WHERE HAS ALL THE GOOD STUFF GONE?

Tracking Wood Preservatives and Coatings via Microscopy

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Introduction. We have joined here today to explore together the many technical aspects of wood protection. In doing so, there is a presumed recognition and appreciation of the desirable properties of wood, a biologically produced renewable material. Among these are strength-to-weight ratio, machinability, relative cost, aesthetic beauty and convertability into a wide range of products.

On the other hand, some of the undesirable features of wood form the basis for the existence of an organization such as yours. Wood/water relationships affect virtually all of the properties of this remarkable material. Users of wood must know the realities of shrinkage and swelling, of susceptibility to decay and to fire. We are therefore concerned with methods of stabilizing wood dimensionally; with drying it while minimizing defects; with introducing appropriate chemicals to help prevent attack by fungal enzymes, bacterial enzymes, insects and marine borers; and also with beautifying wood with protective coatings that retard moisture adsorption and desorption. In addition, building codes may require that some protection against fire be provided by chemical impregnation or coatings. Clearly, the challenges are great in the wood protection industry and the technical background needed to cope with this broad spectrum of scientific areas ranges from wood chemistry, wood physics, biology including mycology and entomology, chemical engineering, timber engineering, and wood anatomy and ultrastructure. The average consumer of wood products has no realization of the

complexity of the problems we face in this field.

In the brief time allotted to me today, I want to address the critical role of wood anatomy and ultrastructure in the wood protection effort. In fact, all wood properties and behavior are affected by wood structure, but for the moment I will restrict the discussion to pathways in wood that allow the movement of chemicals to sites of potential problems. A quick review of the structure of softwoods and hardwoods will be followed by "case studies" to help put this knowledge into context.

Wood Anatomy and Ultrastructure. There are two broad classes of wood, hardwoods (Angiosperms) which are produced by broadleaved trees and softwoods (Gymnosperms) that are the biological products of conifers, mostly but not exclusively with needle-like leaves. The terminology is often confusing because we all know that some "softwoods" are very hard while some "hardwoods" are quite soft. The main point here is that the wood anatomy of these two groups is quite different.

The wood of softwoods consists of only one major cell type oriented longitudinally, that is, along the grain. This is the long, slender element, 3 to 5 mm. in length, called the tracheid. In hardwoods the longitudinal cells may be vessel elements, fibers, fiber-tracheids and other specialized types. Both categories have wood rays running radially from the pith or center of the tree stem to and through the bark. These are made up largely of parenchyma cells, often brick-shaped and assembled in ribbon-like bands.

Softwoods can contain longitudinal and horizonal resin canals, but not all coniferous woods have them. There are none in hardwoods. The key difference between the two

categories of wood is the longitudinal conductive tissue -- tracheids in softwoods and vessels in hardwoods. While there are many other detailed differences, for purposes of this discussion, pathways for liquid penetration are the main concern.

Referring to a few illustrations of these structural details may be useful. In Figure 1, the cross-section of a Douglas-fir log is used to help establish some basic definitions. Bark is the outer covering of a tree stem and while its character will vary greatly from species to species, it will be found on both softwoods and hardwoods. Growth increments or annual rings will also appear clearly on the cross-section or transverse surface. The nature of wood growth is obviously very different in the two broad groups of woods and this is well illustrated in Figures 2 and 3 which are scanning electron micrographs of small cubes of softwood and hardwood, respectively. The major differences in conductive tissue can be appreciated in these photos, but the wide range of tissue types in hardwoods would require a long series of micrographs to adequately demonstrate this feature. In softwoods there is much greater similarity of tissue types because only one longitudinal element is involved: the tracheid.

The major gross pathways for liquid movement through wood can be traced in these same figures, 2 and 3. Each softwood tracheid provides longitudinal conduction along the grain but it must involve lateral movement through connecting bordered pit pairs since the tracheid ends are closed. Therefore flow moves stepwise and requires that the bordered pit pairs are open between neighboring tracheids. In hardwoods the large vessels are made up of vessel elements which are open-ended and connected to form long tubular structures. On the transverse surface (X) of the hardwood the openings to the large vessels are often called

"pores". Note that the pores are surrounded by much smaller longitudinal elements in this example and in most hardwoods. Movement from the large to the smaller elements takes place through pit pairs. Both the coniferous and the hardwood pit membranes will be considered and illustrated later.

Other pathways are the rays which are shown in both the hardwoods and softwoods in Figures 2 and 3. Depending upon the species, these tissue systems can be very effective in conduction of preservative chemicals or other fluids. The resin canals shown in the softwood example have also been found to serve as channels for penetration provided that they are not plugged by dried or hardened resin.

Pit Membranes. One cannot discuss hydrodynamic fluid flow and diffusion in wood without emphasizing the role of pit membranes in the process. In conifers, bordered pit pairs have a closing membrane that has been studied for decades by every available type of microscopy. It remains the center of interest in preservative treatments and in coating applications because of its critical role. Figure 4 is a transmission electron micrograph of a bordered pit membrane in an ideal state for fluid movement from cell to cell. There are large openings between the cellulosic strands that support the central valve-like structure called the "torus". Unfortunately, the majority of bordered pit pairs in the heartwood are "aspirated", closing off the free movement of fluid from one tracheid to an adjacent one. Many of the pit pairs in sapwood are also aspirated, but since each tracheid has a large number of pits in its walls there are enough open passageways to afford penetration of much of the sapwood. Figure 5 is a scanning electron micrograph of Douglas-fir wood allowing a view into the lumens of several tracheids. One bordered pit pair is open to view and an aspirated or sealed pit membrane can be seen.

All of the other pit membranes in conifers (in the simple pit pairs and in the half-bordered pit pairs that connect ray parenchyma cells or longitudinal tracheids and ray parenchyma cells) lack openings that are visible even at the high resolution of electron microscopy. These membranes are essentially two layers of cellulose microfibrils, one from each of the adjoining cells, with an intercellular layer (middle lamella) sandwiched between them. It is very obvious that fluids move across such membranes, or trees could not exist. It must be largely by diffusion which suggests to wood preservers that this would be a desirable method to use except that it is slow and requires patience.

Hardwood pit membranes are all of this same type, having no visible openings. In Figure 6, a transmission electron micrograph of the primary wall in a hardwood, the outline of the pit aperture in the secondary wall is very clear. This is very similar to what can be found in most hardwoods and in the non-bordered pits in conifers.

The Cell Wall. The purpose of wood preservative treatments, and indeed of many coating systems, is to protect the wood substance; that is, the cellulose, hemicelluloses and lignin that make up the cell wall. Since these are vulnerable to attack by wood destroying fungi and insects, it is logical that the wood preservatives should penetrate the cell walls and provide protection by whatever specialized means is designed in the system.

The walls of wood cells are generally three-layered, much like plywood. Any of the layers can be attacked by enzymes from fungi or bacteria, the particular type of attack being characteristic for the organism involved. Fortunately, there are voids in the cell wall especially when some moisture is present to swell the microfibrils and other components apart.

In principle, water-borne chemicals are a better choice for treating wood since water was its natural environment in the living tree. Also, with its so-called "transient capillaries" when in the swollen condition, wood has micro-pathways in its cell walls and chemicals can be deposited effectively at the sites where biological attack can take place. In Figure 7, a transmission electron micrograph of tracheid cell walls in which silver salts have been deposited from solution, we have evidence of the porosity of walls. One can observe that the primary wall region near intercellular spaces appears to have a greater concentration of crystals and presumably, therefore, more openings than in the secondary walls. However, if this micrograph depicted a typical wood preservative, the walls would certainly be well protected.

Detecting Preservatives in Wood. From the above example we have one method of tracing the location of certain chemicals in wood. This approach has distinct limitations which must be recognized. The materials must be electron-dense enough to scatter the electron beam and make it possible to image them. Pentachlorophenol crystals, when this system was acceptable, could be imaged in the TEM (transmission electron microscope). The chemicals would have to be in particle or crystalline form as in Figure 8 which was taken from a study undertaken twenty years ago. Oil-based systems would not be appropriate since the high vacuum system of the TEM would be damaged by volatiles of any kind. In addition, the specimen preparation techniques required for TEM are very limiting and the solvents used in the process would likely dissolve the chemicals. So it must be concluded that while some could be detected with the TEM, it is not a simple nor an advisable approach.

For creosote-treated timber, such as power poles and cross-ties, it is possible to assess penetration by cutting

transverse sections and examining the depth of dark staining. This direct approach does not necessarily present a complete picture because of the chromatographic nature of wood. Some of the oily components, nearly colorless, can migrate far more deeply than the dark-colored material. For these and other types of treatments, tests have been devised that allegedly give an accurate indication of the location of preservatives with a color pattern. For the average practitioner, these results are probably adequate. However, when definitive evidence is required the light microscope or the scanning electron microscope (SEM) with energy-dispersive x-ray analysis must be employed.

The Light Microscope. The basic instrument for wood structure studies, the light microscope, must not be overlooked as a useful tool in all types of wood utilization applications. Small specimens can be sectioned and mounted on a microscope slide for observation by bright field, polarization, phase contrast or differential interference contrast technique, depending upon the thickness of the section. One of these methods is likely to help detect the locations of crystals, particles or liquids in the wood. Perhaps the most powerful method, though, is UV fluorescence, especially for the detection of oils and similar materials. Cell walls penetrated by vehicles or solvents will fluoresce brightly in contrast with those lacking these materials. This method has been used with success particularly with coatings. The results suggest that pigments and the more viscous components of a coating remain on the surface of the wood while solvents and certain vehicles migrate into the walls of cells several cells deep thereby demonstrating again the chromatographic nature of wood.

In light microscopy, there is no concern for the effect

of volatiles on the high vacuum system. It is well suited to dynamic studies in which columns of treating chemicals can be moved along in the cells with pressure from a pencil point or a needle. It is fascinating to see creosote move from tracheids into rays, through bordered pit pairs or resin canals. In cases where wood has absorbed too much preservative, often because of the presence of bands of compression wood, the liquid can be observed "live" even without benefit of a thin section.

The Scanning Electron Microscope. For the past twenty years, the scanning electron microscope (SEM) has become the instrument of choice for many studies relating wood properties or behavior to wood structure. Because of its relatively easier specimen preparation requirements as well as because of its more readily interpreted images, the SEM continues to be widely used in a wide range of scientific applications. Because the SEM column and specimen chamber are under high vacuum, limitations similar to those for TEM use apply. Oily or very volatile components of preservative formulations would quickly contaminate the vacuum system. These restrictions do not apply to systems such as CCA or other water-borne materials that are presumably "fixed" to the wood cell walls. However, these deposits may be too small to be resolved by the SEM which has lower resolving power than the TEM.

Fortunately, EDXA (energy-dispersive x-ray analysis) may be used with SEM and this detection system can be effective even when the materials are not visible in a micrograph. Elements heavier than sodium are detectable provided that they are present in adequate amounts. When pentachlorophenol was used in clear coatings or in vacuum/pressure impregnation systems, chlorine was readily detected and its location could be "mapped" over a comparison micrograph. Figures 9A and 9B illustrate this

very effective method. Figure 9A is a cross-section of a specimen of wood that had been coated with a clear, protective finish containing a significant amount of Penta. This type of finish was very low in viscosity and penetrated the wood very readily. There was relatively little film formation on the surface of the wood and, in fact, it is not easily seen in the micrograph.

When EDXA is used, the location of the Penta, via the chlorine atoms, is indicated by white dots. The concentration of chlorine is very high at the surface and in the cell lumens and walls of the summerwood tracheids. The walls of earlywood tracheids found deeper in the wood suggests that penetration of this system, and particularly of the Penta, is remarkable. It supports the contention that pentachlorophenol can migrate in vapor form, especially at elevated temperatures, and relocate at some distance from its original deposition.

In studies on water-based surface treatments for wood, Desai and Côté (1976, 1980) demonstrated that EDXA was an ideal tool for comparing the behavior of different constituents of a formulation. For example, the pigmented latex component remained on the surface of the wood, the zinc compound penetrated several cells deep but remained in the cell cavities while the sulphur atoms entered the cell walls also at considerable depth in the wood.

This chromatographic separation phenomenon has been seen so many times that it deserves emphasis. It occurs in pressure-treated wood as well as surface coated wood. The formulators assume, for example, that CCA treatment will leave adequate amounts of Cu, Cr and As in all treated areas thus providing balanced protection. Two cases come to mind in which the three components were found to have separated during treatment resulting in incomplete protection. A

Eucalyptus power pole failed after only three years of service and a laminated beam in which the Douglas-fir lumber had been pre-treated before lamination also failed under load.

Where Has All The Good Stuff Gone? In wood preservation treatments and in wood coating applications, there is a major objective: wood protection. Other goals such as improving the appearance of a surface, saving repeated replacement costs, and other ancillary benefits are not always stated though they are important to the consumer. An often unmentioned goal is longevity of the treatment; in other words, effective treatment that will last not only to save replacement costs but also the mess and trouble of additional treatment. The key to successful wood preservation and wood coating processes is in getting the "good stuff" to the critical site in a form that will guarantee its intended function of protecting the wood.

In this brief discussion, the pathways for movement of key components to the right places were described. First the gross or first order channels such as tracheids and vessels, and then the second order openings in the wood cell walls must be penetrated. Otherwise biodeteriorating enzymes can attack unprotected pockets of wood. Chemicals deposited in the cell cavities alone do not necessarily afford adequate protection. Additionally, the effects of chromatographic separation, as in the case of the CCA treated wood, can also lead to inferior results.

In formulating paint, each ingredient is carefully selected to contribute some particular property. Evidently it is assumed that all components will remain together in the final film, which may be the case if a sheet of glass is painted. However, as has been indicated above, wood is unique as a substrate. If one could say that every piece of

wood is the same as another, experience would eventually lead to successful paint formulation. Today's lumber is more variable than ever and may include more reaction wood and a greater number of knots than materials of the past. Even setting aside those concerns, there must be some appreciation for the fact that solvents and vehicles penetrate wood well in advance of other constituents and the film that remains on the wood surface may be quite different from the one that was formed on the glass surface.

While there are test procedures for assessing the efficacy of wood preservation treatments, such as soil block and stake tests, and exposure tests for wood coatings, these are extremely time consuming approaches. Nevertheless, they cannot be set aside since they produce valuable evidence. The notion of exploring potential shortcomings as well as positive factors via microscopy during the developmental phases of a new product or process is suggested as being worthy of serious consideration.

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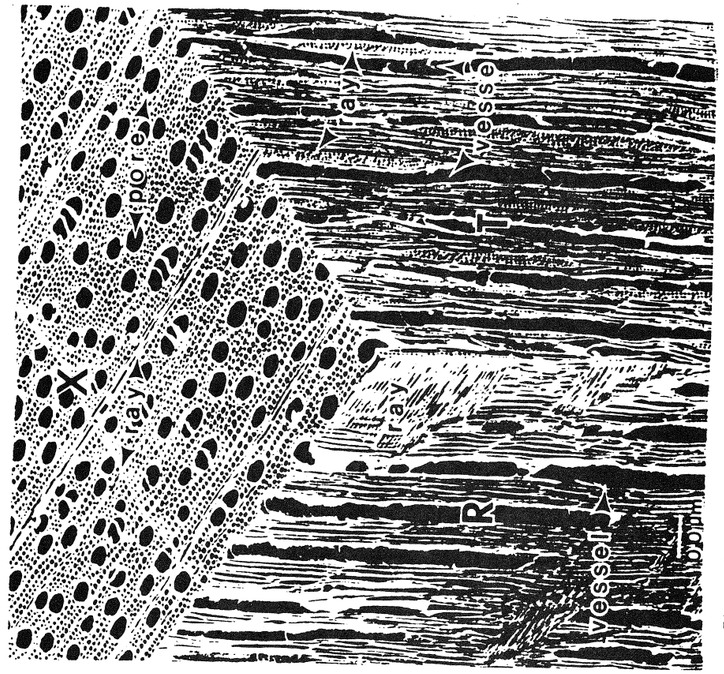

Figure 2. Scanning electron micrograph of a small cube of a typical hardwood showing the transverse (X), radial (R) and tangential (T) surfaces. The vessels appear on the end grain as "pores". Rays can be observed on all three surfaces.

Figure 1. Transverse surface of a Douglas-fir log showing phloem (bark) and xylem (wood) and the location of the cambium at their interface. Note the growth increments (annual rings), the outer sapwood and relatively darker heartwood and central pith.

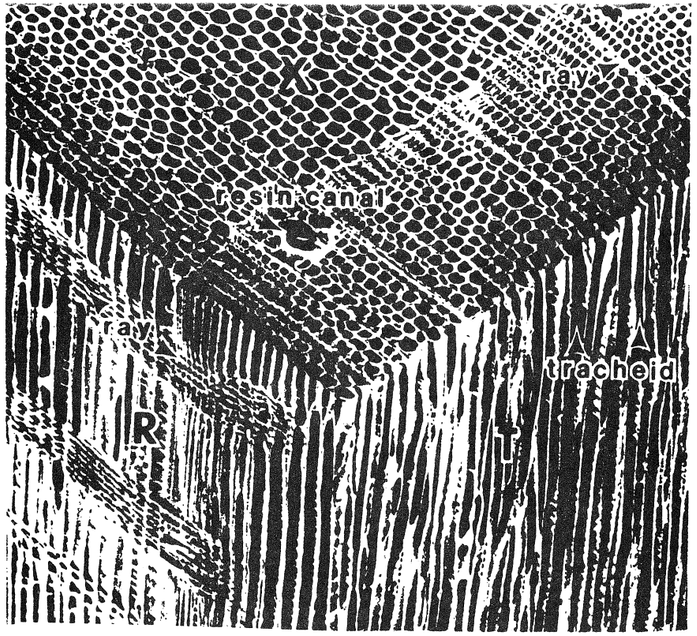

Figure 3. Scanning electron micrograph of a small cube of a typical softwood showing the transverse (X), radial (R) and tangential (T) faces. Note the radially aligned rows of tracheids, the bands of rays and the resin canals.

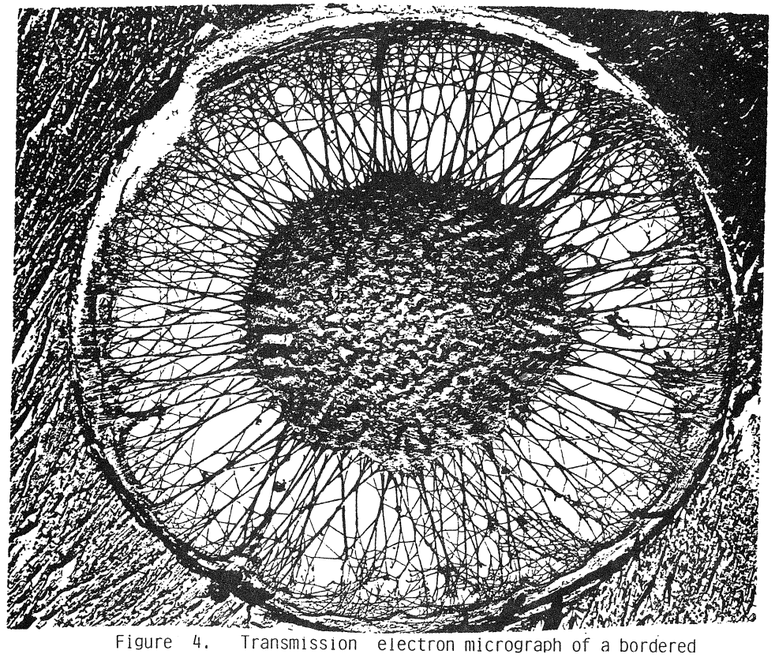

Figure 4. Transmission electron micrograph of a bordered pit membrane in the wood of eastern hemlock. The central torus is suspended by cellulosic strands which allow the torus to move to one pit aperture or the other. The openings allow for free movement of fluid. 6050X.

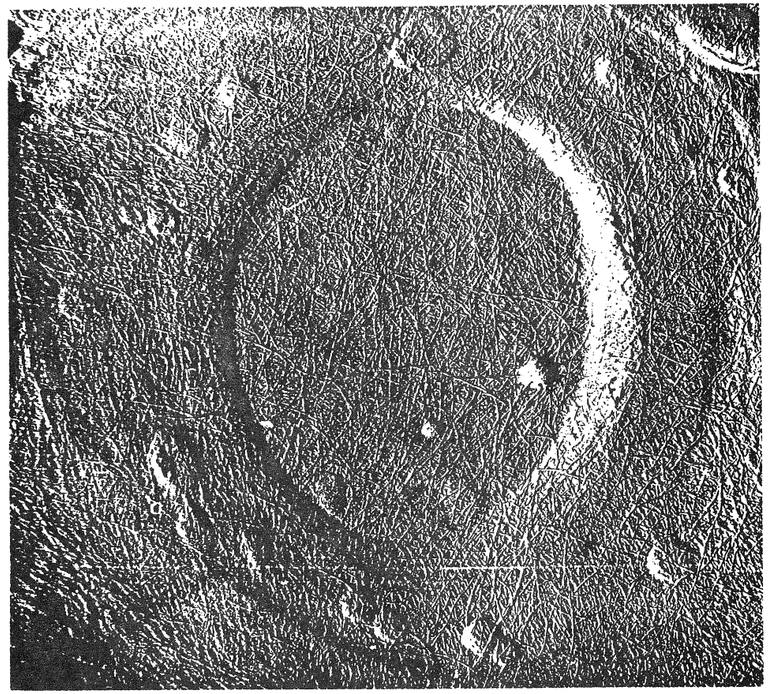

Figure 6. Transmission electron micrograph of the primary wall and pit membrane in a hardwood. Note the randomly distributed cellulose microfibrils and the lack of visible openings for fluid flow. 15,675X.

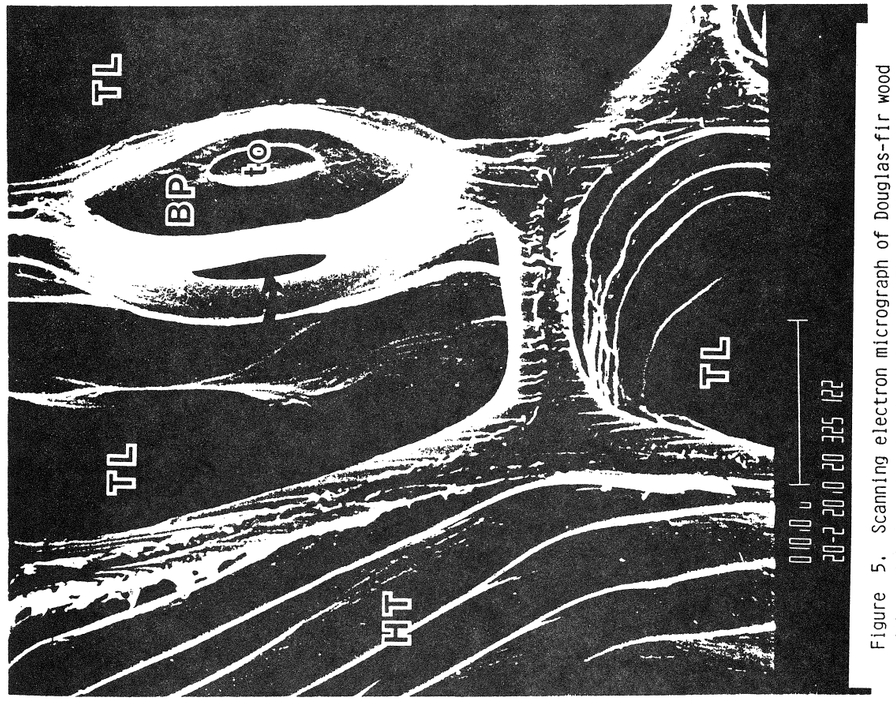

Figure 5. Scanning electron micrograph of Douglas-fir wood with a view into the tracheid lumens (TL) and a bordered pit chamber which were opened via a microtomed cross-section. The bordered pit is aspirated. The walls of the tracheids have helical thickenings in this species. 300X.

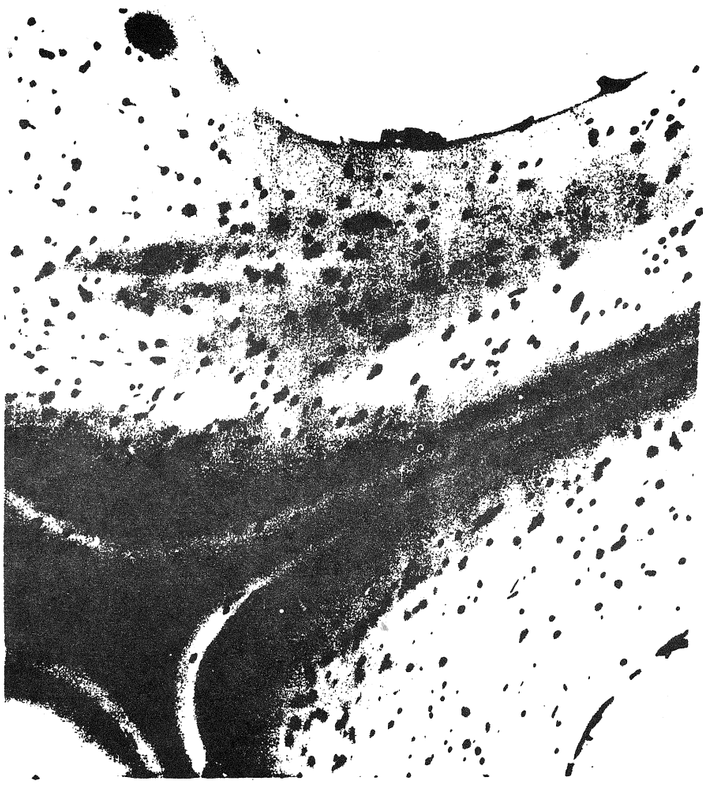

Figure 7. Transmission electron micrograph of a thin section of wood in which a silver salt was deposited from an aqueous solution. The size and shape of the openings in the cell wall may be judged by the nature of the crystals. 9200X.

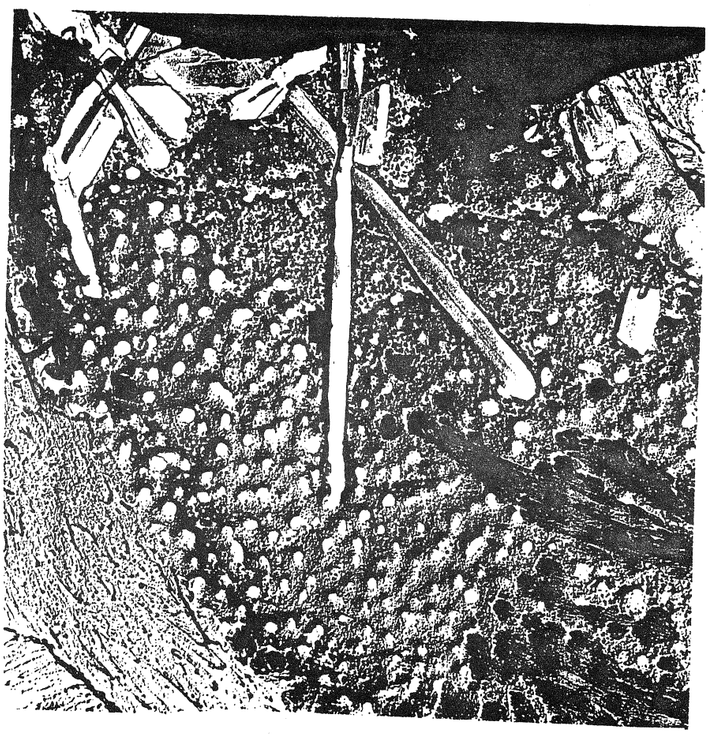

Figure 8. Transmission electron micrograph of pentachlorophenol crystals in a bordered pit chamber of redwood. The penta was introduced by the Cellon process in this study which was done in the late 1960's. 19,600X.

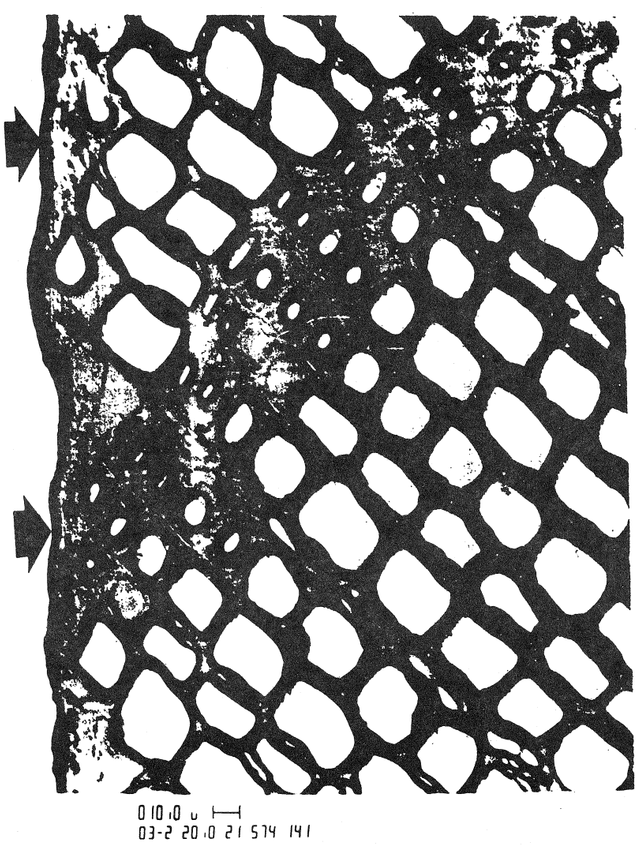

Figure 9A. Scanning electron micrograph of a section of a softwood coated with a clear protective finish containing pentachlorophenol. Note that the coating is difficult to see using the SEM.

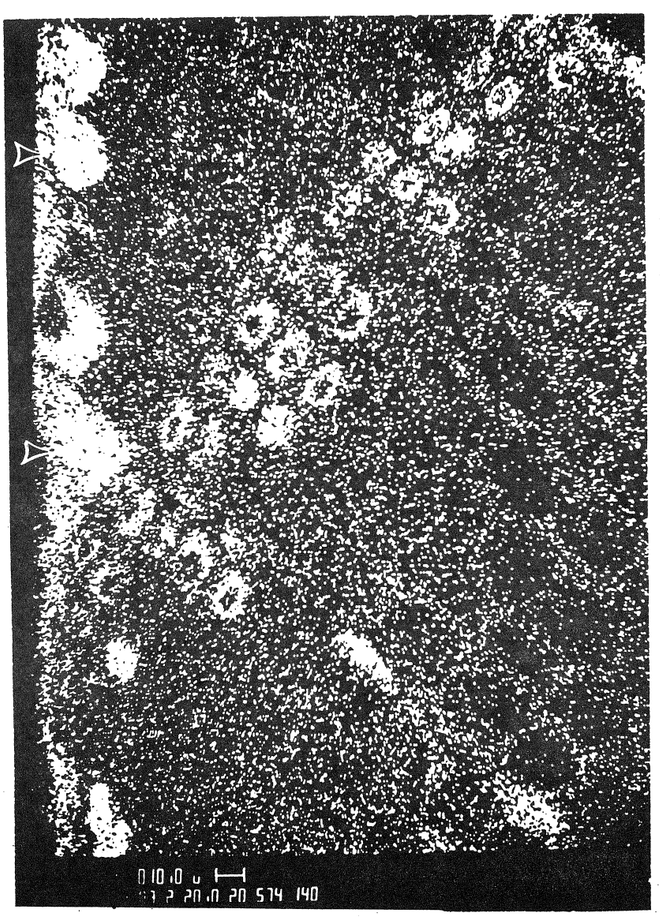

Figure 9B. Element map for Cl, chlorine, in pentachlorophenol prepared by EDXA, energy-dispersive x-ray analysis. Each white dot represents an x-ray generated when the SEM electron beam impinged on the wood cross-section shown in Figure 9A. Note that most of the Cl is held in the coating but the summerwood tracheid lumens and the walls of earlywood cells were well penetrated by Penta.