masschelein-Kleiner (1986) describe a range of microchemical tests to confirm the presence of pigments in layered

samples. Modern organic pigments are more difficult to identify using polarized light microscopy because they lack highly distinctive optical features. Vesce (1942) and McCrone (1982)[1] describe the use of recrystallization and sublimation techniques for their identification.

Infrared microspectroscopy complements polarized light microscopy by providing information on the molecular composition of specific particles and particle aggregates. Numerous pigments have unique infrared spectra, including carbonates, chromates, oxides, silicates, sulfates, the phosphate pigment ivory black, and the nitrile pigment Prussian blue. Many traditional organic pigments—such as indigo and gamboge—and modern dyes, which are difficult to identify by polarized light microscopy, are readily identified using infrared microspectroscopy. Less than 1 µg of sample is required, and analysis is nondestructive, so samples may be used for further analysis.

Scanning electron microscopes equipped with an X-ray spectrometer, as well as electron microprobe analyzers, are used primarily to identify the elemental composition of pigments in particle or layered samples. The range of elements detected depends on the spectrometer used; most X-ray spectrometers detect elements with atomic number 11 (sodium) and above, while others detect atomic number 5 (boron) and above. The secondary use of SEM is for examination of the morphology (shape and texture) of pigments.

Binders and varnishes

Identification of natural paint binders and varnishes in aged samples often proves challenging because these materials lack highly characteristic optical properties, vary in purity, and are especially prone to degradation. Further, binders usually constitute only a minor proportion of paint films and often must be separated from pigment for analysis. Microscopic identification of paint binders and varnishes currently requires characterization of molecular composition using infrared microspectroscopy. Erhardt and coworkers (1988) and Pilc and White (1995) describe systematic approaches for classification of natural coatings and binding media (e.g., oil) using infrared microspectroscopy, followed by identification of specific materials (e.g., linseed oil) using gas chromatography. Derrick and coworkers (1992) and Derrick (1989) describe the layer-specific identification of shellac, copal, sandarac, mastic, and rosin in thin-section samples from coated furniture, using infrared microspectroscopy. Kühn (1960) describes similar specificity in identifying waxes, and infrared analysis of other paint binders, such as oil and egg, have been described in the literature (Van't Hul-Ehrnreich 1970; Meilunas, Bentsen, and Steinberg 1990). Synthetic paint binders and varnishes are readily classified to type and material by infrared microspectroscopy (Lomox and Fisher 1990).

Before infrared microspectroscopy became a practical tool for analysis in the early 1980s, the molecular composition of microscopic samples of binders and varnishes could not be readily determined. Binders and varnishes were characterized by their physical and chemical properties using compound light microscopes and a variety of solubility and melting point tests, as well as microchemical reactions and stains. Caution has to be exercised when interpreting and presenting the results obtained with these techniques; staining techniques, in particular, rely on subjective visual appraisals of color change and are prone to misinterpretation. Gettens and Stout (1936), Plesters (1956), and Mills and White (1994)

review the principal techniques for microscopic analysis of binders and varnishes at different times during this century. Masschelein-Kleiner and coworkers describe a systematic approach for analysis of binding media in cross section, thin section, and particle samples (Masschelein-Kleiner, Heylen, and Tricot-Marckx 1968; Masschelein-Kleiner 1986). Some of these tests involve simple solubility in water, organic solvents, or acids and alkalis. Other tests involve determination of melting point or a specific element, such as nitrogen or phosphorous. Microscopic staining techniques have been used to distinguish between oil and protein binders since the early part of this century; more recently, staining techniques have been proposed for detection of natural resins and carbohydrates. Stains are often used to enhance contrast in synthetic polymers for microscopic examination, but no staining techniques exist for their identification. Ostwald (1935), Gettens (1935), Plesters (1956), Gay (1978), Johnson and Packard (1971), and Masschelein-Kleiner (1986) describe the use of stains that are viewed in visible light. Johnson and Packard (1971), Talbott (1982), Wolbers and Landrey (1987), and Messinger (1992) describe fluorescent staining techniques.

Practical Approaches

Thus far, this article has described several types of samples and microscopic techniques used in the examination and analysis of paint and varnish layers, as well as common applications. This final section describes a practical approach used for analysis of stratigraphy, pigments, binders, and varnishes on a carved bedstead from the collection of Agecroft Hall.

Examination and analysis of the Burderop Park bedstead

Elsewhere in this volume, Elizabeth Howard Schmidt describes the recent art historical and technical investigation of the Burderop Park bedstead at Agecroft Hall. The primary objective of the technical investigation was to determine the finish history of the bedstead and the composition of select layers. Howard Schmidt describes her interpretation of the results obtained by microscopic examination and analysis. Seven layered samples, a painted wooden plug from a bed rail, and a section of carved and decorated molding were studied. Three microscopes were used for the technical study: (1) a compound light microscope equipped for individual or simultaneous oblique visible, epifluorescence, and transmitted polarized illumination; (2) an infrared microscope; and (3) a scanning electron microscope equipped with an energy-dispersive spectrometer.

The wooden plug and molding were placed directly on the stage of the compound light microscope for examination using oblique visible and epifluorescence illumination. By focusing up and down along the edges of paint loss and abrasion, the layers observed in the cross-section samples could be distinguished by their color, fluorescence, reflectance, and thickness (Fig. 6). This permitted layer-specific particle samples to be taken from the plug and the molding instead of the layered samples, which would have required thin-sectioning with a microtome.

The earliest extant layer observed was an amber-colored, fluorescent coating (B in Fig. 6). In cross-section samples, the coating appeared discontinuous and was too thin to be sampled for composition study. On the molding, the layer was observed at areas of paint loss, beneath several lifting flakes of paint, and on the underside of a detached
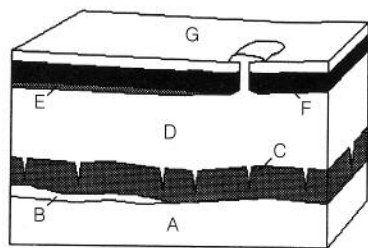

Figure 6

Idealized schematic representation of paint and varnish layers observed in layered samples and on a molding section from the Burderop Park bedstead, Agecroft Hall: A = carved wood substrate, B = discontinuous amber-colored coating, C = fissured red paint layer, D = buff priming and paint layer, E = red graining layer, F = polychrome layers, and G = surface varnish.

flake. The layer was absent from the wooden plug. A series of hardness and solubility tests performed directly on the molding indicated that the coating was extremely brittle and immediately soluble in acetone. These properties usually are associated with, but not necessarily indicative of, natural resins. Solubility testing also provided important practical information that indicated that similar polar solvents could not be used for the conservation treatment. Solvent was wicked beneath the surrounding paint layers, leaving the layers mobile atop the fluid coating; after one hour, the coating remained sufficiently fluid that slight pressure caused it to erupt from cracks several millimeters away.

For characterization, a microgram sample of the powdered coating was removed with a metal probe from a protected area under a lifting paint flake. The sample was transferred directly to a diamond cell used for infrared microspectroscopy. Examination of the sample with the compound light microscope, using epifluorescence and transmitted polarized light, revealed uniform color and fluorescence, and scattered wood fibers within the sample. The diamond cell was transferred to the infrared microscope, and an area of the sample that was void of wood fibers was isolated for transmitted infrared analysis. The infrared spectrum of the sample indicated the presence of a natural resin and was matched with reference spectra for pine resin (Fig. 7). Samples of the wood surface and the red paint layer were analyzed in a similar manner to verify that the coating sample had not been contaminated. Infrared analysis of the wood revealed a mixture that included cellulose (wood fibers). Spectral subtraction of cellulose from the spectrum yielded a *difference spectrum* that compared favorably with pine resin (Fig. 7).

Infrared analysis of the red paint sample revealed the presence of a protein binder and lead white pigment (Fig. 8). A portion of the red paint sample was then dispersed on a glass slide and covered with a mounting medium and cover glass. Analysis using polarized light microscopy confirmed the presence of lead white pigment and indicated the presence of

Figure 7
Partial infrared absorbance spectra of a sample of the first varnish layer from the Burderop Park bedstead (top); one reference sample of pine resin (middle); and the wood surface after spectral subtraction of cellulose (bottom), showing the presence of pine resin.
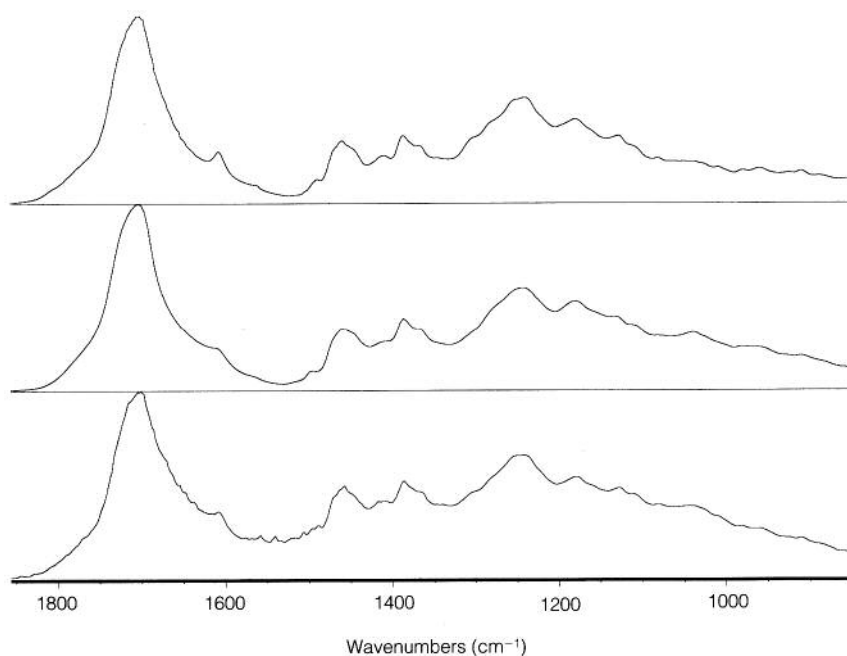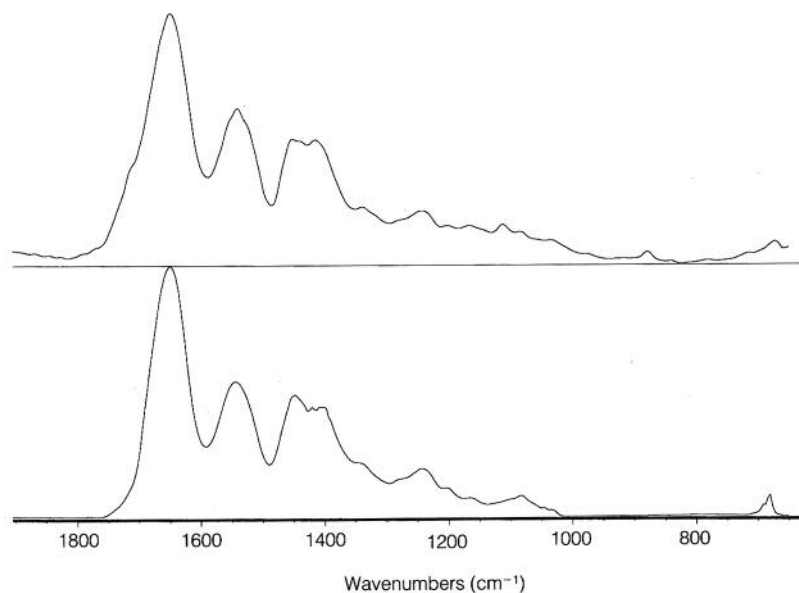
Wavenumbers (cm⁻¹)

Figure 8
Partial infrared absorbance spectra of the first red paint layer from the Burderop Park bedstead (top) and a reference sample of animal glue and lead white pigment (bottom).

red iron oxide pigment. Another portion of the sample was mounted to an aluminum stub, coated with carbon, and analyzed using a scanning electron microscope equipped with an energy-dispersive spectrometer (SEM-EDS), which provided rapid determination of the elemental composition of the paint and confirmed the presence of lead and iron in the sample. In the absence of SEM-EDS, these elements could have been confirmed using a microchemical test for Pb^{2+} and Fe^{2+} ions, respectively. Severe surface fissuring in cross-section samples and cracking and cupping in the molding sample provided evidence that the red paint layer had weathered as a presentation surface before application of the buff-colored paint.

Surface examination also revealed that the buff paint was used beneath each of the polychrome layers and as one of the polychrome colors. Analysis of the buff paint layer revealed the presence of an oil binder, lead white pigment, and a minor amount of red iron oxide pigment. Raking visible light accentuated the surface relief of the molding and revealed that the buff paint layer had migrated to the surface through cracks in the subsequently applied polychrome layers and surface varnish, suggesting that these layers were probably contemporaneously applied as a single finish set. Solubility testing of the surface varnish revealed that it was slowly gelled without dissolution on application of acetone or ethanol. Incident pressure with a metal probe caused the varnish to chip, indicating greater cohesive strength than the amber-colored varnish, which powdered. Infrared analysis revealed the varnish to be a different natural tree resin, possibly copal.

Microscopic examination and analyses indicated the presence of three separate finishes. The first finish consists of pine resin. The second finish consists of lead white and red iron oxide in a protein binder. The third and present finish consists of a buff-colored priming-polychrome layer, a red graining layer, various polychrome layers, and a natural resin varnish.

Conclusions

Since the early 1900s, light microscopy has been the primary tool for examination of the layers constituting painted and coated surfaces, as well

as characterization of component materials. In recent years, electron microscopes have increased the useful magnification and resolution of microscopic images, and spectrometers have been coupled with both compound and electron microscopes to permit rapid analysis of elemental and molecular composition. These techniques permit a wide range of applications that are used by conservators, curators, and art historians in their work to conserve, interpret, and authenticate historic and artistic works. Ongoing developments in digital imaging, optics, and spectroscopy will undoubtedly have a profound impact on the design and use of microscopes in the next century.
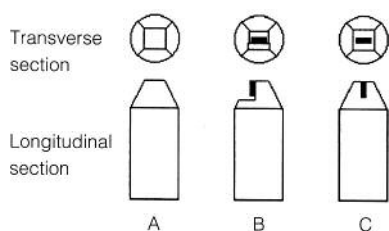
Appendix

Figure 9
Schematic representation of a blank capsule (A), a capsule with a shelf-mounted sample (B), and a slot-mounted capsule (C).
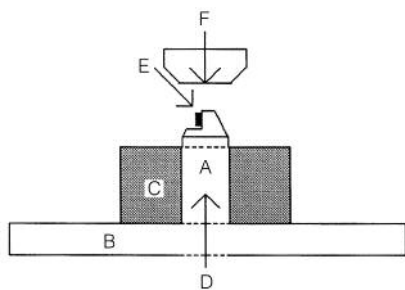
Figure 10
Schematic representation of a capsule-mounted sample (A), being held on a microscope stage (B) with a capsule chuck (C), permitting individual or simultaneous illumination using transmitted polarized light (D), oblique visible light (E), and epifluorescence light (F).

A Nontraditional Approach to the Preparation and Examination of Layered Samples

A nontraditional approach to preparation of layered samples was developed and is used at the Williamstown Center. This approach uses lifting or detached flakes as temporary samples, when possible, for stratigraphic analysis and for provision of subsurface particle samples. If the flake presents a smooth planar cross section, it can be positioned on a tacky adhesive (for example, acrylic resin, poly[ethylene/vinyl acetate] resin, cellulose ether, or wax) and examined with a compound light microscope or a scanning electron microscope. Flakes that do not present a smooth edge may be mounted to a plastic block using a similar adhesive, or held in a spring-loaded microvise, so an edge of the sample can be microtomed to yield a smooth cross-sectional plane. Following examination, the flake may be returned to its source with minimal alteration, using the mounting adhesive as a consolidant. Provided that the flake comes from a representative area, such samples are ideal for use in comparative finish history and evaluation of the progress of surface-related treatment.

A modified capsule-embedding technique for mounting, sectioning, and examining of other layered samples is described in the literature (Martin 1991). Using either an insoluble or a soluble polymer, samples are mounted to a shelf cut into the tip of a capsule block that was cast from a tapered mold (Fig. 9). The top and edges of the sample are left exposed to permit comparative examination with the prepared cross-section edge or the removal of particle samples for composition study. Because the sample is positioned at the tip of the capsule, only a very small amount of material is removed to expose a cross-section plane. The capsule mount is placed in a simple homemade chuck that registers the sample perpendicular to an abrasive sheet, microtome knife, or microscope stage (Fig. 10). Since no leveling medium is used, cross-section samples may be illuminated with transmitted polarized light to observe the presence of birefringent particles in transparent coating layers around the perimeter of the sample. If complete embedment is required for sectioning, additional medium is added to cover the sample. The capsule mounts may be stored in commercially available boxes. This approach has been adopted by many conservation labs and is easily tailored to individual working techniques.

Note

1   Please note errata in McCrone 1982: refractive indexes were transposed for the isotropic blue pigments in Figure 7, and terre verte and verdigris in Figure 8.

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