PENETRATION PATHWAYS OF LIQUID GALLIUM IN WOOD SEEN BY SCANNING ELECTRON MICROSCOPY[1]

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(Received March 1983)

ABSTRACT

In order to understand and to visualize which primary pathways are followed by liquid penetration, specimens of *Pinus sylvestris* L., *Abies pectinata* D.C., and *Fagus sylvatica* L. were impregnated with liquid gallium at a temperature of 50 C and at varying pressures. The gallium was then solidified by cooling, and its location was observed by scanning electron microscopy on specimens previously coated with carbon to prevent redistribution of the gallium.

In softwood the liquid metal penetrated first into the longitudinal tracheids and subsequently into the rays through the cross-field-pitting. The reverse did not apparently occur, however, as radial flow through the rays was negligible. In hardwood only vessels were penetrated. For all three species, penetration uniformly increased with pressure but seemed to reach a maximum at a critical pressure level, 8 bars for pine, 16 bars for fir, and much more elevated for beech. Pit dimensions are obviously important to allow flow at low pressures and in addition, when they are large as in pine, tearing of the membrane facilitates it. Some relationships of these observations to practical aspects of wood preservation are discussed.

Keywords: Scanning electron microscopy, penetration of wood, liquid gallium, *Pinus sylvestris* L., *Abies pectinata* D.C., *Fagus sylvatica* L.

INTRODUCTION

When studying the penetration of liquids into wood, two questions are of particular interest: 1) How much liquid can be taken up? and 2) What pathways does the liquid follow? The theoretical maximum uptake of liquid in initially oven-dry wood is given by void volume, which may be determined by displacement methods: e.g., mercury porosimetry on thin transverse sections (Erickson and Balatinecz 1964; Schneider 1979; Schneider and Wagner 1974; Stamm 1967a, 1967b; Stayton and Hart 1965; Smith and Redding 1964; Van Eyseren 1973). However, when the thickness of the sections exceeds about 2 mm, mercury is no longer able to penetrate all the available void space, but the dimensions of the pathways used can be known.

The determination of principal and successive pathways followed by a liquid is usually difficult. Most workers made microscopic observations of the distribution of the liquid after penetration was complete (Bailey and Preston 1969; Behr et al. 1969; Erickson and Balatinecz 1964; Klein and Bauch 1977) or on a macroscopic scale by cinematographic techniques (Smith and Redding 1964). It is clear, however, that the ultimate distribution does not necessarily indicate the pathways followed during penetration. For example, it has often been advanced that rays are the best pathways, particularly in softwoods. This was proposed

[1] The authors wish to thank Mr. Schnedecker and his team of the Laboratoire de Porosimétrie à mercure et de hautes pressions, Centre de Recherches Atomiques at Saclay, France, and Mr. Orengo and Miss Peant, students, for their valuable help.

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because they generally contain traces of the fluids used (Behr et al. 1969), but this view is not accepted by some workers (Bailey and Preston 1969, 1970; Côté 1963). Rays may well become saturated without being the principal penetration pathway.

Moreover, with preservative solutions that wet the cell walls and may be absorbed in the wood substance, the actual mechanism of penetration may involve pathways additional to those followed by mercury (Bailey and Preston 1969, 1970; Smith and Redding 1964). However, it seems reasonable to assume that the primary pathways followed by mercury give an indication of those followed by preservatives. With Douglas-fir, Bailey and Preston (1970) found optimum pressures for water and petroleum distillate.

Some idea of the pathways followed might be obtained by observing the advancement of the liquid in the wood structure at different stages of penetration. A possible technique would be the use of a compound that may be solidified in the wood structure at any desired degree of advancement. In the work reported here, the objective was to use metal gallium, which solidifies at 29.8 C. The gallium may be introduced into the wood in liquid form and observed as a solid after slight cooling. We used scanning electron microscopy (SEM).

MATERIALS AND METHODS

Two softwoods, *Pinus sylvestris* L. and *Abies pectinata* D.C. and one hardwood *Fagus sylvatica* L. were used. Seven replicate specimens measuring $6 \times 6 \times 10$ mm along the tangential, radial, and longitudinal directions, respectively, were prepared from sapwood of each species. The dimensions were chosen so that the length of the specimen would be several times greater than the average fiber or tracheid length of each species. In order to ensure easy accessibility, all surfaces were cut with a microtome (Choong et al. 1975), and the specimens were oven-dried at 50 C for 24 h and stored over silica gel until the start of the experiments.

Principle

The principle was to introduce liquid gallium into the wood under pressure at a temperature above the melting point (29.8 C) and then to cool the specimens rapidly so that the gallium would solidify in the wood structure. By using different pressures, it is possible to obtain different, well-defined degrees of penetration. Unfortunately, there are no precise data available in the literature on the surface tension properties of gallium. Various authors have reported results that vary according to the substrate and temperature (Harding and Rossington 1970; Mack et al. 1941; Stayton and Hart 1965). In addition, the complex and relatively little understood oxidation phenomena at the surface of gallium exposed to the atmosphere make it impossible to measure reliably the volume introduced into the wood. For these reasons, no attempt was made in the present work to calculate pore radii, and observed penetrations were related directly to the applied pressure.

The apparatus consisted of a specimen chamber, gallium holding tank, and a heating and cooling system, connected by appropriate stepcocks (Fig. 1). Pressures of 1, 4, 6, 8, 10, and 16 bars were used. Each of the seven replicates of the same species was treated separately.

In the penetration experiments, after inserting the specimen an initial vacuum of 5×10^{-3} Torr was applied for 3 h to the specimen chamber. At the same time

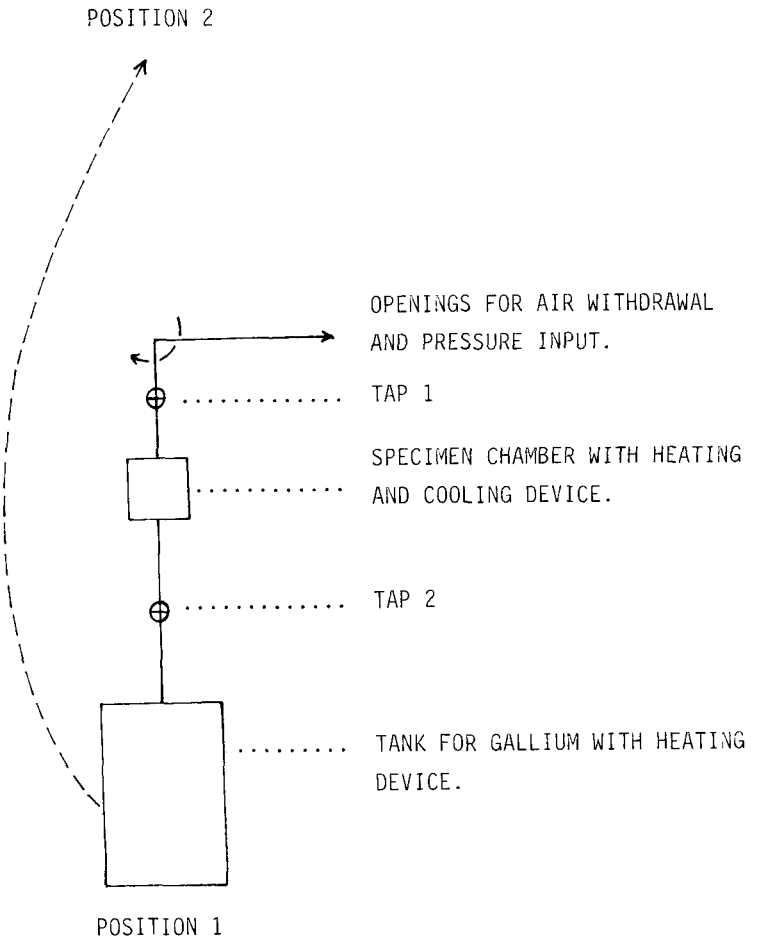

FIG. 1. Apparatus used for impregnation of wood with gallium.

the gallium and chamber were heated to 50 C. Liquid gallium was then admitted to the specimen chamber while the temperature was maintained, and the desired working pressure was applied. After a 20-min pressure period, the excess liquid gallium was withdrawn, and the specimen was cooled under pressure for 12 h by application of solid carbon dioxide packed around the specimen chamber.

On withdrawal, surfaces of the specimens were found to be coated with gallium. The specimens were therefore split down the center of the longitudinal planes for microscopic observation. A simple coat of carbon was applied prior to examination by SEM, to avoid possible changes in the distribution of the gallium that might have occurred as a result of heating that accompanies, for example, gold coating.

RESULTS

Examination of the treated specimens revealed significant differences between species and treating pressures. In the case of *Pinus sylvestris*, it was observed that

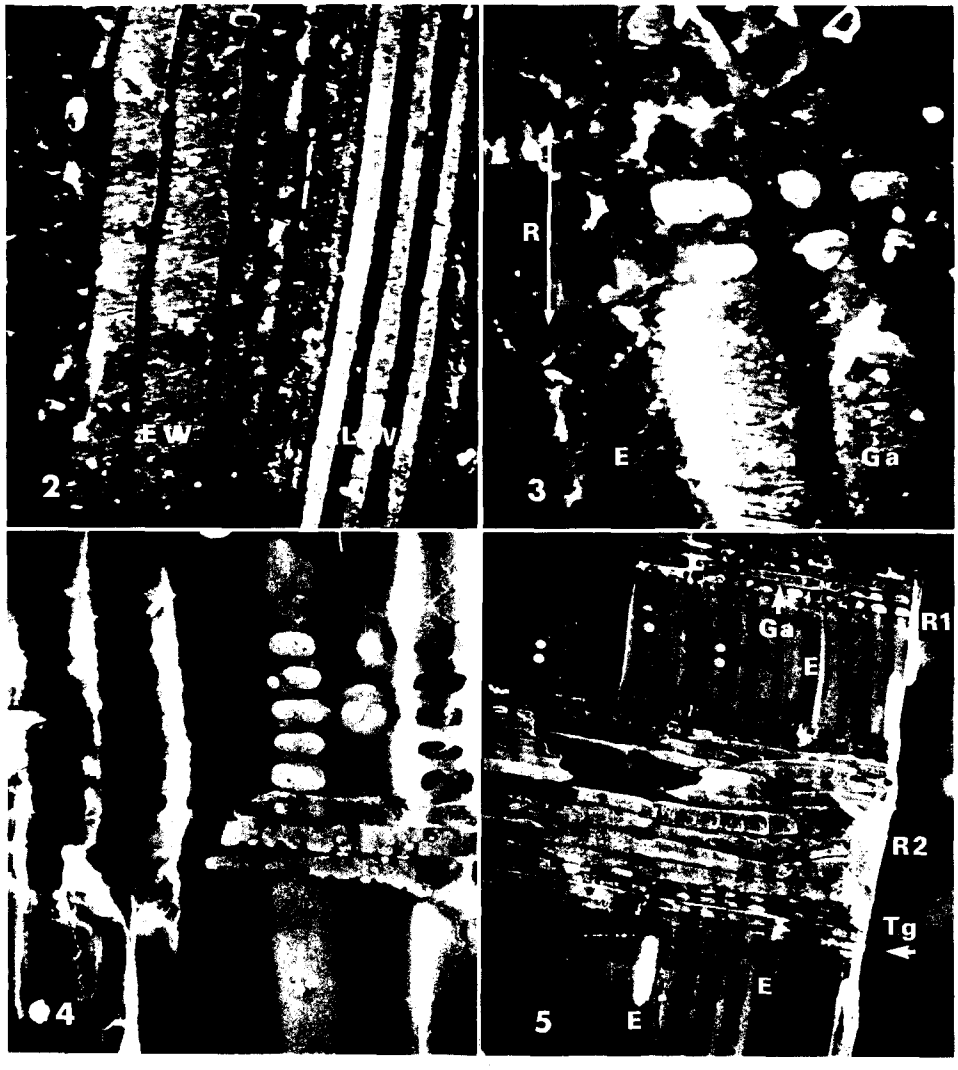

FIG. 2. *Pinus sylvestris:* 4 bars pressure was high enough to drive gallium through tracheids in latewood (LW) with smaller diameters. On the left, earlywood (EW). 300×.

FIG. 3. *Pinus sylvestris:* 4 bars pressure left small drops of gallium (Ga) in the ray (R), coming through the pits from the tracheids underneath. On the left, a tracheid is still empty (E). 900×. Arrow indicates ray height.

FIG. 4. *Pinus sylvestris:* At 6 bars pressure, only one longitudinal tracheid (center) is filled with gallium (Ga). Gallium penetrated from this one through corresponding pinoid pits and even flowed into the transverse tracheids underneath. 300×.

FIG. 5. *Pinus sylvestris:* 6 bars. Two rays open to the tangential (TG) surface. In ray R_1, as in some cells of R_2, no penetration has occurred at 6 bars pressure through the tangential side, but gallium (Ga) appears to have come from the tracheids underneath. Pits corresponding to empty tracheids (E) contain no gallium drops. In ray R_1, gallium started to flow along a cell. The flow was plentiful in ray R_2. 100×.

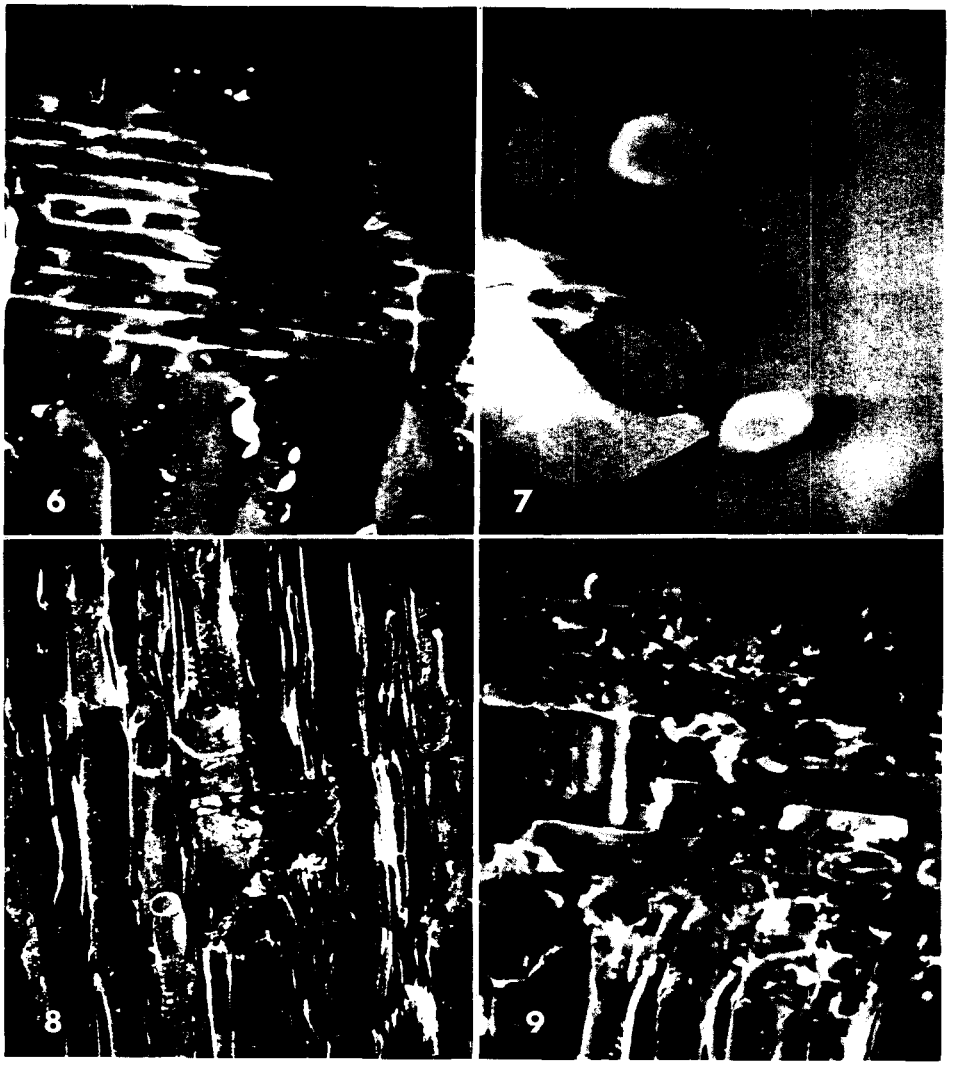

FIG. 6. *Abies pectinata:* At 16 bars pressure, longitudinal tracheids are filled but rays are not. 300×.

FIG. 7. *Abies pectinata:* At 16 bars pressure (detail from Fig. 6), gallium starts appearing in the ray through the cross-field pits from impregnated tracheids underneath. 3,000×.

FIG. 8. *Fagus sylvatica:* At only 1 bar pressure, some vessels are already filled with gallium throughout their length, but fibers and rays are empty. 100×.

FIG. 9. *Fagus sylvatica:* At 16 bars pressure, ray cells remain empty even though they are in contact with full vessels. 300×.

at the lowest pressure (1 bar) the gallium penetrated a relatively short distance in the longitudinal direction—3 mm or less, which is the maximum length of cut fibers. The next highest pressure level (4 bars) was high enough to drive gallium through tracheids along a greater depth about 4 or 5 mm and was sufficient to lead to penetration of some of the smallest latewood tracheids (Fig. 2), whereas

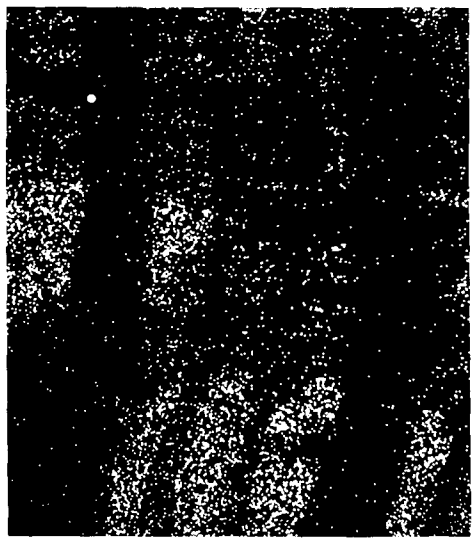

FIG. 10. *Fagus sylvatica:* An X-ray fluorescence micrograph of the same area as in Fig. 9 confirms that only the vessels contain gallium, not the ray.

some neighboring tracheids remained completely empty. About 80% of the tracheids were penetrated.

Some penetration of the rays had also occurred in the form of small droplets of gallium reaching the ray parenchyma cells through the pinoid pits that connect them with the longitudinal tracheids (Fig. 3). The ray tracheids were not penetrated. At 6 bars the amount of gallium found in the ray parenchyma was greater, and droplets of gallium also began to appear in the ray tracheids. Almost complete penetration of *Pinus sylvestris* occurred for pressures greater than 8 to 10 bars.

Careful examination of the samples and the shape of the gallium deposits revealed that, by and large, penetration of the rays occurred through the pits connecting them to longitudinal elements and not as a consequence of flow along their length (Fig. 4). This is also clearly seen in Fig. 5, which shows two rays open to the tangential surface of the specimen block. In ray 1, as in some cells of ray 2, no penetration has occurred through the tangential surface (Tg) or side. Rather, the gallium present in the ray appears to have come from the tracheids in contact with it. On the other hand, the pits in contact with empty longitudinal tracheids (E) contain no droplets of gallium. In ray 1, it appears that gallium had started to flow along the length of a cell. Similar lengthwise flow was much greater in ray 2.

Much the same results were observed in the case of the *Abies* samples. The main difference between these two softwoods, however, is that it took almost twice as great a pressure with the *Abies* to reach the same level of penetration. Thus, with the *Abies* sample, penetration of both longitudinal tracheids and rays was minimal at a pressure of 8 bars. At 16 bars, appreciable amounts of gallium could be observed in the tracheids, which are almost entirely penetrated (Fig. 6) with small drops appearing in the rays (Fig. 7). In agreement with Côté (1963), droplets of gallium in rays lead us to think that the light membrane of the win-

TABLE 1. *Enumeration of the location and degree of penetration of liquid gallium.*

Pressure bars	*Pinus sylvestris*	*Abies pectinata*	*Fagus sylvatica*
16		Longitudinal tracheids filled, drops in rays Fig. 6–7	Vessels filled, tracheids and rays empty Fig. 9
8	Complete penetration	Minimal penetration into cut cells	
6	Rays and transversal tracheids filled from longitudinal tracheids Figs. 4–5		
4	Greater depth penetration. Rays reached through pinoid pits from longitudinal tracheids Figs. 2–3		
1	Penetration into cut fibers less than 3 mm length		Some vessels filled Fig. 8

dowlike punctuations of *Pinus sylvestris* is perhaps easily ruptured under pressure. The small pits found in *Abies* are obviously a factor limiting flow; the same may be said for the pitting in the ray tracheids pits. Movement of gallium from a ray into a tracheid was never observed.

The pattern of penetration into *Fagus* was quite different from that of the two softwood species as might be expected because of its different anatomical structure. At the lowest pressure used (1 bar), some vessels were already completely filled, but gallium was observed in neither the tracheids nor the rays (Fig. 8). Increasing the pressure to 16 bars did not lead to penetration of the tracheids or rays (Fig. 9), and even at this pressure, some vessels were not filled. The lack of penetration of gallium in the rays was confirmed by examination of the same sections used in SEM with X-ray fluorescence microscopy (Fig. 10). So, although the vessels in *Fagus* were penetrable at low pressures, no penetration of either tracheids or rays was observed at the highest pressure used (16 bars).

In all three cases, because of the lack of data on gallium mentioned earlier, no curve could be plotted of the volume versus radius or pressure. In a qualitative manner, the variation of penetration with applied pressure may be seen in Table 1.

CONCLUSIONS

Treatment of wood with liquid gallium that is solidified in situ may be used successfully to plot the flow paths of this liquid into wood in relation to the pressure applied.

In regard to pressure, it was clear that the penetration of gallium does not uniformly increase with increasing applied pressure. On the contrary, it would appear that there is a critical pressure level at which penetration is almost com-

plete. This critical level would appear to be about 8 bars for pine, 16 bars for *Abies*, and much more for *Fagus*. While a slightly lower pressure clearly results in a lower impregnation, a much higher pressure does not induce a significantly greater penetration. If it is accepted that penetration of mercury or gallium may give some indication of pathways available for preservatives in spite of their different wetting properties, then the present findings confirm that to improve impregnation, there should be direct access to longitudinal elements such as tracheids or vessels. Improvement of impregnation may be achieved either by incising or by opening the intervessel, intertracheid, and ray pits by biological or chemical methods.

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