CONSOLIDANT DISTRIBUTION IN DETERIORATED WOOD TREATED WITH SOLUBLE RESINS

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The distribution of synthetic resin consolidant after treatment of deteriorated wood by vacuum impregnation was studied principally by scanning electron microscopy (SEM). The samples had been completely saturated with consolidant solution during treatment, and accordingly, evidence of resin could be found throughout the cross section. However, the resin was not uniformly distributed. Most strikingly, some cells could be observed to have heavy deposits of resin, in some cases completely filling the cell lumen, while adjacent cells contained little or no resin. The percentage of earlywood cells with visible resin deposits in a given sample area was used as an indicator of resin content. It was found that there was greater concentration in the side grain surface layers than in the specimen core. There was also a tendency toward increasing concentration toward the end surfaces but this effect was not as well defined.

Introduction

One of the factors which can be expected to significantly influence the performance of consolidants used for treating deteriorated wood is their distribution within the wood structure following treatment and removal of the solvents. In porous stone, for example, reverse migration of soluble synthetic resin consolidants can take place during the drying phase following impregnation (1). In this process, consolidant solution flows in bulk toward the surface and the solvent evaporates there, leaving behind a high concentration of consolidant in the surface layers. Such uneven distribution of consolidant may be undesirable.

In wood, fluids can move either by bulk flow or by diffusion. Diffusion can take place by movement of vapor through the void structure or by transport of adsorbed fluid within the cell walls (2). In drying wood from the wet state as it is in the living tree, the major part of moisture movement takes place in the form of diffusion (3). Bulk flow, however, also plays a role which can have significant consequences as, for instance, in the development of seasoning stain in redwood (4). In this case water-soluble extractives are carried to the surface where the water evaporates, leaving the extractives behind, causing objectionable patterns of discoloration on the surface.

It was therefore desired to determine whether similar phenomena take place during solvent removal following treatment of deteriorated wood with thermoplastic synthetic resins in solution, by making a microscopic study of consolidant distribution.

Materials and Methods

The material for the present study was taken from matchstick size specimens which had previously been treated with consolidants by vacuum impregnation and then subjected to static bending tests in a study of consolidant effectiveness by Wang and Schniewind (5). Four specimens were selected from each of four groups. Two groups had been treated with 20 percent solutions of Butvar B98, one in ethanol and the other in a 40/60 mixture of ethanol and toluene. The other two groups had been treated

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with 20 percent solutions of Acryloid B72, one in acetone and the other in toluene. These 16 specimens (four treatments with four replications each) formed the main experimental design.

In addition, three specimens treated with 20 percent solution of Butvar B90, two in a 40/60 mixture of ethanol and toluene and one in ethanol were examined. Finally, one specimen treated with a 5 percent solution of Butvar B98 in a 40/60 mixture of ethanol and toluene was included in the study.

The specimens were examined in a Hitachi S-2300 scanning electron microscope (SEM). Initially it was attempted to examine both cross sections and split radial sections, but it was impossible to locate consolidant resin in the radial sections. Accordingly, the examination was confined to cross sections. It was found that the brash fractures that occurred during the previous static bending tests made excellent surfaces for examination. These fractures had taken place at approximately midlength of the 3 x 3 x 50 mm bending specimens. since wood is known to be more permeable along than across the grain, it was suspected that a substantial amount of drying would take place from the end surfaces, possibly leading to differences in the longitudinal distribution of consolidant. To study this, closely spaced serial sections were desired. It was found that by using specially constructed clamping devices which held all four sides of the 3 x 3 mm sticks, one half-length of bending specimen could reliably be broken into six pieces, each approximately 3.5 mm in length. Brash fractures were encouraged by drying the specimens in a desiccator and scoring the tension and the two side surfaces with a razor blade to a depth of 1 to 5 cell diameters at the desired fracture section.

The 3.5 mm lengths were smoothed at one end to obtain a level contact surface. They were mounted on an SEM specimen stub with colloidal carbon. The samples were then dried and sputtercoated with gold. They were viewed in the SEM with an accelerating voltage of 8 to 15 kV at various magnifications. Systematic measurements were made on prints taken at a magnification of 200x, choosing an area of earlywood as close as possible to the center of the cross section (core position) and the other area close to the surface (edge position) and within the same growth ring. occasionally the area near the surface had to be selected from an adjacent growth ring. The examination was confined to earlywood, because the latewood cells were too seriously degraded and distorted for analysis.

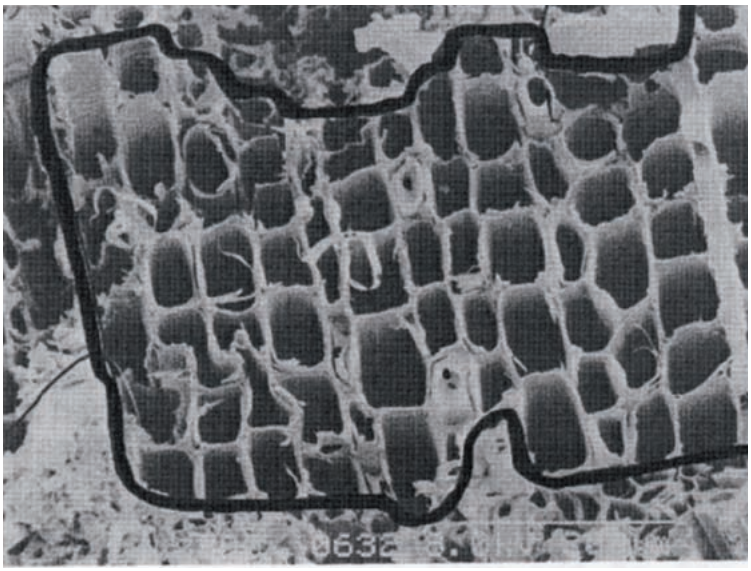

Figure 1. Sample area of 73 cells containing 19.2% cells with plugs or sleeves of consolidant (B98 in ethanol).

On each of the prints used for analysis, a sample area of earlywood was marked out. Depending on ring width, cell size, and image clarity, this area contained from 30 to 139 cells, the average being 85. The number of cells containing solid plugs of resin in the lumen and those that had a thick lining or sleeve of resin in the lumen were counted and expressed as a percentage of the total number of cells in the sample area. An example of such a marked sample area is shown in Fig. 1.

Although plugs and sleeves of resin were counted separately, the combined percentage of all cells containing obvious amounts of resin was used for analysis. statistical analysis was carried out using Statgraphics software and a personal computer.

Results and Discussion

All of the specimens examined showed that the earlywood appeared to be substantially intact, while the latewood showed severe cell distortion and damage, indicating significant deterioration. Fig. 2, a micrograph of an untreated, matched control specimen taken at the boundary between two growth rings, shows latewood cells below and earlywood cells from the following year's growth above. The earlywood cells can be seen to be virtually indistinguishable from undeteriorated wood, and the spiral thickenings typical of Douglas-fir are clearly visible on the lumen surface. Supplementary examination by light microscopy using polarized light confirmed that the wood was bacterially degraded as had been previously mentioned (5), but there was also evidence of softrot damage and in some specimens hyphae of decay fungi (brown rot) were found.

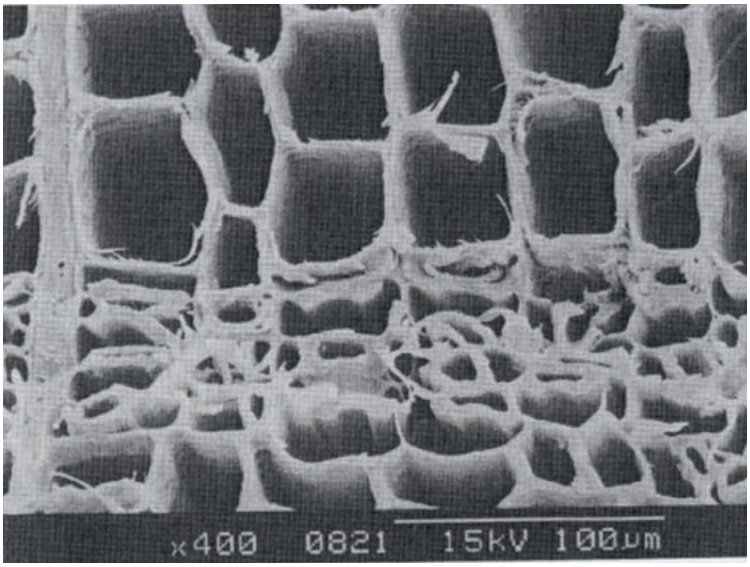

Figure 2. Cross section of deteriorated, untreated Douglas-fir showing nearly destroyed latewood below and apparently intact earlywood above. Note spiral thickenings inside the earlywood cells.

The most striking finding of the SEM examination of specimens treated with consolidant was that many cells contained little if any resin, while others showed either solid plugs or thick inner sleeves of consolidant (Fig. 3). Some plugs seemed to be caps over bubbles. Since most of the samples had been treated with a 20% solution of resin, and since there had been evidence that complete saturation with consolidant solution had been achieved during vacuum impregnation (5), it would have been expected that on average about 20% of the void space in the wood be filled with consolidant. Most cells being

empty shows that considerable bulk flow of solution must have taken place during drying, resulting not so much in a uniform flow toward the specimen surfaces but rather a migration toward and deposition in certain cells which then served as loci for resin precipitation and solvent vapor diffusion.

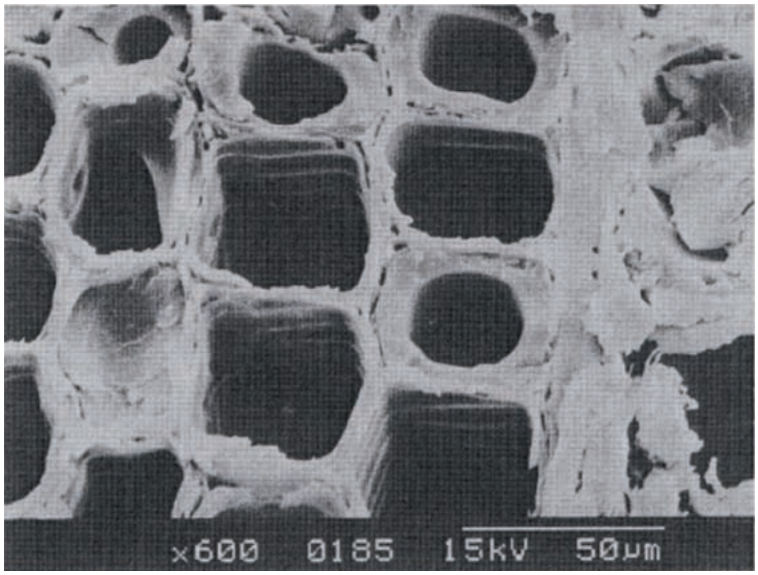

Figure 3. Earlywood cells treated with 20% B72 in toluene. Note solid plug in cell at lower left and thick sleeves of resin toward the top. Spiral thickenings clearly visible in other cells indicating little or no resin content.

There did not appear to be any qualitative differences in the observed pattern of resin distribution that could be attributed to either type of resin or type of solvent, or even concentration of consolidant solution. However, it was noted that in Acryloid B72 the plugs or sleeves of consolidant almost always failed in the same fracture plane as the wood, while in Butvar B90 or B98 tubes of consolidant, identifiable by the spiral thickenings molded on their outer surfaces, could often be seen protruding from the fracture plane (Fig. 4). This may be due to higher tensile strength of the polyvinyl butyral, allowing the sleeves or plugs to be broken at a weak point distant from the overall fracture plane. Since Butvar B98 has been shown to have adhesive qualities comparable to Acryloid B72 in acetone and much superior to B72 in toluene (6), lack of adhesion of the Butvar resins is not a likely explanation for this phenomenon.

The cells containing plugs or sleeves of resin appear to be scattered irregularly throughout the wood structure, and visual examination of cross sections did not reveal any obvious distribution patterns. Plots were made showing the percentage of plugs and sleeves in sample areas near the surface and at the core as a function of distance from the end. Average plots for Acryloid B72 and Butvar B98, each for two different solvents, are shown in Figs. 5 to 8. It must be emphasized that the percentages given refer to the relative number of cells containing significant amounts of resin and are not measures of actual resin content.

The general trend seen in Figs. 5 to 8 is for more cells near the edge of the cross section to have significant amounts of resin than cells in the core, and also an increase in the percentage of cells with resin going from midlength of the specimen toward the end surface. The longitudinal variation is more

Fig. 4. Fracture surface of specimen treated with B98 in ethanol 3.5 mm from the end and close to the edge, showing sleeves and plugs protruding beyond the fracture plane.

clearly evident in the core positions than at the edge. In three out of the four treatments the percentage of cells with resin at the longitudinal position closest to the end is higher in the core than at the edge. This can be attributed to the much greater ease with which fluids move longitudinally through wood (2), so that in this section the longitudinal movement predominates over lateral migration. The plots shown in Figs. 5 to 8 are averages of four specimens each. Plots for individual specimens vary widely, many not showing clear trends.

Average values of the data which form the basis for Figs. 5 to 8, i.e., the data for B72 and B98 excluding B90 and the one specimen treated with a 5% solution of B98, are shown in Table 1. Averaged over all treatments and positions, 15.9% of the earlywood cells contained visible consolidant. Average loading, i.e., gravimetrically determined resin content, was 29.4% for B72 in acetone, 32.2% for B72 in toluene, 28.2% for B98 in ethanol and 31.8% for B98 in ethanol/toluene mixture. The loading was therefore substantially the same for both resin types, but specimens treated with B72 had much lower percentages of earlywood cells containing visible resin as compared to those treated with B98. Solutions of B72 probably tend to migrate to selected cells more effectively owing to their much lower viscosity as compared to solutions of B98. The concept of more resin in fewer cells in the case of B72 is supported by the observation that the ratio of plugs to sleeves was much greater for B72—1.01 and 0.72 in acetone and toluene, respectively—as compared to B98—0.17 and 0.07 in ethanol and ethanol/toluene, respectively. The type of solvent appeared to have less of an effect.

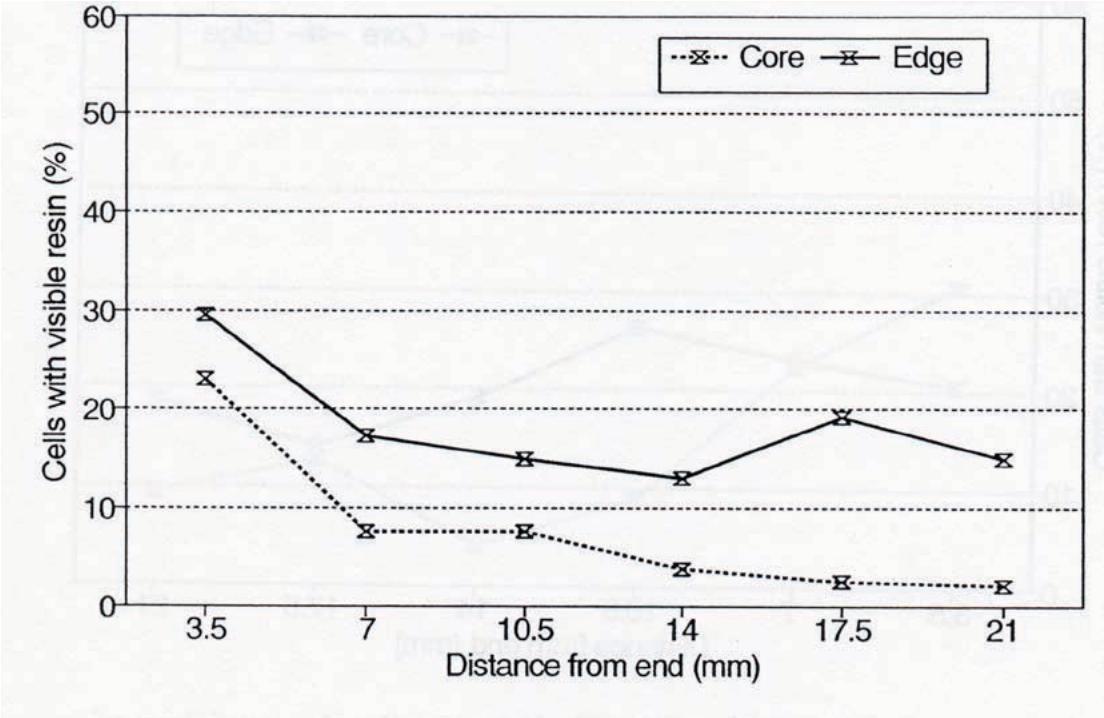

Figure 5. Percent of cells with visible resin in specimens treated with 20% B72 in acetone vs. location.

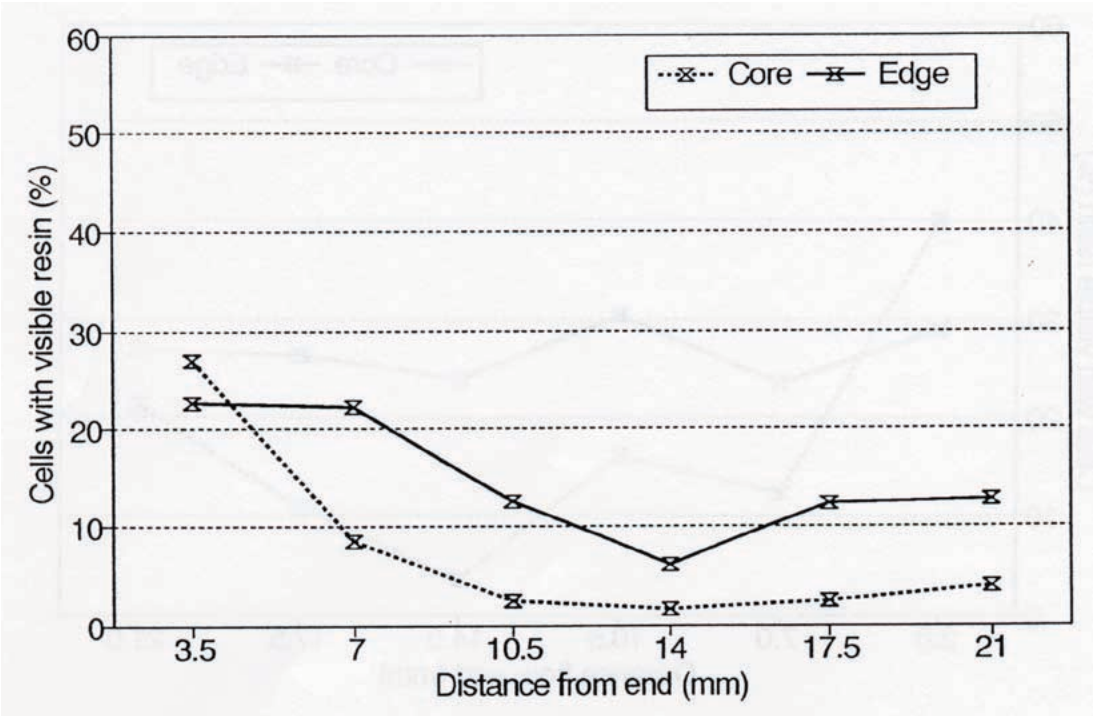

Figure 6. Percent of cells with visible resin in specimens treated with 20% B72 in toluene vs. location.

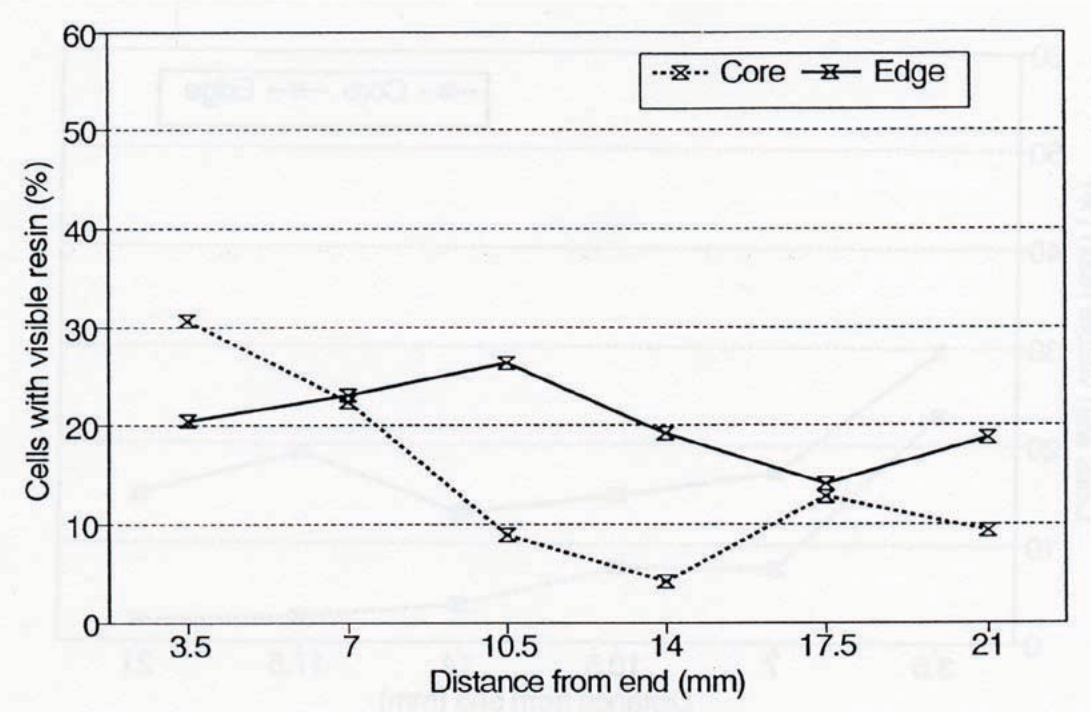

Figure 7. Percent of cells with visible resin in specimens treated with 20% B98 in ethanol vs. location.

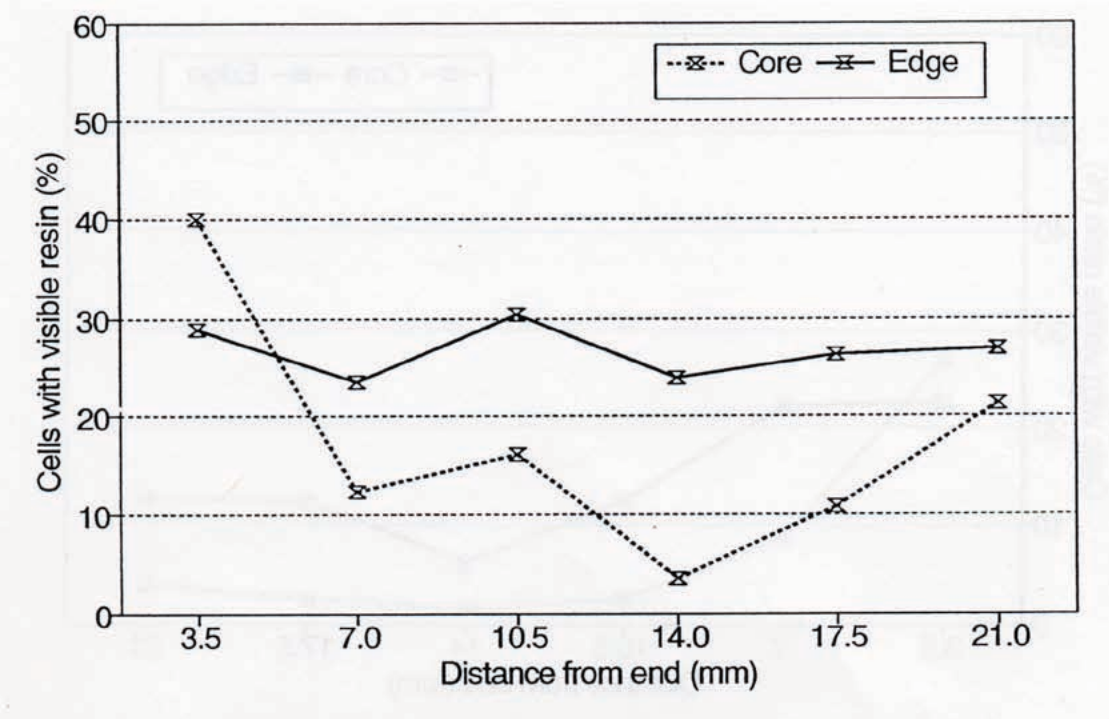

Figure 8. Percent of cells with visible resin in specimens treated with 20% B98 in ethanol/toluene vs. location.

Table 1. Percent of cells with visible resin according to treatment, and longitudinal and lateral position.

Factor	No. of Observations	Average (%)	95 Percent Confidence Limits for Average (%)
Grand average	192	15.9	14.1 / 17.7
Treatment:			
B72/acetone	48	13.2	9.7 / 16.8
B72/toluene	48	10.7	7.2 / 14.3
B98/ethanol	48	17.6	14.0 / 21.2
B98/eth/tol	48	22.1	18.5 / 25.6
Long. position:			
3.5 mm	32	28.6	24.3 / 33.0
7 mm	32	16.1	11.7 / 20.4
10.5 mm	32	14.9	10.6 / 19.3
14 mm	32	10.6	6.3 / 15.0
17.5 mm	32	12.0	7.6 / 16.3
21 mm	32	13.2	8.9 / 17.6
Lateral position:			
Core	96	11.5	9.0 / 14.0
Edge	96	20.3	17.8 / 22.8

For longitudinal position, Table 1 shows that the location closest to the end of the specimens had by far the greatest percentage of cells with consolidant, with much less variation among the other positions. Lateral position within a given cross section indicates a substantially greater percentage of cells with visible resin near the cross section edge as compared to the core.

The data were subjected to an analysis of variance and associated statistical tests. The results of the basic three-way analysis of variance are shown in Table 2. All of the main effects--treatment (resin/solvent combination), longitudinal position, and lateral position--were found to be statistically significant at better than the 1 percent level. Tukey multiple range tests showed that effect of treatment was due to resin type alone, solvent type showing no statistically significant effect. However, while B72 in toluene was significantly different from B98 in either of its solvents, B72 in acetone differed significantly only from B98 in the ethanol/toluene mixture. The significance of longitudinal position was entirely due to the high percentage of cells with resin at the end position. All other longitudinal positions were not significantly different from each other. All of the findings are reflected in the 95 percent confidence limits in Table 1. Where the intervals overlap, the differences are not statistically significant, whereas significant effects are characterized by intervals that do not overlap.

Table 2. Analysis of variance for treatment and position effects

Source	Sum of squares	d.f.	Mean square	F-ratio	Signific. level
Treatment	3591.8	3	1197.3	7.69	< 0.01
Long. pos.	6836.8	5	1367.4	8.78	< 0.01
Lat. pos.	3763.4	1	3763.4	24.16	< 0.01
Residual	28354.2	182	155.8		
Total	42546.2	191			

No statistical analyses were made for the specimens treated with B90 but the results for the few specimens examined were similar to those for specimens treated with B98. The one specimen treated with 5% B98 in ethanol/toluene also showed a similar pattern of migration, but since the loading was only 7.5% there were far fewer cells with visible resin.

A preliminary investigation into using ultraviolet (UV) light microscopy showed some promise in determining consolidant location in wood. Experimentation with various embedding and microtoming techniques showed that sections thin enough for transmitted UV microscopy could be prepared if a low yield of usable sections could be tolerated. Best results so far were obtained without embedding and cutting sections 20 to 40 micrometers thick. Various stains were tried to accentuate the contrast between wood and consolidant. Toluidine blue, which masks the natural fluorescence of wood, worked well. If a stain could be found that stained the consolidant preferentially and also incorporated an element above oxygen on the periodic chart of elements, consolidant location could also be investigated using an energy dispersive x-ray analyzer. The very limited work to date indicates that consolidant location as determined by UV microscopy agrees with the SEM results. UV microscopy could provide more detailed information within individual cells by allowing more closely spaced serial sections. It also promises to be better suited for determining consolidant location in badly deteriorated latewood.

The results have shown that there is consolidant migration during solvent evaporation by bulk flow from the interior toward specimen end and side grain surfaces. There is also internal migration to selected cells so that in earlywood the consolidant appears to be concentrated on average in only 16 percent of the total number of cells. Since in the case of B72 the polar acetone which is adsorbed by wood and causes substantial swelling gives nearly the same results as non-polar toluene which does not swell wood, the diffusion of solvent vapor appears to take place through the porous structure rather than by diffusion through the cell walls in the form of solvent vapor bound to internal sorption sites. One can only speculate as to why the consolidants become concentrated in selected cells. One possible explanation might be that the resins form chemical complexes with tannins or decomposition products within the wood which causes precipitation of resin, providing loci for further precipitation as the process continues. It is not clear whether plugs and sleeves extend over the entire length of cells. In some cases plugs could be seen in association with bubbles, so that plugs and sleeves may alternate in the same cell. Some protruding sleeves and plugs were quite long, up to 1.3 mm, suggesting that if resin is present it extends over the entire length of the cell.

Acknowledqements
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