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Distribution, concentration and bonding factors affecting the performance of water repellents applied to wood

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In the name of God most Merciful most Gracious

ONE BLESSED WITH KNOWLEDGE OF
SCIENCE IS BLESSED WITH ENDLESS GOOD.

The Holy Qur'an

DISTRIBUTION, CONCENTRATION AND BONDING FACTORS AFFECTING THE PERFORMANCE OF WATER REPELLENTS APPLIED TO WOOD

by

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To the memory of

MY FATHER and FATHER-IN-LAW

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SUMMARY

The effects of water repellent solution concentration, distribution of various components and wood-water repellent bond type were studied using Corsican pine (*Pinus nigra*) and European beech (*Fagus sylvatica*) wood. The resin component protects treated wood by forming an impermeable coating on cell lumina, whilst the wax gives protection by hydrophobic action. Increased concentration and treatment severity cause deeper penetration and increased loading and provide better protection. Water repellents are distributed in highest concentration at the treated end and in gradually decreasing amounts inwards.

Weathering rapidly reduces the effectiveness of the coating action, because in the absence of hydrophobes water is able to gain rapid access to all treated capillaries. However, hydrophobic treatments continue to provide protection to inner wood even after end grain degradation, because water is able to penetrate treated cells only to the depth of the degraded zone. Loss of water repellent effectiveness in the surface zone due to weathering occurs even though hydrophobic substances remain. This is almost certainly associated with degrade of wood structure and wood-deposit bond.

Pine specimens were treated with alkylchlorosilanes and alkylene oxides and double treated with an epoxide and a resin-wax water repellent to study the performance of chemically bonded treatments. Both silane and epoxide treatments proved to be resistant to exposure. Silanes provide initial water repellency similar to that provided by resin-wax and are far more resistant to weathering. Loss of effectiveness of silane treatments is attributed to wood degrade enhanced by the effect of HCl produced in the reaction. Stabilization obtained by epoxides is extremely resistant to exposure. Reduced water absorption, due to OH-group blocking and cell-wall bulking, but no water repellency is shown by epoxy-treated wood. The full potential of water repellents applied to stabilized wood was not realized due to problems encountered in applying resinous solutions to epoxy treated wood.

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PART 1

BACKGROUND AND LITERATURE REVIEW

1.1 Wood - A Complex Porous Medium

In most porous media only the void spaces take part in the conduction of fluid. The walls surrounding them have little effect on the phenomenon. In wood, however, certain liquids contained within the capillaries are able to move into their walls. The ability for this to occur is dependent upon the molecular structure of the flowing fluid (Scheidegger, 1974). Non-swelling liquids, not having a chemical affinity with the cell wall, flow through the effective pore spaces without interacting with the cell wall polymers. Water, on the other hand, is adsorbed into the cell wall until the latter is fully saturated. This occurs at about 30% moisture content and is known as the fibre saturation point (FSP). The water is believed to be held there by hydrogen bonding (Stamm, 1964; Wenzl, 1970).

It is thought that the sorbed water forms first a monolayer and subsequently multilayers up to ten molecules thick. The swelling and shrinking of wood is the result of sorption and desorption of this water. Above the FSP, water occurs in the cell lumina as free water which has no effect on the dimensional stability of wood. The cell lumina, however, provide important water pathways allowing rapid access to interior cell walls. Dimensional instability of wood due to water sorption is disadvantageous to its use as a construction material. During use wood continually adsorbs and desorbs water. This cyclic process sets up stresses in the structure of wood leading to the development of cracks, checks and changes in the overall geometry of carefully machined artefacts.

Attempts to impart water repellency and dimensional stability to wood have so far met with limited success. Processes involving transport of water repellent chemicals into wood have to take into consideration the nature of the fluids, their flow characteristics and their interaction with wood. Water repellents and stabilising chemicals have to be transported through the cell structure in order to gain access to interior surfaces for protection of large specimens to be achieved.

The rate and magnitude of treating solution uptake which can be achieved, depend largely on the diameter and tortuosity of the flow paths. There is a tremendous variation in these parameters in wood, not only between but also within species. Variations are immense even within a single tree, depending upon a host of factors. Wood specimens from different heights, from juvenile or mature wood or from wood formed early or late in the growing season in the same tree may behave quite differently. These differences are due to differences in wood anatomy and hence any study of the nature and distribution of chemical coatings or reactants within the porous structure must take the anatomy of wood into consideration.

1.2 Gross Structure of Wood

Structural elements in wood responsible for fluid conduction vary between as well as within species depending on a number of factors. Wood formed early in the growing season differs from that formed later (Stamm, 1964). This is more obvious in the trees of temperate zones where seasonal climatic variation is greater than in tropical regions. In the tropics, conditions suitable for active growth occur throughout the year.

Marked differences are seen between the conduction pathways of Angiosperms or hardwoods and Gymnosperms or softwoods. In softwoods, tracheids form the axial fluid transport pathways. Transverse movement of fluids takes place through pits interconnecting axial elements and through rays (Isenberg, 1963). In hardwoods, vessels are responsible predominantly for the axial transport of fluid. Fibres and rays connected to these vessels build up a supplementary system for axial and radial transport of fluids.

In softwoods, the early wood tracheids are wide and thin-walled, with the radial width exceeding the tangential width. As the growing season progresses, the cell walls go on thickening, but the radial width of the cells decreases. At the end of summer, this process becomes quite pronounced, the radial width diminishing to as little as a third and the cell wall thickness, in some cases, exceeding three times that of cells formed early in the growing season (Stamm, 1964). The latewood tracheids are narrower and thicker-walled (Jane, 1970). Thus, the early wood lumina are likely to offer easier fluid conduction passages than those of the late wood cells. This effect is, however, offset by the greater incidence of pit aspiration in earlywood than in latewood (Phillips, 1933; Petty, 1972; Comstock and Côté, 1968). Aspiration plays a dominant role in the fluid flow mechanics of tracheids (Banks, 1971b; Bolton and Petty, 1977). In most hardwoods, the latewood vessels are thicker-walled, smaller in diameter and fewer in number compared to those in earlywood.

Wood is composed of complex structural arrangement of a number of different types of cells. The structure of softwoods is simpler than that of hardwoods. Between 90 and 95% of the softwood volume may consist of axial tracheids. These are longitudinal cells which fulfil the dual function of sap conduction and tree support. They are hollow, tubular cells, tapered and closed off at the end. Generally, they are 2.5 to 7mm in length (Wenzl, 1970), averaging about 3.5mm (Kollmann and Cote, 1968). In transverse width they range between 0.015 to 0.08mm, but most fall between 0.02 and 0.05mm (Kollmann and Cote, 1968). Their ends are rounded in radial section and rather more pointed in tangential plane (Banks, 1974). Cross-sectionally, they are square or polygonal in shape (Wenzl, 1970; Jane, 1970; Isenberg, 1963). Axial tracheids in juxtaposition overlap one another over about one third of their length. Axial fluid transport takes place from tracheid to tracheid through interconnecting bordered pits (Wenzl, 1970; Stamm, 1964).

Of the rest of the softwood volume, some species may have up to one percent longitudinal resin canals. They have no role in the conduction of fluid in the living tree but may contribute a little to liquid conduction in dried timber. The remaining 5-8% of the softwood bulk volume consists of ray tissues. These tissues extend horizontally in the general direction of pith to periphery and help in the radial conduction of sap in wood. The ray tissues may be of four types: (i) ray parenchyma, (ii) strand tracheid, (iii) ray tracheid and (iv) resin canal.

The roughly rectangular ray parenchyma cells measure approximately 0.2 to 0.5mm in length and 0.01 to 0.05mm in breadth. Fluid transport between these cells occurs in all directions through simple pits in adjacent cells (Phillips, 1948). Interconnection between ray parenchyma and longitudinal tracheids generally occurs by way of half bordered pits (Phillips, 1948; Jane, 1970).

Strand tracheids are not of regular occurrance. They are formed from the fusiform initials of the cambium. Several transverse partition walls or septa may form inside the strand tracheid to divide it into several sections. Each of these sections may develop into individual strand tracheids (Jane, 1970). These brick shaped cells are similar to the parenchyma cells but their walls are provided with bordered pits (Jane, 1970). Communication between these rays and the tracheids occurs through small bordered pits. Strand tracheids are usually found associated with vertical resin canals and sometimes with parenchyma cells and in the boundaries of the growth rings.

Ray tracheids develop from ray initials of the vascular cambium and are present in the rays of many softwood species. One or more rows of these cells may form the upper and lower margins of the ray cells or may sometimes be interspersed among the ray parenchyma. Ray tracheids are similar to ray parenchyma cells in most respects except that the former are provided with bordered pits in place of simple pits. Fluid flow between adjacent cells occurs by way of the intercellular pitting briefly described.

The axial elements in hardwoods are more varied than those in softwoods. Hardwood fibres are short and usually range from 1 to 1.5mm in length (Stamm, 1964). Tropical species yield even shorter fibres (Razzaque and Siddique, 1977). The average diameter of hardwood fibres is 0.015mm. They are arranged less orderly in the tree than are softwood tracheids. The fibres are interspersed with shorter, thinner walled parenchyma cells and much wider vessels. Four or five types of elements, vessels, parenchyma, libriform fibre, tracheid and fibre tracheid are present in hardwoods in proportions varying with species (Table 1.1; Huber and Prütz, 1938).

Vessels are formed from axial rows of cells, by the partial or complete disappearance of their end walls. They vary enormously in size in different woods and are responsible for most axial fluid conduction in the tree. This is facilitated by the fact that they are joined end to end by extremely porous structures, called perforation plates (Tsoumis, 1968; Jane, 1970). The vessels thus form continuous longitudinal channels for the transport of fluid. They may constitute as little as 6.5% and as much as about 35% of the total volume of wood (Kollmann and Cote, 1968). In some species the vessels are dispersed quite uniformly throughout the growth rings. These are known as diffuse porous species. In these species the variation in vessel diameter is only a few fold. A second group of hardwoods, known as ring porous woods, has much larger and abundant vessels in the early spring wood, than in the latewood (Wenzl, 1970; Wardrop and Davies, 1961; Hunt and Garrat, 1967).*

Table 1.1 Proportion of different elements in wood *

Species	Average Volume Percent			
Softwoods	Fibres	Wood rays	Wood parenchyma	Vessels
Spruce (*Picea excelsa*)	95.3	4.7		
Pine (*Pinus sylvestris*)	93.1	5.5	1.4	
Larch (*Laryx europaea*)	91.2	8.8		
Fir (*Abies pectivata*)	90.4	9.6		
Hardwoods				
Horse Chestnut (*Aesculas hippocastamon*)	76.1	15.5		8.4
Birch (*Betula verrucosa*)	64.8	10.5		24.7
Ash (*Fraxinus excelsior*)	62.4	14.9	10.6	12.1
Aspen (*Populus tremula*)	60.9	12.7		26.4
Oak (*Quercus pedunculata*)	58.1	29.3	4.9	7.7
Beech (*Fagus sylvatica*)	37.4	27.0	4.6	31.0

Parenchyma cells are arranged radially in hardwood, as in softwood. Additionally, longitudinal parenchyma cells are usually present in hardwoods. In hardwood, rays are several cells wide and make up a larger proportion of the wood bulk than do the rays in softwoods (Table 1.1). The large volume of the ray cells may abcount for the greater radial diffusion rate compared to that of tangential rate observed in hardwoods (Burr and Stamm, 1947).

The libriform fibres or sclerenchyma are short and thin walled and their cross sections are usually circular or oval.

Intermediate forms of fibres between vessels and libriform fibres are known as tracheids and fibre tracheids in hardwoods. However, their proportion is very low. In beech, for example, they amount to only 0.4 to 1.2% (Wenzl, 1970).

1.3 Ultrastructure of wood

1.3.1 Cell wall structure

Wood cells are formed in the cambium initially with the outermost wall enveloping the entire cell (Jane, 1970). Later, a secondary layer (S) forms inside the initial or primary (P) layer. Preston (1934) and other workers demonstrated secondary wall of plant cells to be conspicuously straited and laminated (Wardrop and Dadswell, 1952a; 1952b; Emerton and Goldsmith, 1956; Hodge and Wardrop, 1950). The secondary wall is now recognized to consist of three layers, S_1, S_2 and S_3, outer, middle and inner layers respectively. There is some evidence of the presence of a fourth, S_4, layer in the secondary wall, but its existence remains a subject of controversy. The presence of a warty layer has, however, been established in some species. It forms the innermost layer of the secondary wall lining the lumen (Fengel, 1969).

Cells in the xylem of a tree remain bound together by the matrix substance. This intercellular material forms the middle lamella (ML). The ML, in most cases, remains in intimate union with the primary wall. The primary wall, averaging only 0.2 μm in diameter, is sometimes difficult to distinguish from the ML. To obviate the difficulty, the ML and the primary walls of two bordering cells are given the collective name of compound middle lamella (CML; Jane, 1970). The primary wall, thin as it is, strongly influences the swelling and shrinking properties of wood fibres (Stamm, 1964).

As the growing cell approaches maturity, the much stiffer secondary cell wall begins to be deposited (Wardrop and Harada, 1965). The secondary wall, extending from the primary cell wall into the lumen, constitutes the bulk of the total cell wall, ranging from 1.5 to 4.5 μm in thickness (Table 1.4). The S_1 and S_3 layers are thinner compared to the S_2 layer (Fig. 1.1).

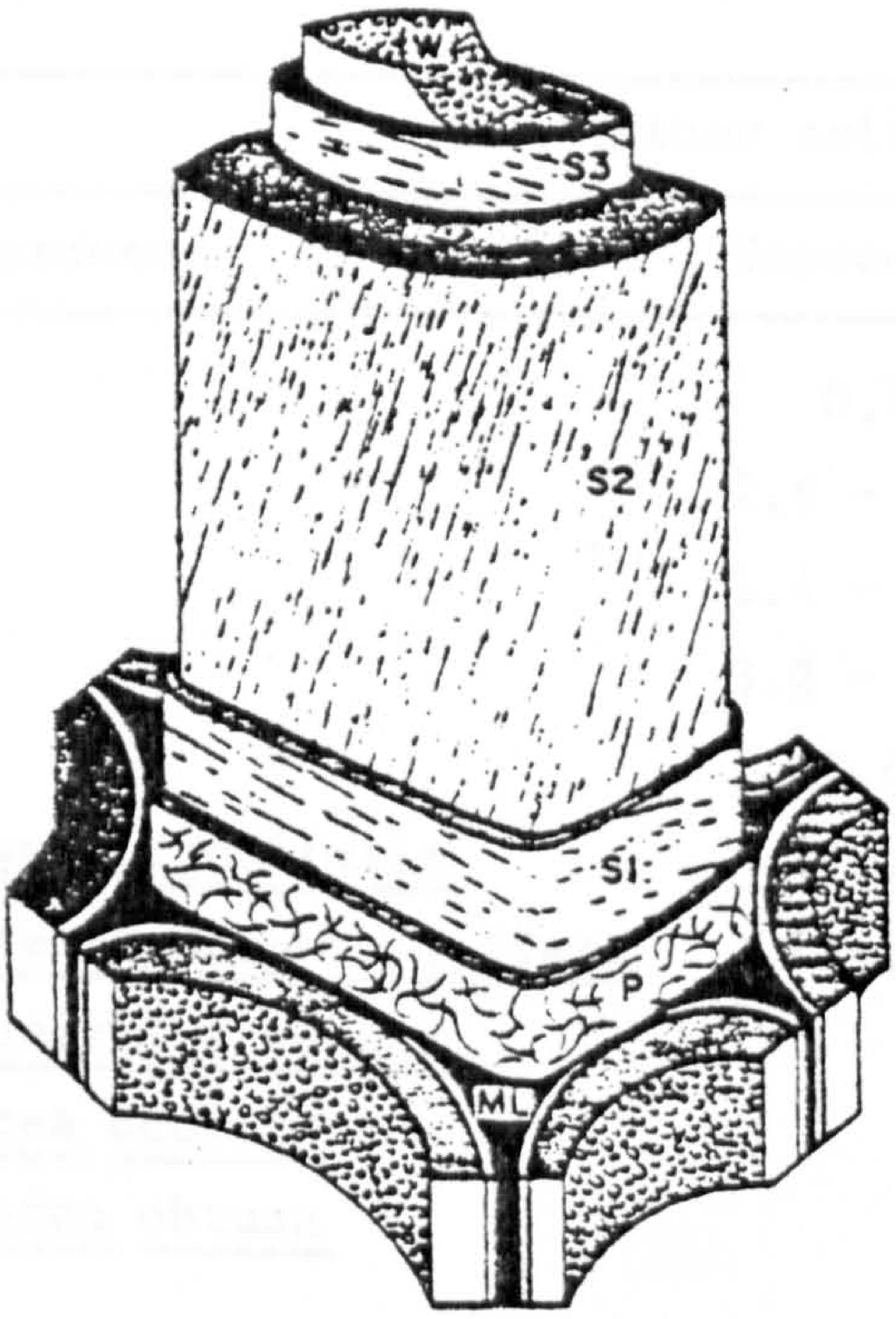


Figure 1.1 Schematic diagram of the cell wall of wood cells. This is a generalized plan applicable to many cells in both softwoods and hardwoods (Côte', 1981). ML = middle lamella, P = primary wall, S_1, S_2 and S_3 = layers in secondary wall, W = warty layer.

1.3.2 Cell wall composition

In nearly all species 90 to 95% of wood is comprised of cellulose, hemicellulose and lignin. These natural polymers constitute the cell wall material. A major portion of the remaining 5-10% may be removed by extraction with water or organic solvents without altering the structural nature of wood. There is considerable variation in the amount and distribution of extractives between species, within a particular species and throughout the wood of a given tree (Buchanan, 1963).

Table 1.2 Variation in some extractive content in wood (Mutton, 1962; Hillis, 1962)

Species		Ether soluble extract (%)		Polyphenol in wood (%)
Softwood	Hardwood	Sapwood	Heartwood	
Abies balsama		0.95	0.74 - 1.18	
Pinus echinata		2.6 - 3.8	3.9 - 13.3	
P. palustris		1.4 - 2.7	3.6 - 20.3	
P. ponderosa		3.2 - 4.8	2.7 - 9.9	1.0
P. strobus		5.46	3.62	
	Fagus grandifolia	.19-.26	.38 - .57	
	Lireodendron tulipifera	.13-.27	.43 - .58	
	Eucalyptus wandoo			16.0
	Hopea odorata			10.0
	Shorea obtusa			6-7

Extractives are not essential components of wood cell structure and as such they, along with the minerals, are collectively known as extraneous materials. They include polysaccharides, polyphenols, terpenes, resins, essential oils, alkaloids, gums, mucilages, waxes and other colouring and odouring substances (Table 1.2). They influence the hygroscopicity, density, permeability, durability and several other properties of wood (Narayanamurti, 1957; Wangaard and Granados, 1967). Resinous materials in softwoods and oils and oleoresins in hardwoods usually account for most of the extractives.

Cellulose, hemicellulose and lignin are not evenly distributed across the cell wall. Their distribution varies greatly between species. Inter-tree and intra-tree variation in the distribution of the chemical components in the same species may occur depending on location within the stem, growth conditions and age (Harlow, 1952; Fengel, 1969).

Broadly speaking, 45-50% of the cell wall material in softwood species is cellulose. Of the rest, 20-35% is hemicellulose and 25-30% is lignin (Fengel, 1969; Koch, 1972). In hardwoods, comparatively more hemicellulose and less lignin (15-25%) is present in the cell walls (Koch, 1972).

The true middle lamella contains up to 85% lignin. The remaining 15% has a high percentage of hemicelluloses and pectins and little or no cellulose. The primary wall being very thin, the combined middle lamella as a whole is also highly lignified (Fig. 1.2; Scott et al., 1969; Bentum et al., 1969; Fergus et al., 1969). Although the secondary wall is less lignin rich, because of their greater mass, the bulk of the lignin content of wood cells is located there and not in the CML (Fengel, 1969). In fact, only about 35% of the cell lignin is located in the CML, the rest being distributed throughout the other cell wall layers (Berlyn and Mark, 1965).

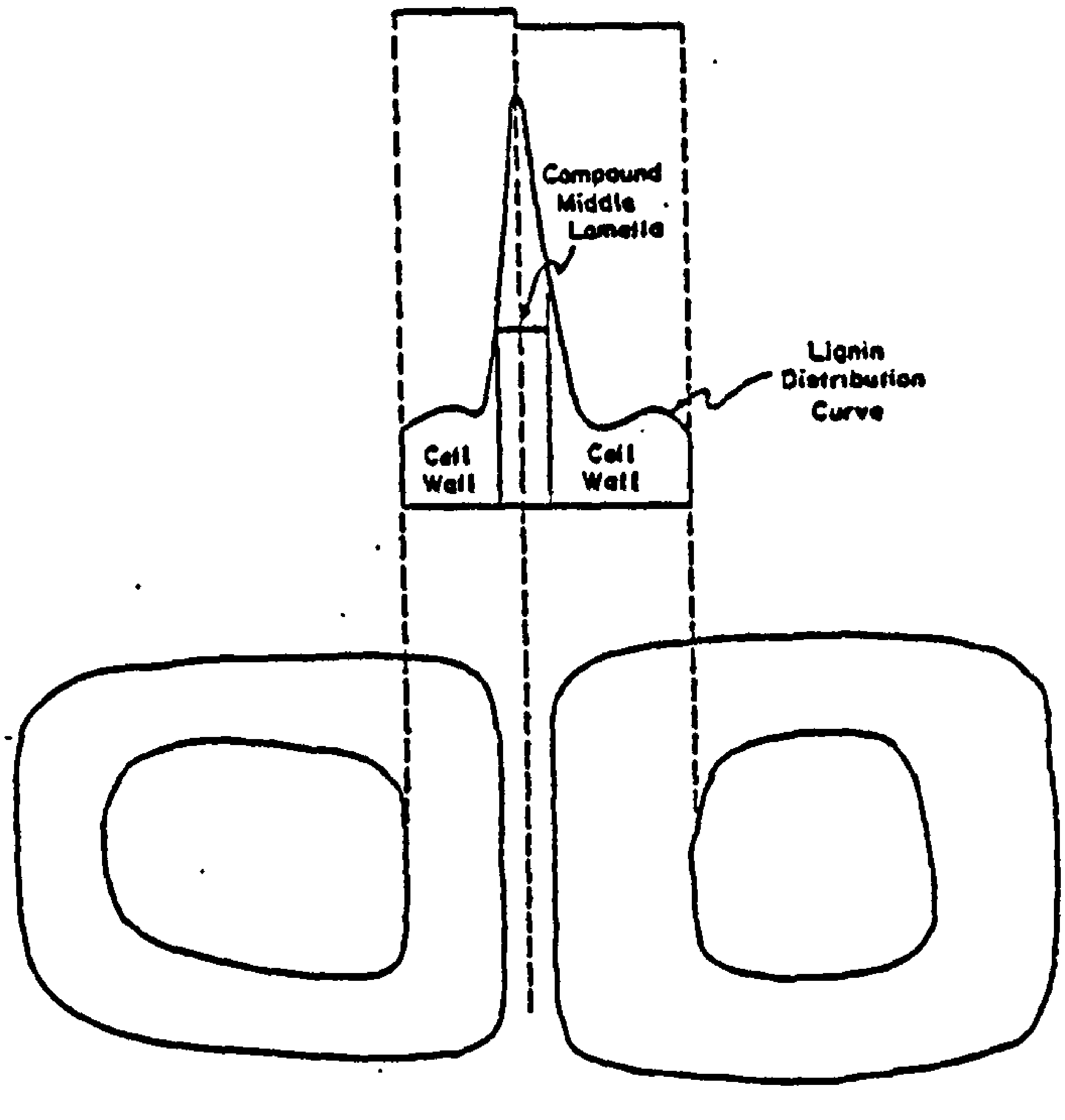


Figure 1.2 Schematic design of lignin distribution in middle lamella and cell wall (modified drawing on the plan of R.E. Mark, 1967).

The primary wall is comprised of substantial quantities of all the three major chemical components. It has less lignin compared to the true middle lamella and a higher proportion of cellulose and hemicellulose than in the secondary walls. Most of the cellulose is located in the S_2 and S_3 layers of the secondary wall (Table 1.4; Fengel, 1969).

The chemical nature of the warty layer is not very clear. When the cell wall polysaccharides are dissolved chemically, a lignin skeleton is left. Electron micrographs of the lignin skeletons show a high concentration of lignin lining the lumen (Berlyn and Mark, 1965). This fact, along with the observation that white rot fungi, secreting lignolytic enzymes, and not brown rot fungi, secreting only polysaccharidases, can fully dissolve the warty layer, indicates the presence of lignin in the warty layer (Fengel, 1969).

Table 1.3 The composition (gravimetric) of softwood cell walls (Fengel, 1969)

	Cellulose	Hemicellulose	Lignin
Early wood	49.8	19.1	31.1
Late wood	52.8	17.6	29.6

Table 1.4 The relative volume (%) composition of cell wall layers (Fengel, 1969)

Cell wall layer	Earlywood	Latewood	Cellulose	Hemicellulose	Lignin
CML	15.0	10.0	12.4	25.6	62.0
S_1	12.2	7.6	34.5	35.5	30.0
S_2 and S_3	72.8	82.4	55.7	14.3	30.0

1.3.3 Organization of the cell wall constituents

Cellulose is supposed to be the fibrous framework substance giving form and structure to the cell wall (Koch, 1972; Fengel, 1969). It shows a considerable degree of organization or crystallinity. Polarization microscopy, X-ray and electron defraction studies give convincing evidence of the crystalline or partially crystalline nature of cellulose (Mark, 1940; Hagglund, 1951; Farmer, 1967; Preston, 1965; Ritter and Stillwell, 1934). The hemicelluloses may show a limited degree of crystallinity (Wise and Jahn, 1952). Lignin is amorphous in nature (Kollmann and Cote, 1968; Stamm, 1964).

The cellulose and hemicellulose molecules are aggregated into bundles to form microfibrils of indefinite length and from 100 to 300 Å in width (Wardrop, 1964). X-ray and small angle X-ray scattering indicate that the crystalline regions have a diameter of 50 - 100 Å (Kollmann and Cote, 1968). These values are in excellent agreement with the size of the microfibrils observed by electron microscopy (Stamm, 1964). Cellulose behaviour deviates from that expected of a perfect crystal. This is explained by the fact that the cellulose molecular chains end within the microfibrils, causing dislocation within otherwise perfect crystalline lattices (Wilkie, 1970; Muhlethaler, 1969; Fig. 1.3). Further, cellulose chains emerging from a single crystallite may enter other adjacent crystallites through disorientated amorphous zones (Howsmon and Sisson, 1954).

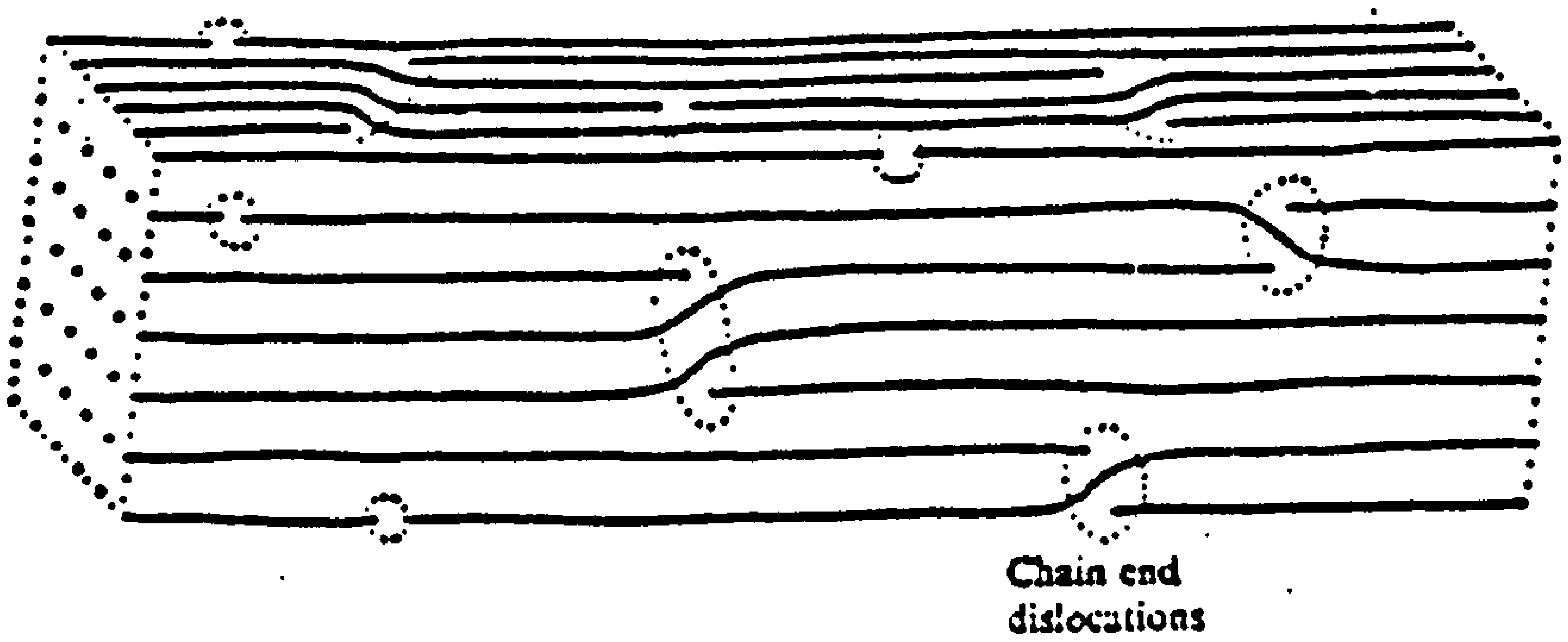


Figure 1.3 Cellulose microfibril chains ending within the fibrils causing dislocations within otherwise perfect crystalline lattices.

Besides the disorder arising out of the chain end dislocations and cellulose chains passing through disoriented amorphous zones, considerable disorder may be caused as a result of cellulose molecules lying on the surface of the microfibril. These molecules are less strongly bound to the microfibril than those lying in the interior of the microfibril and lead to surface disorder (Statton, 1967; Muhlethaler, 1969; Wilkie, 1970). Within the less organized regions cellulose is likely to be in intimate association with non-cellulosic polysaccharides. Water is able to enter freely through those zones and is adsorbed by the available OH-groups (Stamm, 1964). On the other hand, water cannot penetrate the lattice of the crystallite (Mark, 1952).

The microfibrils join together to form lamellae. The lamellae are differentiated from each other by slight changes in the microfibril angle (Fengel, 1969). Each cell wall layer comprised of several lamellae, has a characteristic microfibril orientation relative to the axis of the cell (Figures 1.4; 1.1; Table 1.5; Thomas, 1977; Kollmann and Côté, 1968*).

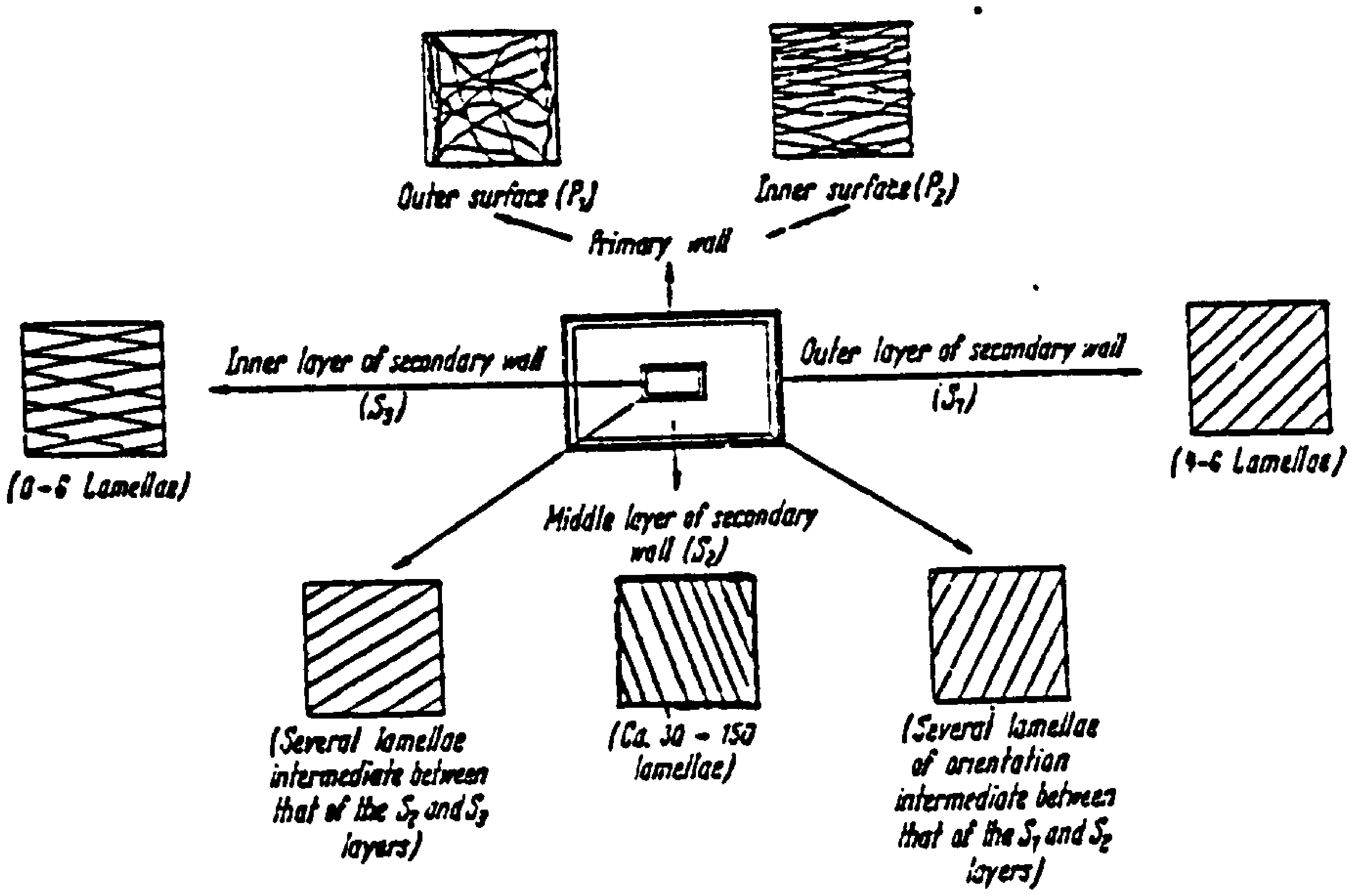


Figure 1.4 Characteristic microfibril orientation of cell wall layers*

Table 1.5 Thickness and microfibril angle of various cell wall layers (Kollmann and Côte', 1968)

Layer	Relative thickness (%)	Angle of orientation made by microfibrils with cell axis (0^o)
P_1	1	Random
P_2		Approaches 90
S_1	10-22	50-70
S_2	70-90	10-30
S_3	2-8	60-90

1.4 Liquid flow in wood

Flow through unblocked porous media is described by Darcy's Law:

$$Q = \frac{KA\Delta P}{\eta l} \qquad \text{Equation 1.1}$$

where Q = volumetric rate of flow;
A = Cross-sectional area of specimen, normal to flow direction;
ΔP = Pressure drop across specimen;
l = Specimen length;
η = Fluid viscosity;
K = Permeability constant.

From Equation 1.1 it can be seen that the permeability constant 'K' is independent of specimen geometry. It has been shown that flow through wood often deviates markedly from Darcy's Law (Banks, 1974, 1981; Bramhall, 1971; Bolton, 1980). The deviation in air dried sapwood has been shown to be due to the high degree of bordered pit aspiration encountered, especially in earlywood. This leads to a situation where K in equation 1.1 is not a true constant, but decreases approximately exponentially with increase in specimen length (Bramhall, 1971):

$$\frac{dQ}{dt} = \frac{KAe^{-bl}\Delta P}{\eta l} \qquad \text{Equation 1.2}$$

where e = Natural logarithmic base; and
b = A positive constant determined by experiment.

When b = 0, $e^{-bl} = 0$ and the equation reverts to Darcy's.

A rather similar effect is encountered with hardwoods. In this case, the partial blocking is generally attributed to the occurrance of tyloses, gum deposits etc. in the vessels. In practice, this partial blocking leads to uneven distribution of impregnant materials in treated wood (Chattaway, 1949; Koran and Cote, 1965; Jane, 1970). This is likely to have a marked effect on the performance of wood preservatives, water repellents and dimensional stabilising treatments.

1.4.1 The wood water system

The interaction of wood with water influences most of the processes involved in the utilization of wood as a building material (Stamm, 1952; Howsmon & Sisson, 1954). The presence of moisture above a certain level in wood to be used for constructional purposes makes it subject to subsequent drying in use, leading to dimensional change. Moreover, wood destroying organisms are active at moisture content above about 20%. Thus, drying of wood to be used for building purposes is a necessity. Even after drying to a reasonable moisture content, wood exposed to fluctuating sources of water (rainfall, changing relative humidity) will change its moisture content in sympathy with the fluctuations. In many environments, wooden building components are subjected to periods of high and low moisture content. This gives rise to dimensional changes which impose mechanical stress onto the individual wood pieces and onto the components fabricated from them. Furthermore, such fluctuations may from time to time allow the wood to remain sufficiently wet for periods long enough to allow significant fungal degradation to occur.

1.4.2 Water flow into wood

Mass flow of liquid into the gross capillary structure in the absence of an applied pressure differential is controlled by the so-called capillary pressure, arising from the interaction of surface forces associated with the walls of the capillary (wood in this case) and the flowing liquid (water). Capillary pressure, Pc, is defined by the Jurin equation thus:

$$Pc = \frac{2\gamma \mathrm{Cos}\theta}{r} \qquad \text{Equation 1.3}$$

where Pc = Capillary pressure;

γ = Surface tension of liquid;

θ = Contact angle of water with capillary wall;

r = Capillary radius.

Examination of equation 1.3 shows that Pc can assume both positive and negative values depending on whether θ is greater or less than 90^o. Where $\theta < 90^o$, Cos θ and hence Pc is positive and the liquid flows spontaneously into the capillary. For values of $\theta > 90^o$, however, Cos θ and Pc are negative and an external force to overcome this negative pressure is needed to cause capillary penetration to occur.

Substitution of the capillary pressure term into the integrated form of Darcy's equation (non-steady state) gives rise to equation 1.4 below, which describes the non-steady state flow of liquids into unblocked porous media of uniform pore radius.

$$V = A \left(\frac{2kt}{\eta}\right)^{\frac{1}{2}} \left(\frac{2\gamma \text{Cos}\theta}{r}\right)^{\frac{1}{2}} \qquad \text{Equation 1.4}$$

where V = Volume of liquid absorbed in time 't';

A = Cross-sectional area of specimen;

k = Permeability constant;

η = Liquid viscosity

γ = Liquid surface tension

θ = Contact angle;

r = Capillary radius.

It must be borne in mind that for wood this equation is further complicated by two factors.

1) Wood, especially air dried wood, is not a totally unblocked medium and hence flow through it is not accurately described by Darcy's Law (Sec.1.4).

2) The capillaries comprising wood structure are not uniform, hence flow occurs more rapidly through some than others (Banks, 1981).

Even with these constraints, however, it is clear that the rate of liquid penetration of wood due to capillarity is strongly dependent on the contact angle θ (see equation 1.3).

1.5 Methods of diminishing water uptake and dimensional instability in wood

Water is strongly sorbed by the free OH-groups in wood. If these reactive groups are rendered hydrophobic or at least inert to the action of water, hygroscopicity is substantially reduced or eliminated. Ideally, if the OH-groups in cellulose and lignin could be reduced to hydrogen groups, significant reduction in hygroscopicity could be achieved (Stamm, 1964). All the known methods of wood hydrogenation, however, lead to breakdown of cellulose and lignin to lower molecular weight products, thus degrading the desirable mechanical properties of wood.

In practice, reduction in the rate or amount of water sorption and dimensional change is generally achieved by employing either:

1) physical or mechanical treatments, or

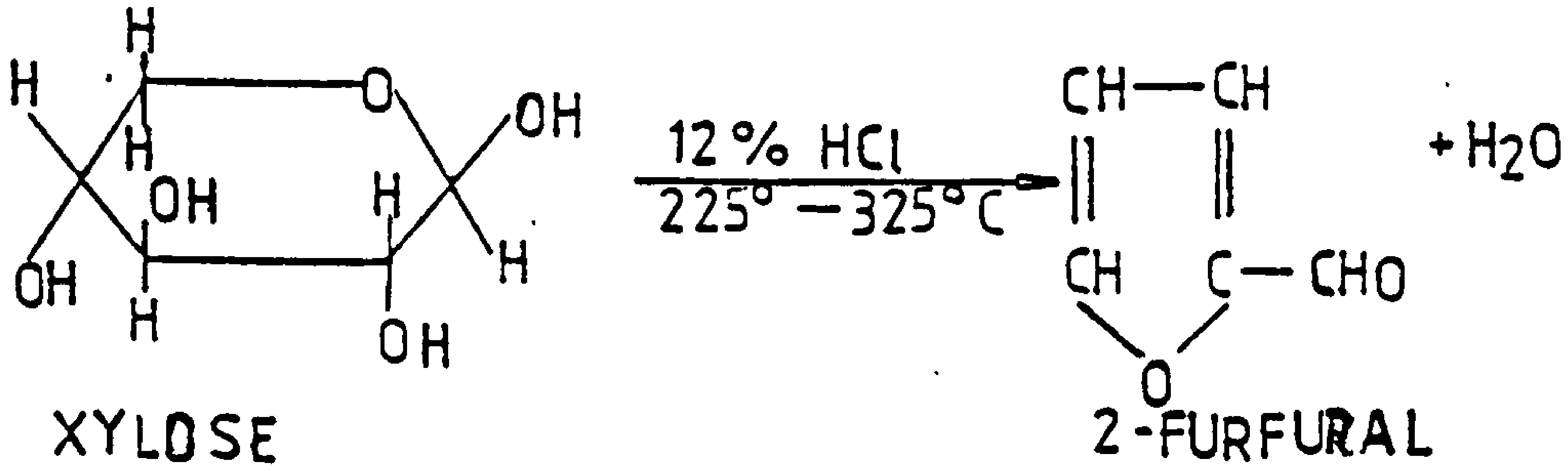
2) chemical treatment to reduce hygroscopicity.

1.5.1 Physical and mechanical treatments

The anisotropic swelling of wood in the longitudinal and tangential directions can be minimized by cross-laminating odd number of veneers to form plywood. Cross-lamination does not prevent swelling, but it changes its direction so as to nullify the swelling effect and limit it to a few tenths of a percent in the length and width directions (Stamm, 1964).

Attempts have also been made to stabilize wood by subjecting it to controlled heat treatment. This causes some loss of water of constitution accompanied by the breakdown of the more hygroscopic hemicelluloses (Stamm, 1959 ; Seborg et al., 1953). The breakdown products furfural polymers, being less hygroscopic, afford some degree of dimensional stability (Shafizadeh and Chin, 1977).

$$\text{Hemicellulose} \xrightarrow[\text{hydrolysis}]{\text{Acid}} \text{Pentoses} + \text{Hexoses}$$



Increased dimensional stability may also be achieved by bulking the cell wall capillaries in wood. Various organic substances and inorganic salts have been used with varying degrees of success, but their water solubility and deliquescence detracts from their value.

Synthetic resins applied as monomers or pre-polymers and cured *in situ* to form homopolymers or wood/plastic copolymers have been used with some success (Choong and Barnes, 1969). These treatments which may reduce instability by a combination of

1) mechanical constraint due to hard cured polymer within cell lumina,
2) cell wall bulking by polymer bonded within the cell wall, and
3) pore blocking, making water access difficult,

are often effective but tend to be expensive because a large volume of chemical is needed to fill the cell cavities (Rowell and Gutzmer, 1975).

Of all the physical treatments, the application of surface coating agents to protect wood by forming a physical barrier, is the most widely used. It is well known that paints, varnishes and lacquers in a drying oil medium form tough films on wood surfaces which give effective reduction in the rate of water ingress.

It has been found that a two coat application of a well formulated paint or varnish (based on natural drying oils or alkyd resins) can give a water excluding efficiency of up to 95%. Water excluding efficiency (WEE), variously termed as water repellent efficiency (WRE) or degree of efficiency is calculated as:

$$\mathrm{WEE} = \frac{\mathrm{AU}-\mathrm{AT}}{\mathrm{AU}} \times 100 \qquad \text{Equation 1.5}$$

where AU = Water absorption by untreated specimens in a given time, and
AT = Water absorption by treated specimens in the same time.

These coatings, however, deteriorate with time rather quickly. Change of relative humidity and temperature over a relatively short period can lead to the formation of checks and cracks. Once a paint or varnish coating starts to breakdown, water uptake rate is increased and further deterioration occurs more rapidly (Borgin and Corbett, 1973). Vasisth et al. (1974) using SEM and light microscopy observed the development of microchecks in all weathered painted wood surfaces. Even three coats of paint were shown to lose their efficiency in less than a year (Stamm, 1964). To try to extend the effectiveness of coatings, techniques to introduce them into the cellular structure as internal lumen coatings, have been developed (Stamm, 1964). It has been found that they are more effective when they are formulated to contain a hydrophobic (water repellent) component (Borgin and Corbett, 1973; Purslow, 1966).

1.5.1.1 Principles of water repellency

In section 1.5.1 it has been shown that to a first approximation, the volume of water (V) absorbed as a result of capillary pressure is given by equation 1.4. From this equation it is apparent that

$$V \propto Cos\theta^{\frac{1}{2}} \qquad \text{Equation 1.6}$$

(θ = wood/water contact angle)

In the wood/water system, θ is the only variable of Equation 1.4, which can be externally manipulated. A surface which is wetted by water, allows water to spread over it in a continuous film. A water repellent surface allows the water to stand in separate droplets covering the minimum possible surface area. At the periphery of these droplets the water air interface forms an angle with the solid surface. This angle, enclosed within the water phase is known as the contact angle (Figure 1.5).

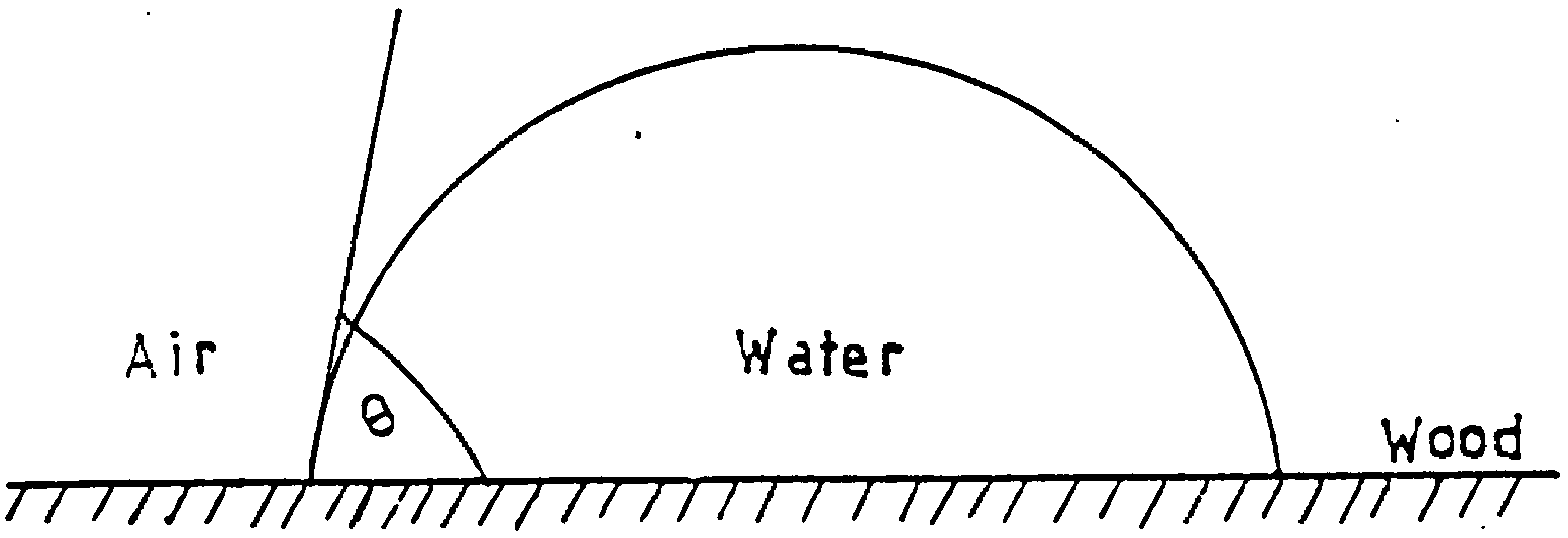


Figure 1.5 Contact angle (θ) of water on wood surface.

The condition for existence of a finite contact angle was first propounded by Young (1805). He explained the existence of the contact angle in terms of the liquid-solid adhesive forces and the liquid-liquid cohesive ones. If the cohesive forces within the liquid are greater than those of adhesion with the solid, there will be a finite contact angle. The larger the cohesion, compared to the adhesion, the larger the angle, which may theoretically be as large as 180°. In practice the largest angle ever measured on a smooth surface is about 115° (Adam and Jessop, 1925; Ray and Bartell, 1953; Adam and Elliott, 1962). On the other hand, if the adhesion is equal to or greater than the cohesion, the liquid will completely wet the solid and the contact angle will be zero. The condition can be quantitatively expressed by the Young-Dupre equation:

$$W_{SL} = \gamma_L (1 + \mathrm{Cos}\theta) \qquad \text{Equation 1.7}$$

where W_{SL} = Work of Adhesion;
γ_L = Surface free energy of liquid;
θ = Contact angle.

The right hand side of the equation contains easily measurable quantities γ_L and θ, liquid surface free energy or surface tension and liquid/solid contact angle respectively. When WSL is smaller than $2\gamma_L$ there is a finite contact angle. As WSL increases, the contact angle decreases till it becomes zero, at which point WSL = $2\gamma L$. At the other theoretical limit of a contact angle of 180°, there is no adhesion between the liquid and the solid.

The contact angle is dependent not only upon the free energies (Good and Kotsidas, 1979), of the solid, liquid and solid-liquid interface but also on the RH and temperature at which it is measured and the time lapse after initial contact. The initial moisture content and swelling (Adam, 1964) of the solid and the surface roughness of the solid also influence the contact angle (Borgin, 1965; Bikerman,1968). Of these factors all but the last mentioned one can be externally controlled. However, wood surfaces are always rough, no matter how carefully they are prepared. Even after careful microtoming, cut cells give rise to a complex form of roughness at a microscopic level (Fig. 1.6).

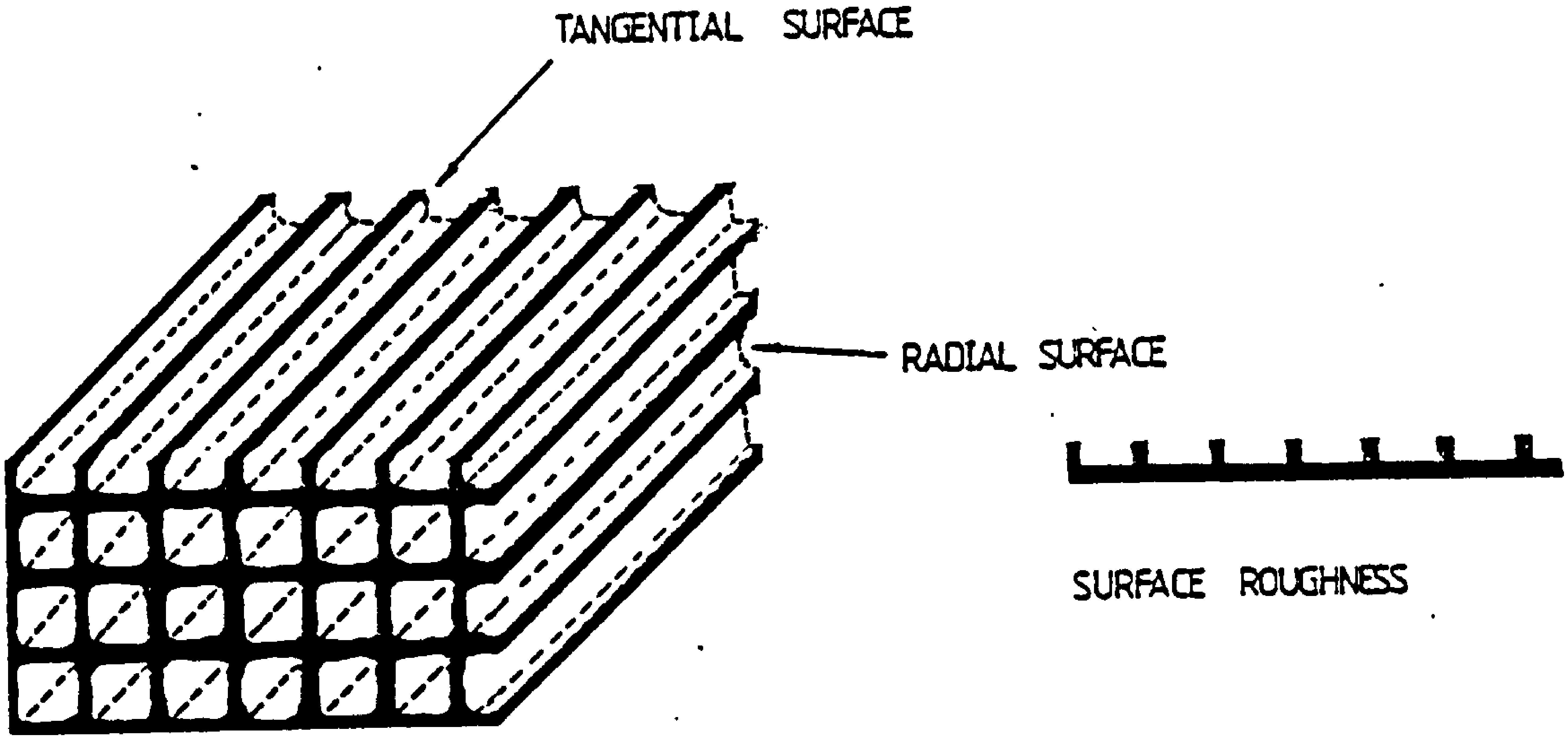


Figure 1.6 Surface roughness due to sectioning of vessels, tracheids and fibres

From Young's equation it is seen that

$$\gamma_S - \gamma_{SL} = \gamma_L \text{ Cos } \theta \qquad \text{Equation 1.8}$$

where γ_S = Surface free energy of solid;

γ_L = Surface free energy of liquid;

γ_{SL} = Interfacial energy of solid-liquid interface;

θ = Contact angle.

This equation strictly applies only to perfectly smooth surfaces. For rough surfaces whose real area is 'r' times the apparent area, Equation 1.6 becomes,

$$r\,(\gamma_S - \gamma_{SL}) = (\gamma_L \text{ Cos}\theta)$$

Hence, $$\gamma_L \text{ Cos } \theta' = r\gamma_L \text{ Cos } \theta$$

where θ' = Contact angle measured on rough surface,

or $\text{Cos } \theta' = r \text{ Cos } \theta$ (Wenzel, 1936).

The practical implication of this is that for values of θ less than 90°, θ' is decreased by surface roughness, whilst for $\theta > 90^\circ$ it is increased.

For untreated wood surfaces Θ is generally of the order of 0-30° or so (Nguyen and Johns, 1978; 1979; Borgin, 1965), and hence liquid water is able to enter the pore space spontaneously, the roughness factor re-inforcing this effect. Hydrophobic substances (water repellents) applied to wood increase the contact angle to values around 100-115°, giving rise to a negative value of Cos Θ and hence resistance to water penetration, which is more apparent on rough surfaces than smooth ones. This is the principle of water repellent treatments applied to wood (Nguyen and Johns, 1978; 1979).

It is clear from the discussions made in the preceding section that an effective water excluding treatment which will totally stabilize wood against dimensional changes is yet to be developed. However, water repellent treatment preventing or greatly reducing the rate of water uptake by capillarity has been shown to be effective in reducing the initial rate of water uptake and hence, dimensional instability of wood in use (Purslow and Williams, 1978). Evidence regarding the long term effectiveness of water repellents applied to wood is ambiguous. For example, using 'T' shaped jointed specimens, Purslow and Williams (1978) report significant loss of effectiveness of many formulations after one or two years' exposure to the weather. On the other hand, Feist and Mraz (1978b) report work carried out in the U.S.A. demonstrating effectiveness of fairly similar formulations over a twenty year period. From the above studies it seems likely that much of the apparent difference in performance is related to differences in the geometry of the test specimen and the severity of exposure. It is possible, however, that apparently trivial formulation differences in the type of solvent and fungicide used might also contribute to the differences.

Broadly known as "water repellents", these formulations generally have two components in an organic solvent vehicle, in addition to fungicides and insecticides. One of the components is the true water repellent or hydrophobic substance. This is usually a hydrocarbon (paraffin) wax or sometimes a silicone or organometallic material. The other, whose function is to disperse the hydrophobe and bond it to the wood cell wall is a natural or synthetic resin or in some cases a drying oil. In addition to its role as a dispersant/bonding agent, the resin component in the formulation is believed to form a coating on the cell walls including the pit openings. As a result, it may act as a mechanical barrier to liquid water flow complementary to that due to the hydrophobic effect (Stamm, 1964; Voulgaridis, 1980). As a mechanical water barrier, however, the film is far from perfect, since it is believed that imperfections occur during film formation (Borgin, 1961).

The use of resin alone in the formulation, therefore, may be expected to restrict the water sorption and swelling rate to a relatively minor degree. It has been shown by Voulgaridis and Banks (1979) that treatment of pine with resins gave rise to a low degree of water resistance, whereas in beech such treatments showed marked effectiveness in reducing the rate of water uptake. This has been ascribed to structural differences between the species tested. It is believed that the fine pit pores interconnecting vessels and fibres in beech are more effectively coated by the resin than the much larger bordered pit membrane openings in pine.

1.5.1.2 Chemical nature of water repellents

A variety of chemical substances are available for commercial utilization as water repellents, to be applied to wood. The principle requirement is that the component groups should be nonpolar, i.e. having little affinity for water. Examples are waxes, hydrocarbons and silicones. Conceptually, it is attractive to think of water repellent chemicals containing a polar end capable of bonding to wood, well separated from the hydrophobic tail (Borgin and Corbett, 1969). This idea has not been developed, however. Currently used formulations as mentioned earlier, usually contain a resin or a drying oil to act as the keying agent between the cell wall and the hydrophobic material. These are generally dissolved in a hydrocarbon solvent and deposited into the cell lumen by immersion, vacuum or pressure treatments. After the solvent evaporates, the water repellent constituents form a deposit on the cell lumens including the pit areas. The nature and mode of operation of the deposit depends on the type of materials used.

The resins used may be natural or synthetic. A variety of resins, alkyd, straight chain hydrocarbon, hydrogenated resin ester, coumarone/indene etc., have been used from time to time. The presence of the hydrocarbon groups within the resin may contribute some hydrophobicity to the treated surface. By and large, however, the hydrophobicity comes from the paraffinic component of the formulation. The higher alkanes or the paraffins of the general formula C_nH_{2n+2} present methyl groups at the treated surface, giving rise to contact angles of over 90° (Adam, 1941). Paraffin waxes on smooth surfaces give contact angles varying from 105° to 114° (Adam, 1963).

Borgin (1961) found that water in the cell wall up to the FSP does not affect the absorption of water repellents at all. Whereas, water present in the lumen as free water drastically cuts the absorption of water repellents by wood. This points to the fact that water repellents are unlikely to penetrate cell walls (Stamm, 1964). This is to be expected, given their general non-polar character.

The water repellent deposit is believed to be held on the internal surfaces of wood by Van der Waal's forces. These bonds are rather weak, ranging between 1 and 15 KJ/mole (Higgins, 1977). Loss of effectiveness of water repellent treatments may be due to the effect of three different factors acting either independently or in combination. These are:

(a) changes in the wood substrate;
(b) adhesive failure between wood and the deposit;
(c) cohesive failure of the deposit.

(a) Changes in wood substrate: Under weathering conditions wood swells and shrinks in sympathy with atmospheric humidity changes and as a result of wetting by rainfall etc. Water repellent treatment slows down but does not prevent these processes. Ultimately the stresses brought about by these changes cause wood degradation manifested by end grain defibrillation (Voulgaridis, 1980) and checking, microchecking and splitting of longitudinal surfaces (Borgin and Corbett, 1973). It is likely that the microscopic effects associated with these macroscopic changes weaken or destroy the wood resin bond.

(b) Wood-deposit adhesive failure: Adhesive failure of the wood-deposit bond has been explained by Borgin (1965; 1968) as a process of "preferential wetting". As a result of water gaining access to the cell wall by way of flaws in the deposit or by slow molecular diffusion through it, it is suggested that the weak Van der Waal wood-deposit bond is replaced by a stronger wood-water hydrogen bond (see Figure 1.7).

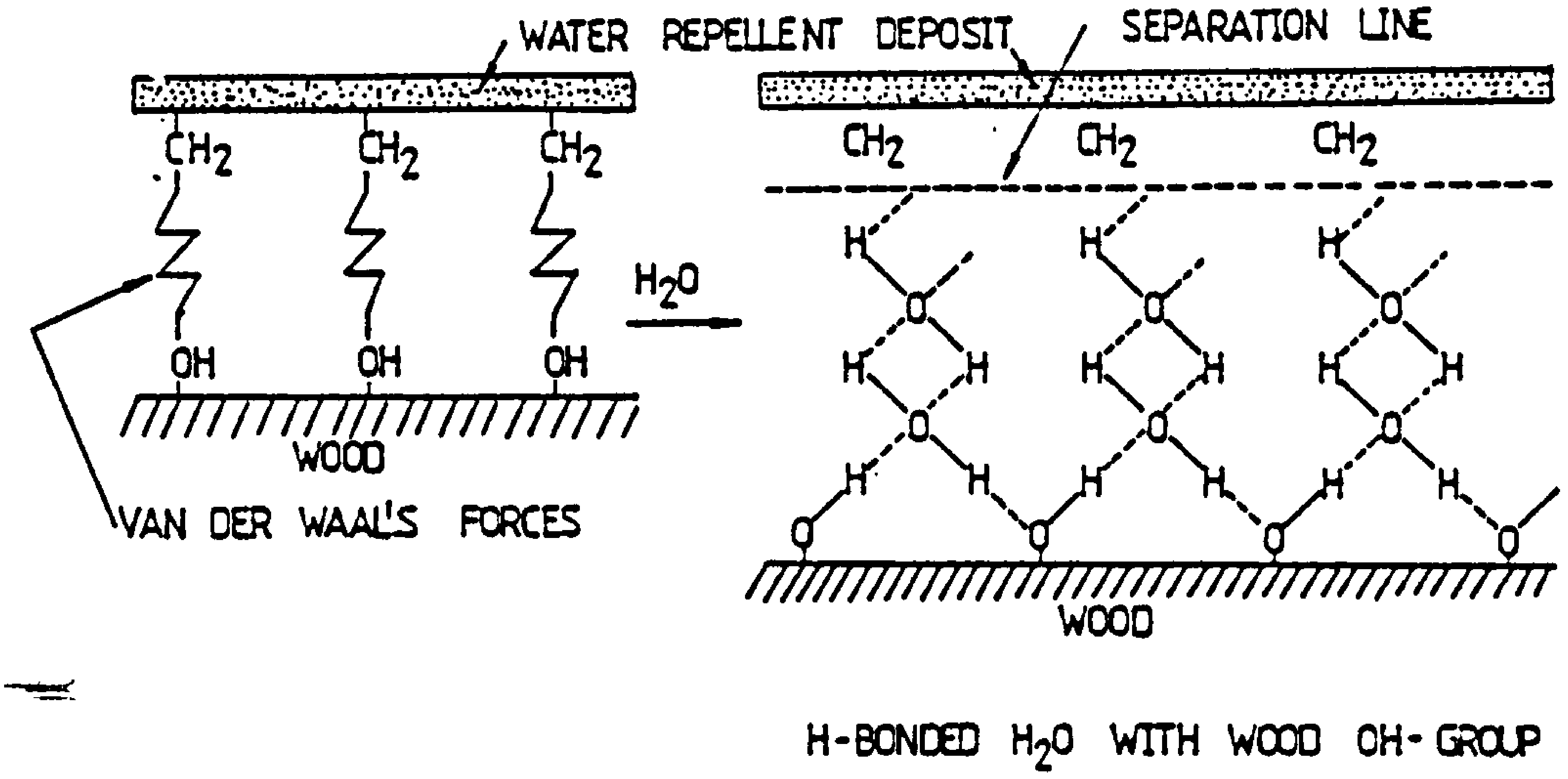


Figure 1.7 Stronger wood-water hydrogen bonding displaces weakly bonded water repellent deposits from wood surface

The reaction is thermodynamically favourable in that a solid surface of high surface free energy attempts to reduce this surface free energy by absorption of vapours and gases. By this process, it is suggested that water wets wood and physically displaces the water repellent coating from it (Borgin, 1968). It should be recognized, however, that no experimental evidence has been offered to support this hypothesis.

(c) Cohesive failure of the deposit: It is possible that shrinking and swelling stresses imposed on the deposit might bring about some cohesive failure due to fatiguing. It is known that paint coatings frequently fail by such processes. At the microscopic levels involved in internal cell coatings with water repellents it has not been established to what extent this type of failure does in fact occur (Fig. 1.8).

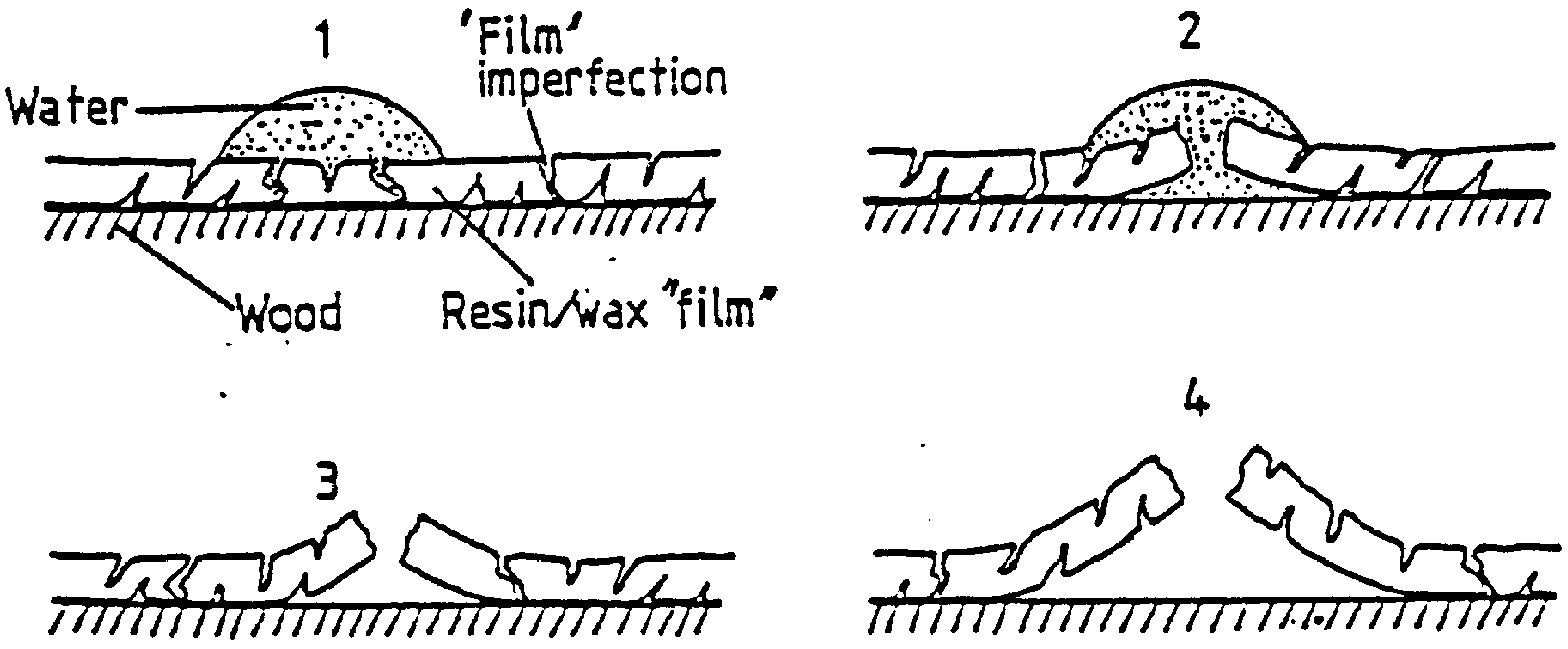


Figure 1.8 Preferential wetting due to film imperfection, aggravated by shrinking and swelling stresses may lead to cohesive failure.

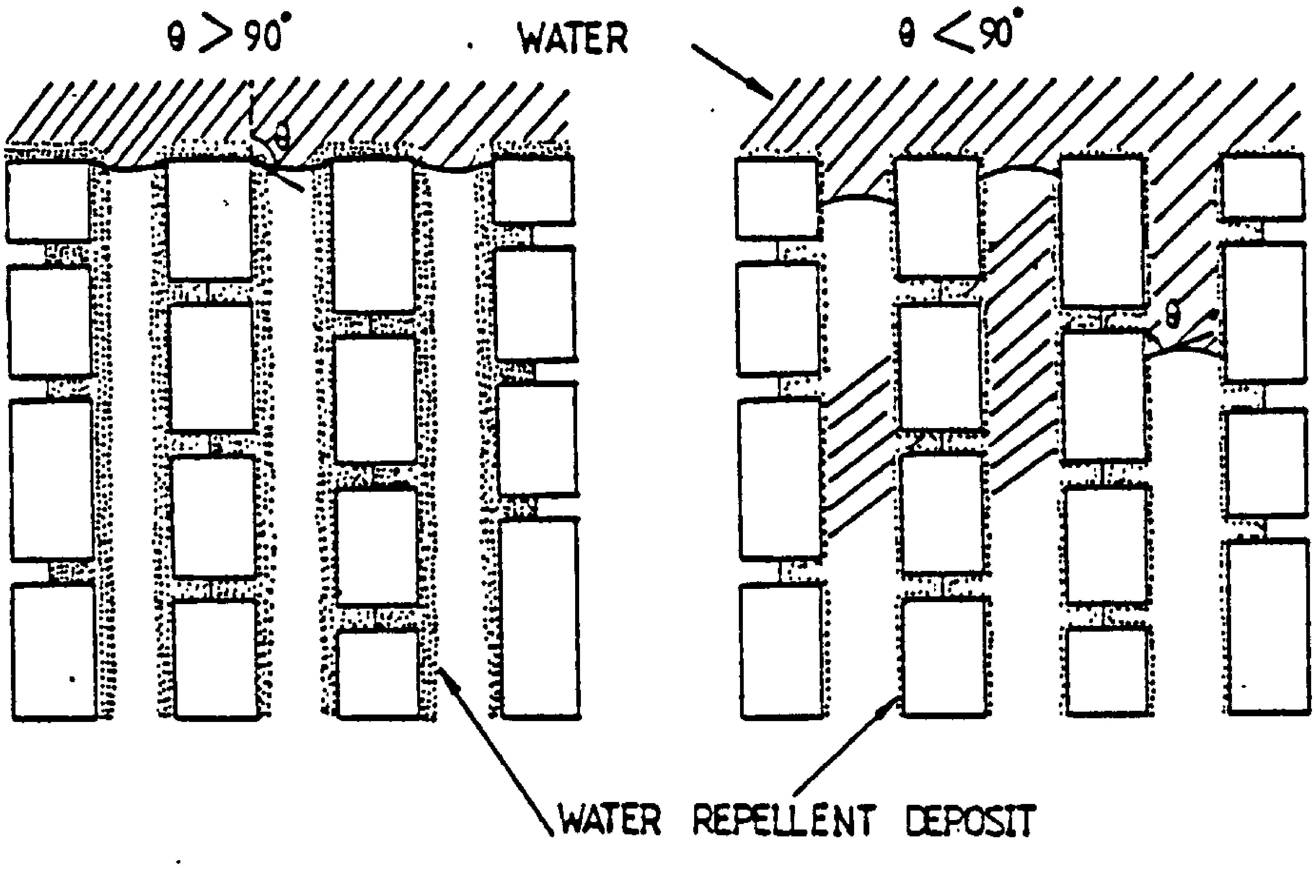


Figure 1.9 Thick deposit or deep penetration of water repellents in wood, in practice, provide better protection

1.5.1.3 The effects of distribution and concentration of water repellents on their performance

When a hydrophobic material penetrates into wood and coats or impregnates the cell walls to the extent that the capillary system is made hydrophobic, water penetration will be restricted in the system (Borgin, 1965). Theoretically, a coherent monomolecular layer should be sufficient to bring about the effect. Provided the hydrophobic layer remains perfect, deep penetration of wood with the hydrophobic deposit should be unnecessary (Fig. 1.9).

In practice, it has been found that deeper or complete impregnation leads to a more durable effect (Borgin, 1965). This is probably due to the fact that the deposit in immediate contact with a water source is gradually degraded due to the processes described above. Where deep impregnation is achieved, as this degradation goes on, fresh undegraded deposit is exposed offering continued good protection.

During impregnation of wood with solutions based on volatile non-swelling solvents and subsequently during the evaporation of the solvent, complex intercellular distribution phenomena are likely to occur. It has been shown by Cockroft (1957) using solutions of creosote in petroleum solvent that the deposit (creosote) tends to concentrate towards the exposed surfaces after the solvent has evaporated. This effect, which is due to liquid phase capillary flow towards exposed surfaces induced by the solvent evaporation from the cut ends of the capillaries (rather like sap streaming in trees) must lead to uneven distribution. Hence it may be that even deposition over cell surfaces is not attained in practice.

Working with water repellent treated Corsican pine (Pinus nigra) and European beech (Fagus sylvatica) sapwood specimens, Voulgaridis (1980) demonstrated a marked tendency for water repellent effectiveness to be greatest at the exposed (transverse) surfaces of his specimens than at distances a few centimetres from these surfaces. The effectiveness gradient was found to be much less marked in beech than in pine, illustrating the difficulty of drawing general inferences about the effect.

It was observed by Banks (1973) that the solution uptake by thin wafers (0.65mm in the fibre direction) of Scots pine sapwood was not significantly affected by variation in water repellent concentration over the range 0.2-5% wax in a 10% resin solution. However, progressively better performance was obtained with the increase in wax concentration over this range. Purslow and Williams (1978) found that higher wax levels from 0.2% to 1% in a 10% (W/V) resin formulation provided improved water resistance in long term L-joint field trials.

Using relatively long specimens Stalker (1972) observed that the presence of resins and waxes in organic solvents reduce the penetration of the solution into the wood. All this evidence point to the importance of the concentration of the water repellents in penetration and performance in treated wood.

Palejowski (1980) working with 10cm long beech specimens of 2x2cm cross-section obtained about 50% reduction in water absorption compared to untreated controls after treatment with a 10% resin solution. Addition of wax in the formulation up to 2% cut the water uptake by total of 75%. Further wax concentration up to 5% had little further effect on the water repellency. Artificial weathering decreased the water repellent effectiveness in all the specimens, but the general trend of better protection for the specimens treated with higher concentration formulations persisted even after exposure to cyclic wetting and drying over a period of 20 days. These results indicate that the protection afforded to wood by water repellent treatment may be strongly dependent on the distribution and concentration factors (Voulgaridis and Banks, 1979).

1.5.2 Bonding factors affecting the performance of water repellents

To assess the strength of the bond formed between wood and water repellent deposit, Voulgaridis (1980) measured the tensile strength of pine and beech specimens bonded with water repellent substances as the adhesive. The results obtained from this work indicated that the addition of paraffin wax in the proportion normally used in water repellent solutions to the resins caused a marked decrease (70%) in the strength of bond between the deposit and wood. After 20 heating cycles (12 hours heating at 25°C followed by 24 hours cooling at room temperature in each cycle) the bond strength increased in the case of resin bonds by about 100% for the pine specimens and by about 200% in the case of beech blocks. The strength of resin-wax bonds subjected to this treatment decreased slightly in the case of pine and very substantially with the beech blocks. Cyclic wetting (12 hours soaking at 25°C followed by 12 hours air drying at 35°C) for 5 cycles led to an average reduction of bond strength with both pine and beech of 65-70%. At the most extreme a few bonds in beech lost all their adhesive property as a result of this treatment.

These results suggest that the weakness of the bond formed between wood and conventional water repellents may lead to easy detachment of the deposit from the cell wall during exposure to the weather. This might well contribute to the observed fall off in performance after exposure (Fig. 1.10). If the loss of effectiveness associated with the above effect is significant, the use of water repellent substances, able to form stronger bonds (e.g. H-bonds or covalent bonds) with the cell wall, may lead to enhanced long term performance.

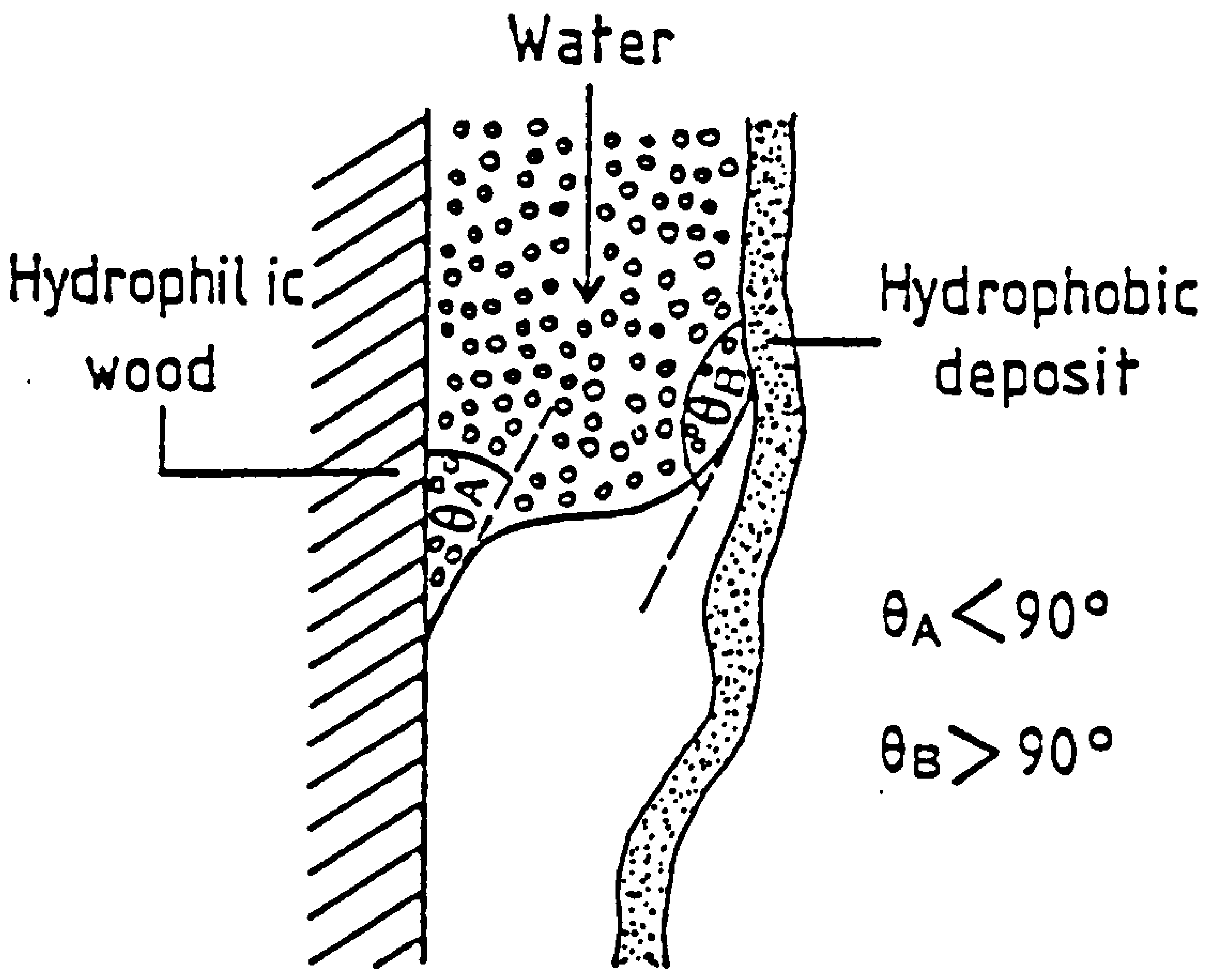


Figure 1.10 Water repellent deposits detached from cell wall form hydrophilic-hydrophobic interfaces

There is no record of a chemical treatment applied to wood with the main purpose of imparting water repellency. On the other hand, a great deal of work is reported describing methods devised to impart dimensional stability. These treatments are generally based on the reactions of wood hydroxyl groups to form acetal or ester linkages (Meyer and Loos, 1969; Rowell, 1975). Dimensional stabilization maybe achieved by the following mechanisms:

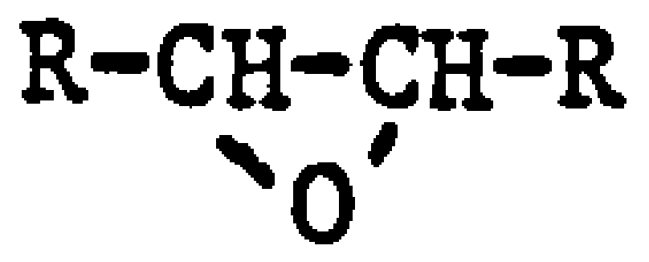
1) Cross-linking of hydroxyl groups on adjacent polymer chains, preventing sorption of water by the reacted sites, and limiting the amount of water sorption which can be accommodated by those remaining unreacted.

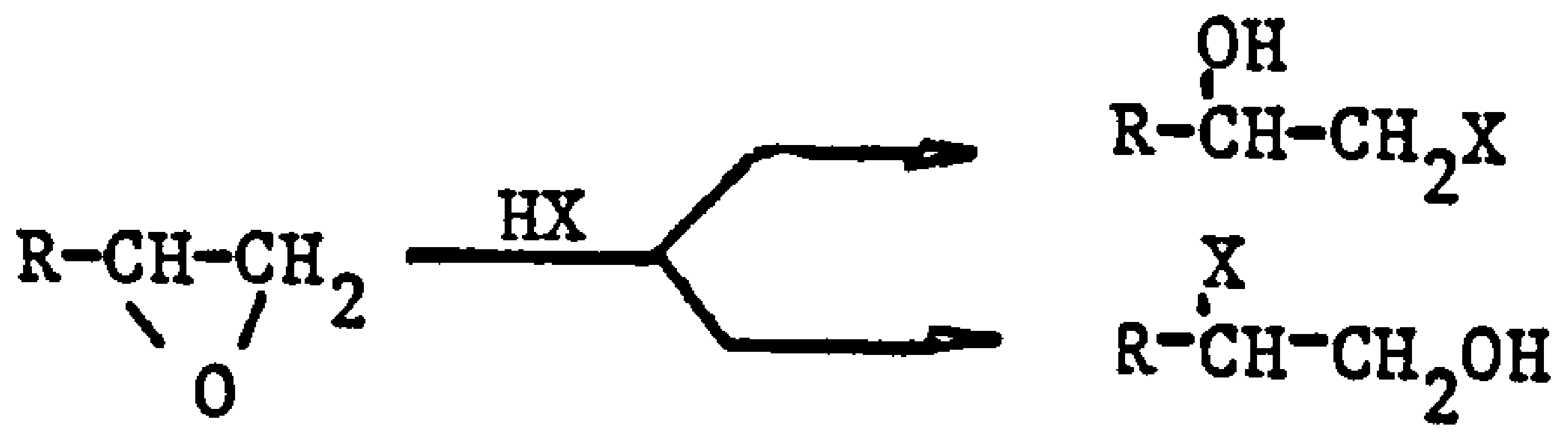
2) Blocking of hydroxyl with, for example, ester groups which have a low potential to form hydrogen bonds with water.

3) Introduction of bulky chemical groups into the cell wall which retain it in or near to its fully swollen state (Stamm, 1964).

In the following sections two types of reactions are discussed by which it is thought possible to produce hydrophobic wood surfaces.

1.5.2.1 Reactions with epoxides

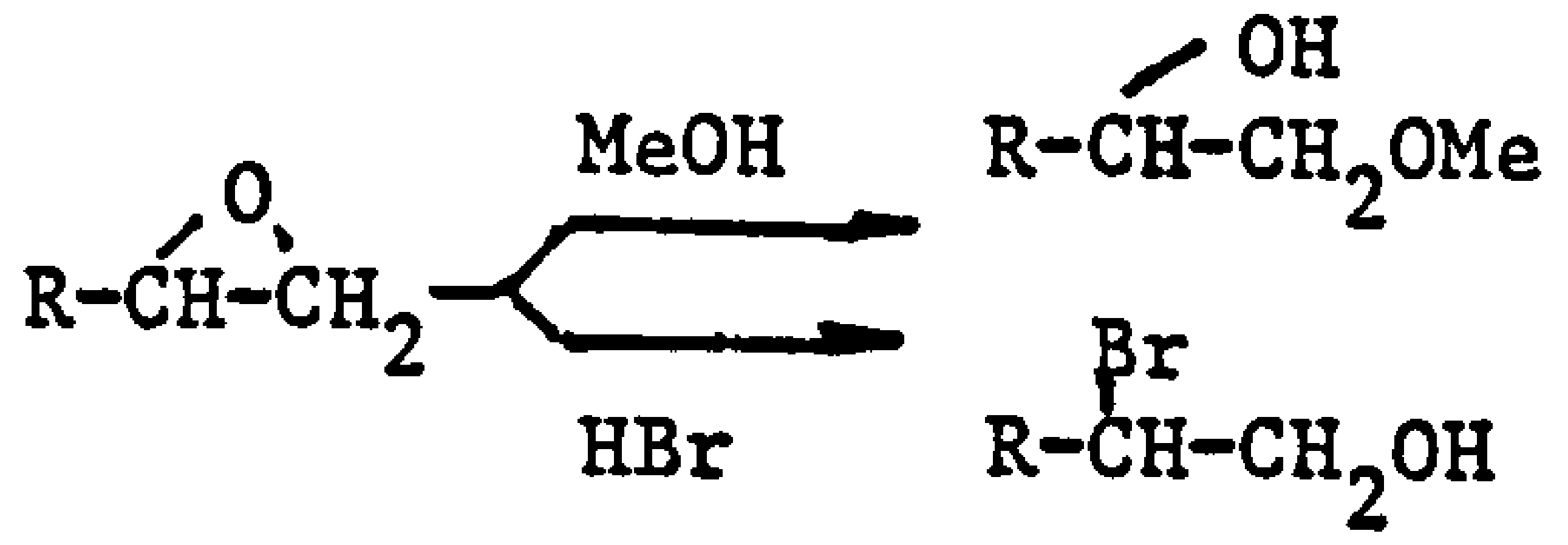
Epoxides with the general structure  $R-\underset{\diagdown O \diagup}{CH-CH}-R$ are a very reactive group of compounds. Through ring opening reactions they present two functional groups on adjacent carbon atoms. Opening of the ring and selective cleavage of the C-O bond to the less substituted or more substituted carbon atom takes place according to the electrophilic or nucleophilic nature of the reagent system used (Kirk, 1973). The reaction may be represented as



$$R-\underset{\diagdown O \diagup}{CH-CH_2} \xrightarrow{HX} \begin{cases} R-\overset{OH}{CH}-CH_2X \\ R-\overset{X}{CH}-CH_2OH \end{cases}$$

where 'X' is an electrophilic or nucleophilic group.

When an electrophilic (acidic) reagent is used (e.g. HBr) protonation of the epoxide oxygen leads to selective cleavage of the epoxide ring so that the bromine becomes attached to the more substituted carbon atom (II below). With a nucleophilic (basic) reagent, such as methoxide ion, MeO$^-$, the less substituted carbon atom is attacked by methoxide as in I giving the 1-methoxy 2-hydroxy compound:



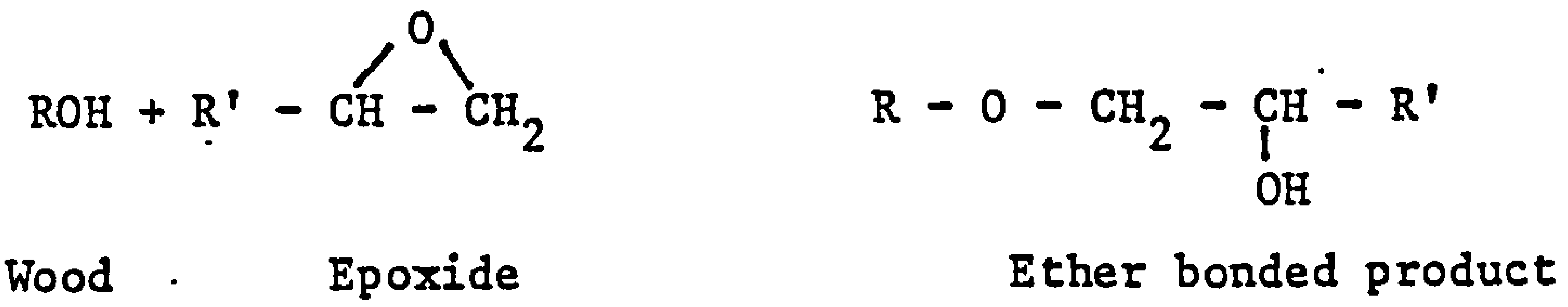
(I)

(II)

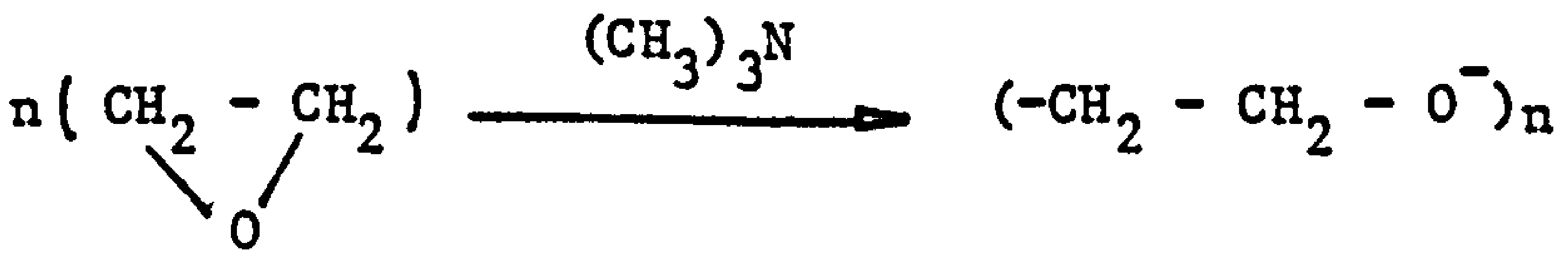
Several epoxides have been shown to react readily with wood. McMillin (1963) obtained cell wall bulking and dimensional stability by reacting wood with ethylene oxide in the gas phase. The simplest of epoxides, this monomer has a relatively high proportion of oxygen, a small molecule and an ether function which has relatively high hydrogen bonding capacity. All these factors tend to assist it to enter the amorphous areas of the cellulose with comparative ease, causing significant swelling of the cell wall.

It has been suggested that by the use of longer chain epoxides, e.g. propylene oxide, the rate of sorption might be decreased due to the hydrophobic character of the propyl chain (Schuerch, 1968). The lower ratio of oxygen to carbon in propylene oxide however, might inhibit its entry into the cell wall and it might act effectively as a hydrophobic coating, decreasing the rate, but not the amount of moisture absorption. Contrary to this theoretical idea, Rowell and his coworkers (Rowell, 1975; Rowell and Gutzmer, 1975; Rowell et al., 1976; Rowell, 1978) showed propylene and butylene oxide to penetrate the cell wall effectively. Butylene oxide, probably due to its larger molecular size and greater activation energy needs more vigorous reaction conditions to achieve a rate of reaction comparable to that achieved with propylene oxide.

Epoxides react with wood hydroxyl groups in the presence of a basic catalyst to yield an ether bonded compound but leaving an additional primary or secondary alcoholic group in the ether bonded wood product:



Ethylene oxide reacted with wood in the vapour phase with triethylamine catalyst yields various polymerized products (McMillin, 1963). The presence of abundant hydroxyl groups in wood is believed to give rise to chain transfer. The homopolymer chain formed by ethylene oxide probably proceeds thus:



Theoretically, this chain may be very long. But the chain transfer process breaks the molecules to shorter chain products with the formation of alkoxide ions:

$$-(O-CH_2-CH_2)n-O-CH_2-CH_2-O^- + \underset{\text{Wood}}{ROH}$$

$$-(O-CH_2-CH_2)n-O-CH_2-CH_2OH + RO^-$$

This process keeps the molecular weight of the reaction products low (Schuerch, 1968).

By using a bifunctional epoxide, e.g. butadiene diepoxide,  in addition to the effects described, it is believed that cross-linking between adjacent polymer chains may be induced, giving rise to improved dimensional stability for a given weight gain (Schuerch, 1968).

Dimensional stability is believed to result from a combination of reduction in hydrophilic property due to elimination of hydroxyl groups and "bulking" effect. McMillin (1963) believed that the advantage of gas phase reaction over liquid phase impregnation was that the polymers were produced on and within cell walls without filling the lumen and vessels.

Treatment with epoxides has been shown to give anti-shrink efficiency (ASE) up to 82% depending on the weight gain brought about by the reactions (Liu and McMillin, 1965; Barnes *et al.*, 1969). The optimal weight gain seems to be about 33%. Above this level of treatment cell wall rupturing can occur allowing the wall to swell above the green volume, leading to a decrease in ASE (Rowell and Gutzmer, 1975).

$$\left(\text{n.b.}\quad \text{ASE} = \frac{\text{Swelling Coefficient control} - \text{Swell. Coeff. treated}}{\text{Swell. Coeff. Control}}\right)$$

Equation 1.9

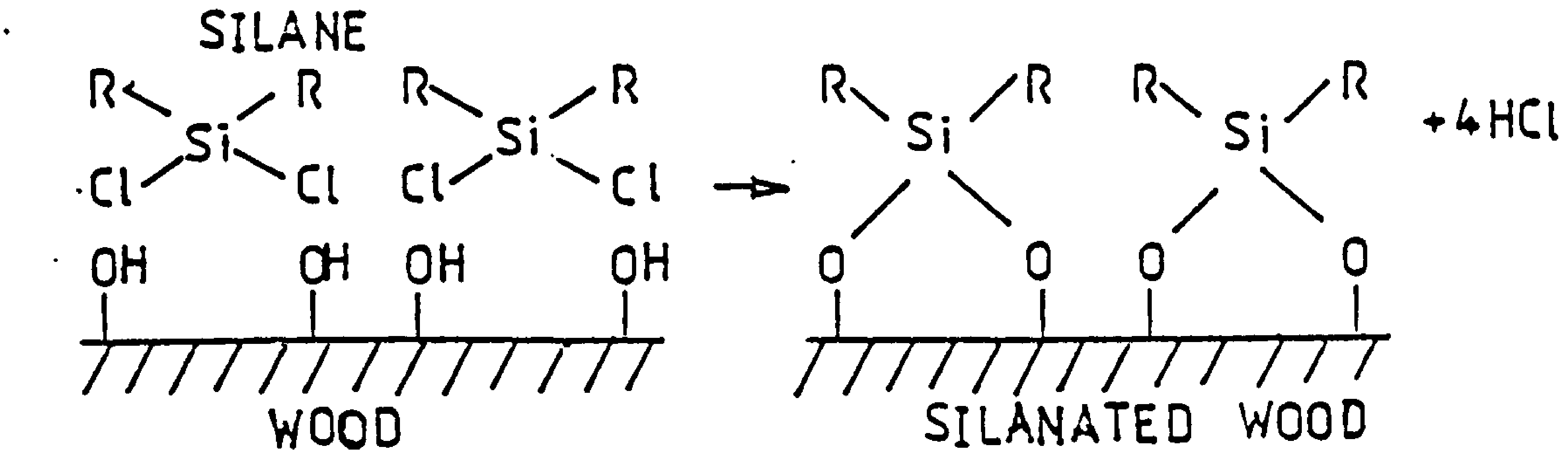
The stabilization achieved by epoxide reactions has been shown to be resistant to the effects of prolonged exposure to water (Rowell, 1978). Furthermore, and importantly, it has been established that the strength properties of the treated wood are unimpaired (McMillin, 1963).

1.5.2.2 Silanes as water repellents

Many of the hydrides and alkyl substituted hydrides of silicon (silicones) like those of carbon are known to exhibit strong hydrophobic properties. Only a limited amount of work has been done on the use of silicones, polyalkyl siloxanes and especially organochlorosilanes to impart water repellency to wood. With textile and other synthetic fibres, however, silicon based compounds have shown their potential as water repellents. Contact angles of 90° or higher were obtained with polymethyl or polydimethyl siloxanes.

The commonly used water repellents are deposited on the wood cell lumens and held there by Van der Waal's forces. Chlorosilanes, on the other hand, are considered to be effective covalent cross-linking agents for fibres having nucleophilic groups. Multifunctional silanes may react to form inter or intra-molecularly cross-linked products (Varma and Bandyopadhyay, 1975). The replacement of active hydrogen atoms in organic compounds by the silyl group reduces the polarity of the compound and with it the likelihood of hydrogen bond formation with moisture (Stevens, 1981). Chlorosilane vapours have been shown to impart good water repellency in treated cotton, nylon and polyvinyl alcohol fibres (Gagliardi, 1966; Varma *et al.*, 1973a;1973b;Varma and Bandyopadhyay, 1975).

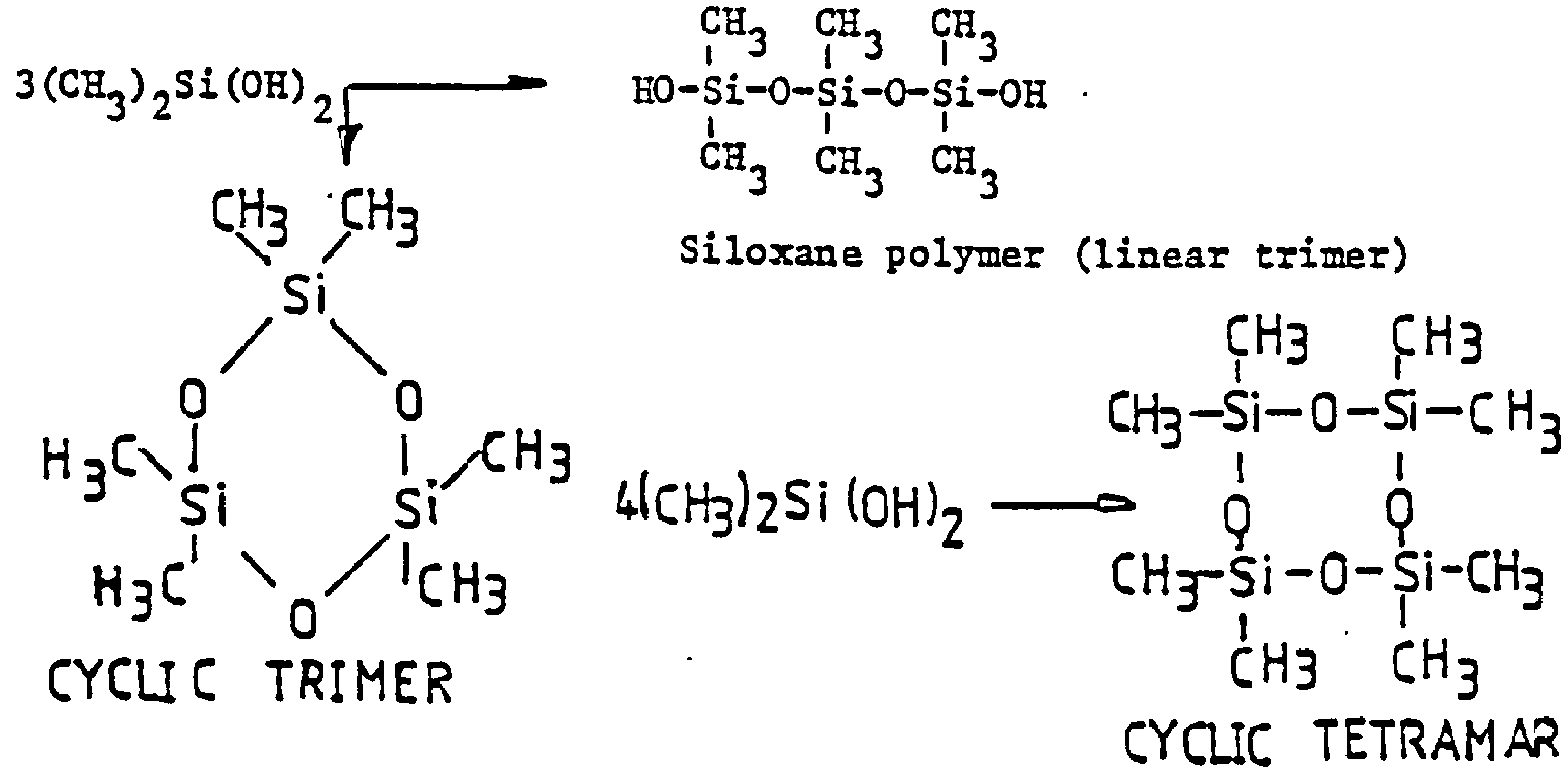
When silicon tetrachloride ($SiCl_4$) is reacted with wood, chemical modification takes place and the decay resistance of the treated wood is increased (Owens *et al.*, 1980). Silanes (e.g. dimethyl dichlorosilane) may react with the hydroxyl groups of the wood components chemically to form covalent bonds. The silylcellulose produced is much less polar and less able to form hydrogen bonds with water than is the original unmodified cellulose (Marian, 1973).



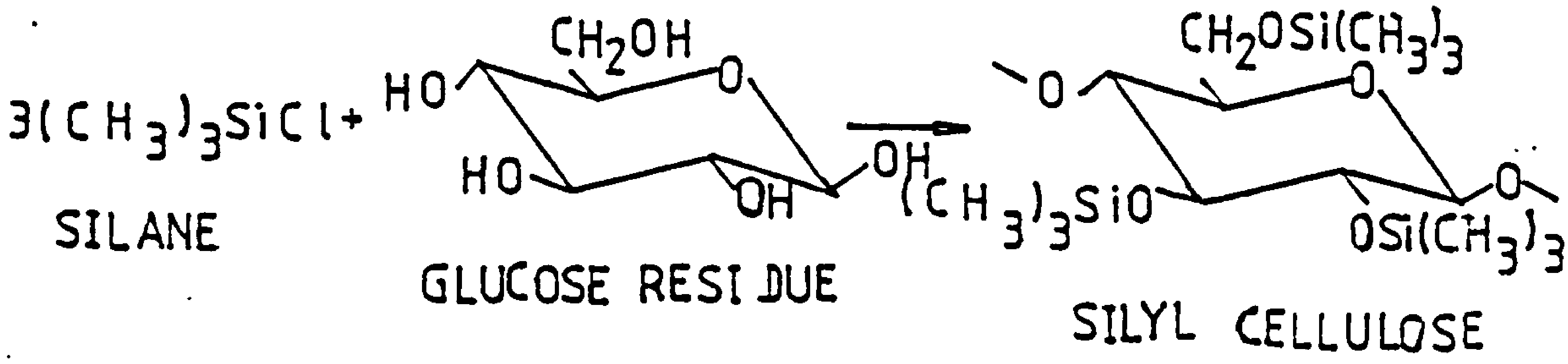
Methyl groups in silanated wood point away from reacted wood surface

Silanes may form silanols with the water present in wood, which in turn may polymerize to siloxanes. Wood surfaces coated with siloxane polymers may account for some of the water repellent properties in silanated wood (Rochow, 1951; Robbart, 1957):

$$\underset{\text{DMDCS}}{(CH_3)_2SiCl_2} + 2H_2O \longrightarrow \underset{\text{Silanol}}{(CH_3)_2Si(OH)_2} + 2HCl$$



Schuyten et al. (1948) obtained up to three silyl groups attached to each glucopyranose ring by reacting trimethyl-chlorasilane with wood:



The HCl formed as byproduct is believed to lead to significant hydrolytic degrade of the wood during the reaction. To try to overcome this effect several workers have suggested using acid acceptors in the reaction mixture, to neutralize the acid as it is formed (Pierce, 1968; Stevens, 1981).

Many chlorosubstituted silanes, e.g. CH_3SiCl_3, CH_3SiHCl_2, $(CH_3)_2SiCl_2$ and even quite long chain homologues, such as n-doderyl trichlorosilane, $CH_3-(CH_2)_{11}SiCl_3$ have been shown to react readily with wood.

1.6 Evaluation of water repellency and dimensional stability

Water repellents retard the rate of penetration of water in wood, but do not check the ultimate amount of water adsorbed (Borgin, 1965). All methods, therefore, for evaluating the efficiency of water repellents are based on the rate of water absorption by or rate of swelling of the treated wood specimens. Ideally, field tests using large specimens are desirable to give a sound evaluation of water repellency. However, results of such tests differ from one exposure site to another, due to variation in climatic conditions. Partly as a result of this problem, laboratory tests using various types of specimen have been developed over the years in various countries.

Many workers have used rather small specimens in such laboratory tests (Borgin, 1961). For example, Oliver (1963) described a test method using specimens of dimensions 2.5 x 2.5 x 0.6cm. Since then, several workers have used specimens of approximately similar dimensions quite satisfactorily (Banks, 1970a;Borgin and Corbett, 1971; 1974; Voulgaridis, 1980).

Laboratory test methods with small specimens are mostly based on the comparison of the degree of swelling in the tangential direction or water absorption of treated and untreated controls during immersion in water for a defined period (usually 30 minutes). Water repellent efficiency (WRE) is calculated as the reduction in swelling or water uptake achieved in treated specimens, expressed as a percentage of the untreated control value, i.e.

$$\mathrm{WRE} = W = \frac{S_o - S_t}{S_o} \times 100 \qquad \text{Equation 1.10}$$

when S_o and S_t are swelling or water uptake in the control and treated specimens respectively.

A rather different method of expressing water repellency has been suggested by Banks (1971a;1973). This is based on the idea of estimating the time taken to achieve a defined proportion of the maximum change in dimension brought about by water sorption. The benefit of this form of expression is that it is functionally related to the diffusion coefficient. See, for example, the Boltzmann form of Fick's general diffusion law:

$$D = \frac{\pi L^2 \Delta a^2}{16t} \qquad \text{Equation 1.11}$$

where D = Diffusion coefficient;

L = Specimen length in flow direction;

Δa = Increase in tangential length in time 't' (as a fraction of maximum length increase),

i.e. 't', the time taken to achieve fractional dimensional increase Δa varies inversely with diffusion coefficient: $d \propto \frac{1}{t}$.

Measurement of contact angles of water repellent treated wood specimens has also been widely used as a method of assessing water repellency (Borgin, 1961; Gray and Wheeler, 1959; Marian and Stumbo, 1962; Rak, 1975). Various methods are in use for measuring contact angle. Tilting plate and sessile drop methods have been found to be satisfactory for wood specimens (Rak, 1975; Gray and Wheeler, 1959; Voulgaridis, 1980). Electrical resistance measurement (which is related to moisture content) has also been used as an alternative to water absorption or swelling measurement (Vermass, 1976).

In bonded water repellent treatment of wood the hydrogen atom of the wood OH-group is generally replaced by a larger group from the treating chemical (see Sect. 1.5.2.1 and 1.5.2.2). As a result, there is usually a substantial gain in weight in the treated wood. The weight percent gain (WPG), in most cases, gives a rough idea of the extent of chemical modification achieved by the treatment. The dimensional stability attained by such treatments is evaluated as anti-shrink efficiency (ASE), the percentage reduction in equilibrium swelling and shrinking caused by the treatment (Stamm, 1964).

To calculate ASE, the volumetric swelling coefficient of the control and treated specimens are calculated as,

$$S = \frac{V_2 - V_1}{V_1} \times 100 \qquad \text{Equation 1.12}$$

where V_2 and V_1 are saturated and dry volume respectively.

$$ASE = \frac{S_o - S_t}{S_o} \times 100$$

where S_o and S_t are volumetric swelling coefficients of the control and treated specimens respectively (Equation 1.9; sec. 1.5.2.1). ASE values are usually cited in relation to particular weight gains achieved in the treatments.

1.7 Scope of the present work

A lot of work has been reported on the methods of application and evaluation of water repellents either in isolation or in conjunction with wood preservatives. The mechanism of the performance of the water repellents in treated wood and their breakdown by physical factors point to several areas where there is inadequate knowledge to allow a full understanding of water repellent performance.

The objective of the present work is to investigate the pattern of distribution, interelationship of distribution and concentration and effects of concentration and distribution factors on the performance of water repellents in wood. Furthermore, investigations are carried out into the influence of these factors on the rate of loss of effectiveness of water repellents in wood due to effects of simulated weathering factors (moisture and heat).

Finally, an attempt is made to assess the benefit of inducing covalent bonding between wood and water repellent to improve long term effectiveness.

PART 2

WATER REPELLENT CONCENTRATION AFFECTING THE PERFORMANCE OF TREATED WOOD

2.1 Objectives

In the water repellent solutions used to treat the wood specimens in the experiments described below, a paraffin wax has been used as the hydrophobic agent and a straight chain hydrocarbon resin as the dispersing medium. From the integrated form of Rideal-Washburn's equation (Morgan and Purslow, 1973; Voulgaridis, 1980), regarding penetration of fluids in a capillary medium, it is clear that the amount of solution absorbed must be dependent upon the nature of the wood substrate and the treating solution and the time they remain in mutual contact. As solution penetration is dependent upon the capillary radius, it is likely to vary from species to species depending on the characteristics of their fluid flow paths. Hence this study is based upon the use of two different wood species (a hardwood and a softwood), having different types of conducting pathway.

It is known that wax deposits in wood cells make them resistant to water penetration by increasing the contact angle made by water with the treated wood to more than 90°. The resin is also believed to be very important in dispersing and binding the wax component more securely to the wood substrate. It is also thought that resin may itself contribute to protection against water sorption by forming a mechanical barrier to water penetration. In addition to the above variables, concentration of resin and wax was varied to examine the effect of differences in retention of each of these components.

The responses of these variously treated wood specimens under weathering conditions are of utmost importance in the practical application of water repellents. Investigations were carried out, therefore,on the behaviour of the two components at various concentrations exposed for varying periods of simulated weathering.

2.2 Water repellent effectiveness in long specimens

2.2.1 Preparation of wood specimens and treating solutions

2.2.1.1 Selection of wood

There is a great variation in the permeability of various species both in softwoods and in hardwoods. Keeping this in mind, it was decided to select two rather permeable species, Corsican pine (*Pinus nigra*) and European beech (*Fagus sylvatica*) in order to achieve a treated zone extending over a reasonable distance.

Because of its higher permeability, sapwood from both the species was chosen in preference to heartwood. Variation in ring width and consequent variation in the proportion of earlywood and latewood affect permeability, sorption and swelling characteristics of wood. This variation between different pieces of wood may significantly influence the water repellent properties of treated specimens (Purslow, 1965). To minimise this effect, specimens were selected from stems with no less than 4 and no more than 7 growth rings per cm (Figure 2.1a). All specimens were taken from clear, straight-grained and defect-free zones of wood. Some of the relevant wood properties of the two species are summarised in Table 2.1 (Voulgaridis, 1980; Farmer, 1972).

Table 2.1 Some physical properties of Corsican pine and European beech wood

Property	Corsican pine	European beech
Anatomy	Softwood with resin canals	Diffuse porous hardwood
Permeability	Sapwood permeable	Axially permeable
Dimensional swelling (0%-FSP)	Tangential 7.5% Radial 4.0%	Tangential 12% Radial 6%
Density (Kg/m^3)	500	720

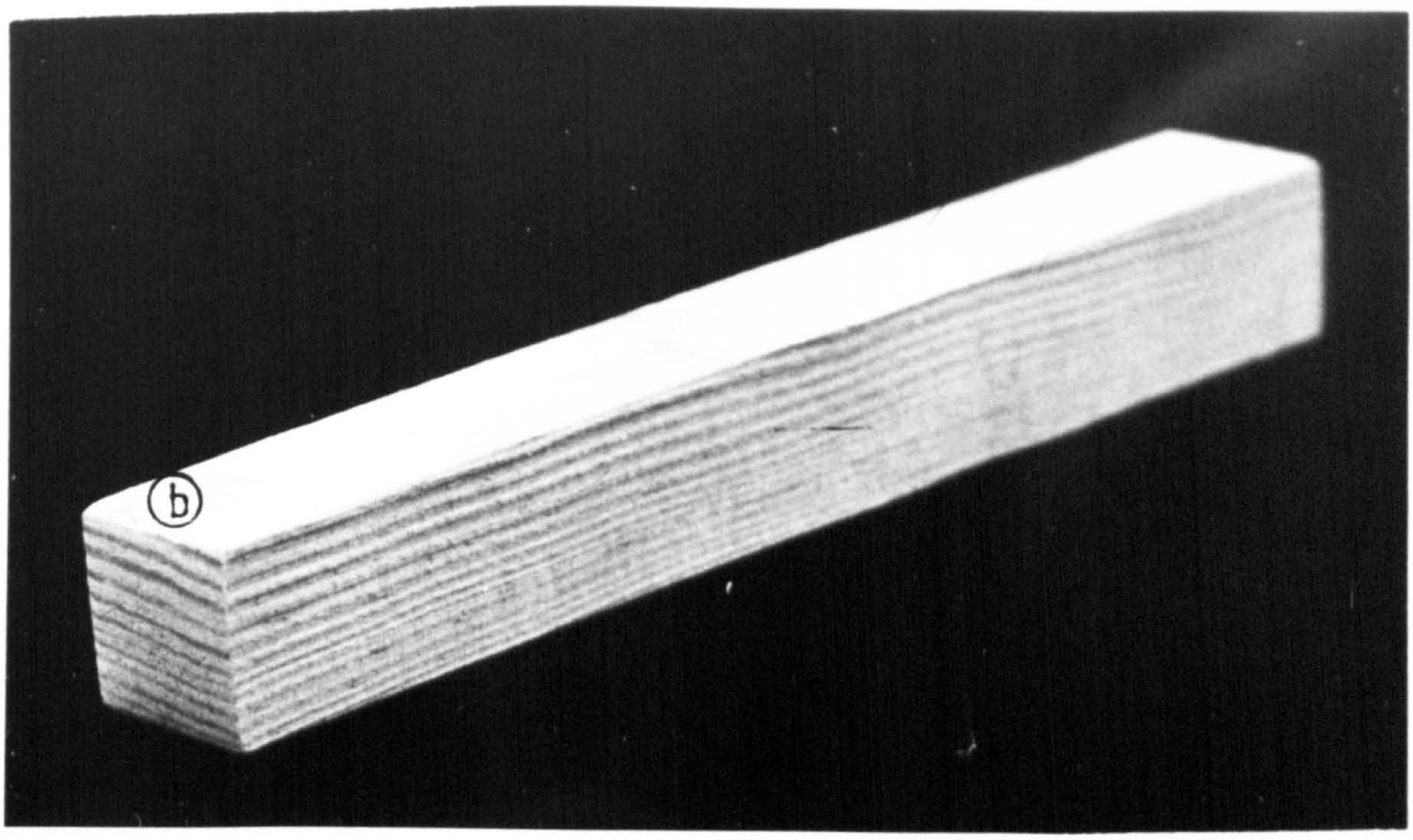


Figure 2.1a. Specimens showing clear wood and straight grain. 4 to 7 growth rings per cm.

Figure 2.1b Preparation of 15 cm. long specimens with control wafers from off-cuts.

2.2.1.2 Cutting of specimens

Specimens of both Corsican pine and European beech were taken from single logs for a particular experiment. Sticks 20cm long and 2x2cm in cross-section were produced from defect-free wood. The sticks were orientated in such a way that two parallel lateral faces were tangential and the other two radial to the longitudinal stem axis. The sticks were then trimmed at either end to give 15cm long specimens. From the trimmings 6mm thick, transverse sections were taken from either end as control specimens (Figure 2.1b). These were monitored for maximum swelling and the data obtained were used as the basis for estimation of the time to half or quarter swell of treated specimens. The wafer specimens from off-cuts as well as the long specimens were equilibrated at 20°C and 65% RH before further manipulation.

2.2.1.3 Treating solutions

It is thought that resins play a prominent role in water repellent formulation by forming a coherent and strongly bonded coating on the wood surfaces, whilst waxes give a strong hydrophobic action (Voulgaridis and Banks, 1979). A straight chain hydrocarbon (SCH) resin* showing good film-forming and water-repellent properties (Voulgaridis, 1980) has been used alone or in conjunction with a low congealing temperature paraffin wax in this work. White spirit was used as the solvent. This is a complex mixture of petroleum hydrocarbons. Some of the relevant properties of the solvent, resin and wax obtained from technical literature are listed below. (see Table 2.2).

The equilibrium contact angles as cited in Table 2.2 were measured using thin films of resin, wax and resin-wax mixture deposited onto glass microscope slides. The measurements were made at 20°C by the sessile drop method (Gray and Wheeler, 1959; Rak, 1975). For each deposit, contact angle measurements were made with 20 separate drops.

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*The straight chain hydrocarbon resin used throughout is Escorez 1102 produced by the ESSO Company.

Table 2.2 Properties of the chemicals forming treating solutions

SCH Resin		Paraffin wax		White spirit	
Softening pt. (Ring & Ball)	100°C	Melting pt.	49°C	Boiling range	150-198°C
Specific gravity	0.97	Congealing pt.	49°C	10% vol. distilled at	163°C
Bromine no. (Cg/g)	15	Initial Contact Angle	108°C	50% vol. distilled at	170°C
Acid No. (Mg KOH /g)	<1.0	Wax 10% + resin ~~10%~~ Contact Angle with water	103°C	90% vol. distilled at	184°C
Flash pt. (coc)	285°C			Dry point	196°C
Contact angle (with water)	86°C			Vapour density	>1.0
				Sp. gravity at 20°C	0.772
				Viscosity	0.88
				Aromatic content	18%
				Flash pt. (Abel closed cup)	38°C
				Evaporation rate (n-butyl acetate = 1)	0.19

Solutions of the resin and resin-wax in white spirit were prepared, gentle heat being applied to aid solution. The solutions were then cooled to 20°C and maintained at that temperature. 11 formulations as given below were used in this study.

1. 10% solution of resin (R_{10})
2. 11% solution of resin (R_{11})
3. 12% solution of resin (R_{12})
4. 15% solution of resin (R_{15})
5. 20% solution of resin (R_{20})
6. 10% resin + 1% wax ($R_{10}W_1$)
7. 10% resin + 2% wax ($R_{10}W_2$)

8. 10% resin + 5% wax ($R_{10}W_5$)
9. 10% resin + 10% wax ($R_{10}W_{10}$)
10. 11% resin + 1% wax ($R_{11}W_1$)
11. 18% resin + 2% wax ($R_{18}W_2$)

2.2.2 Treatment of wood specimens with water repellent solutions

There is a very large difference in liquid permeability in the radial and tangential directions between pine and beech wood. To monitor the effect of factors brought about by this difference, therefore, only longitudinal penetration of water repellent solutions was permitted. This was effected by sealing all the lateral faces and one transverse face of the long specimens with a styrene resin (ABS solvent cement). Three coats of the cement were found to prevent any liquid penetration through the coating. After curing of the styrene resin the specimens were again equilibrated at 65% RH and 20°C before water repellent treatment.

All surfaces excepting one transverse face remaining sealed the specimens were vacuum impregnated using an initial vacuum of 200 mm of Hg. After application of the initial vacuum, the specimens were immersed in the treating solution and pressure was allowed to return to atmospheric. The specimens were held in this condition for 3 minutes. The solution was then drained and the specimens wiped clean of superficial liquid. They were then weighed to assess the solution absorption. The specimens were then stored in a ventilated room at 65% RH and 20°C for 15 days to allow partial evaporation of solvents to occur. Initial experiments revealed that complete solvent evaporation under this condition takes an inordinately long time. To save time after partial evaporation the specimens were kept for 12 hours at 35°C in a force draft oven and then equilibrated at 65% RH and 20°C for the next 12 hours for 15 consecutive days. Thereafter they were equilibrated at 65% RH and 20°C until constant weight was attained.

2.2.2.1 Water repellent uptake data

Water repellent absorption data are shown in Table 2.3. Beech, in general, can be seen to absorb more solution than pine with both resin and resin-wax formulations. Solution absorption varies little in beech with variation in concentration. Hence there is a marked increase in solids retention with increase in concentration.

Table 2.3 Water repellent absorption in Corsican pine and European beech after 3 minutes vacuum treatment

Water repellent formulation %	PINE (12 replicates)		BEECH (12 replicates)	
	Solut. abs. per stick ± stand. dev. gms.	Calc. solids content gms.	Solut. abs. per stick ± stand. dev. gms.	Calc. solids content, gms.
Resin 10	4.20(0.28)	0.42	5.30(0.51)	0.53
Resin 11	4.10(0.37)	0.45	5.29(0.58)	0.58
Resin 12	3.93(0.42)	0.47	5.22(0.33)	0.63
Resin 15	3.82(0.49)	0.57	5.10(0.41)	0.77
Resin 20	3.67(0.38)	0.73	5.06(0.54)	1.12
Resin 10 + Wax 1	3.23(0.46)	0.36	4.62(0.71)	0.51
Resin 10 + Wax 2	3.14(0.38)	0.38	4.51(0.68)	0.54
Resin 10 + Wax 5	2.65(0.62)	0.40	4.27(0.64)	0.64
Resin 10 + Wax 10	2.57(0.48)	0.51	4.04(0.58)	0.81
Resin 11 + Wax 1	3.48(0.47)	0.42	4.87(0.51)	0.58
Resin 18 + Wax 2	3.12(0.46)	0.62	5.04(0.62)	1.01

In pine, solution absorption can be seen to decrease slightly with increase in concentration of resin and resin/wax solutions.

It is noticeable that the incorporation of wax decreases absorption more than equivalent amounts of resin. Presumably there are viscosity effects, more significant in pine because of the finer pores involved in fluid transport. However, even with pine, for each series (resin only or resin-wax) solids retention increased systematically with increasing concentration.

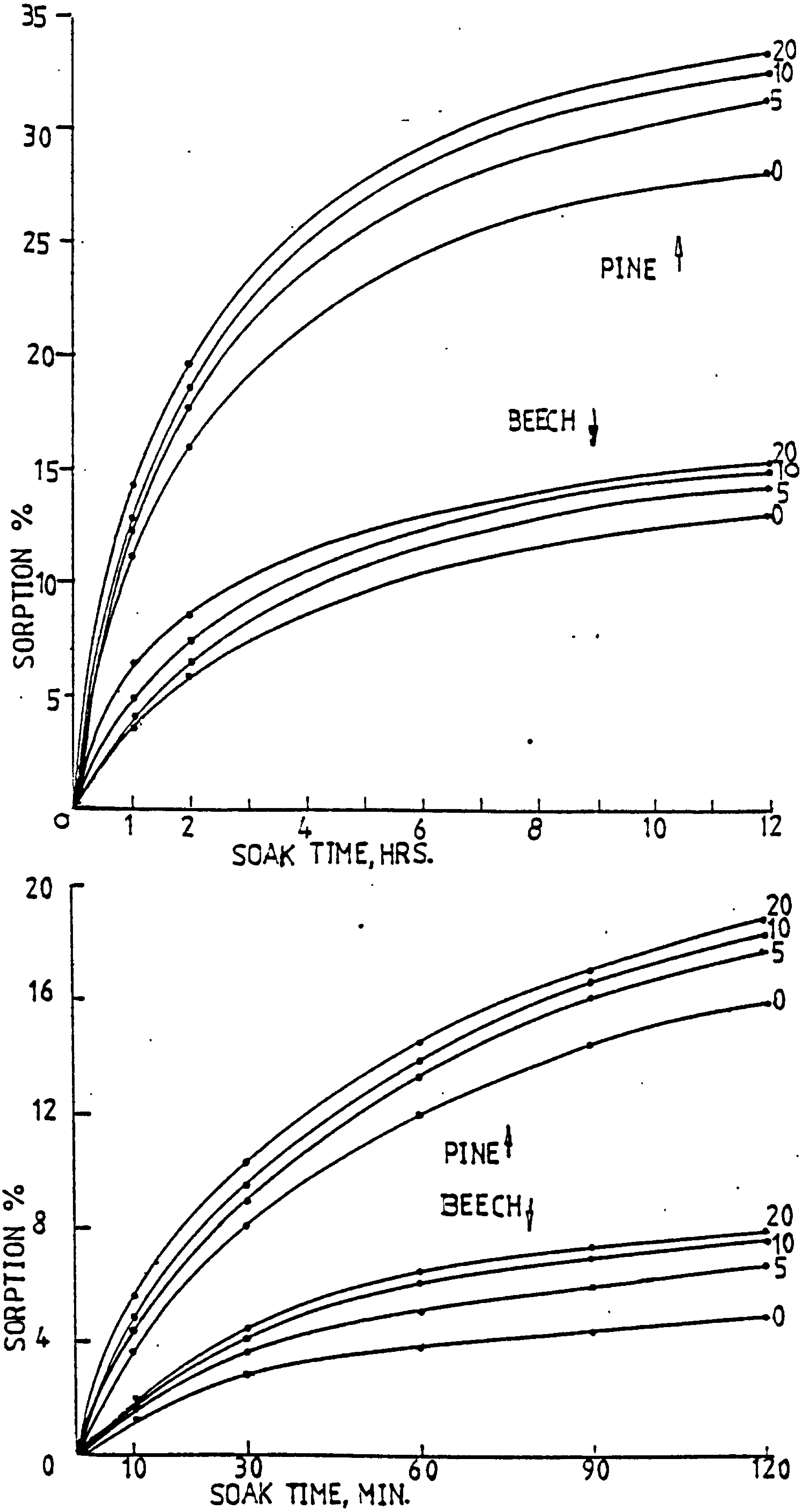


Figure 2.2 Water absorption by pine and beech untreated control long specimens (coated on all but one transverse face) after 0, 5, 10 and 20 weathering cycles (9 replicates).

2.2.3 Simulated weathering procedure with long specimens

Corsican pine and European beech specimens were subjected to 0,5,10 and 20 soaking and drying cycles. Each cycle consisted of 12 hours of immersion under 8 to 13cm of mildly agitating deionized water at 25°C followed by drying for the same period at 35°C in a force draft oven. After subjecting them to the required number of cycles the specimens were dried for a week at 35°C and then equilibrated to constant weight at 20°C and 65% RH.

2.2.4 Assessment of water repellency of whole specimens

The equilibrated (at 20°C and 65% RH) control and treated specimens were evaluated for water repellent effectiveness by measuring the rate of water uptake during immersion in water. The specimens were submerged under approximately 10cm of mildly circulating deionized water in a water bath maintained at 25°C. The specimens were removed from the water bath at intervals of 1,3,5,10 and 15 minutes and thereafter every 15 minutes for the first 2 hours. They were wiped clean of surface water and quickly weighed before being replaced in the bath. The whole process was carried out with only a few specimens at a time to ensure a minimum possible time lapse between soaking periods. At the end of the 2 hour period the specimens were allowed to soak in the water bath for a further period of 10 hours giving a total soak time of 12 hours. Water absorption was measured finally after this period.

2.2.4.1 Water absorption by untreated control specimens

The rate of uptake of water by both pine and beech control specimens are detailed in Appendix I, Table 1 and Figure 2.2. About 13% water was absorbed by beech specimens in 12 hours soaking when all but one transverse face was sealed. About double this amount was absorbed by pine in a similar time. (In the absence of sealant, water sorption would be considerably greater due to significant absorption through the other transverse face and the lateral faces).

It was observed during the first few cycles that checks developed in the ends of the specimens. This is probably due to stresses developed during the periods of alternate wetting and drying.

Figure 2.3 Rates of water absorption by pine long specimens after 0, 5, 10 and 20 weathering cycles (3 replicates). Curve nos. represent: 1=10% resin; 2=11% resin; 3=12% resin; 4=15% resin; 5=20% resin; 6=10% resin + 1% wax; 7=10% resin + 2% wax; 8=10% resin + 5% wax; 9=10% resin + 10% wax.

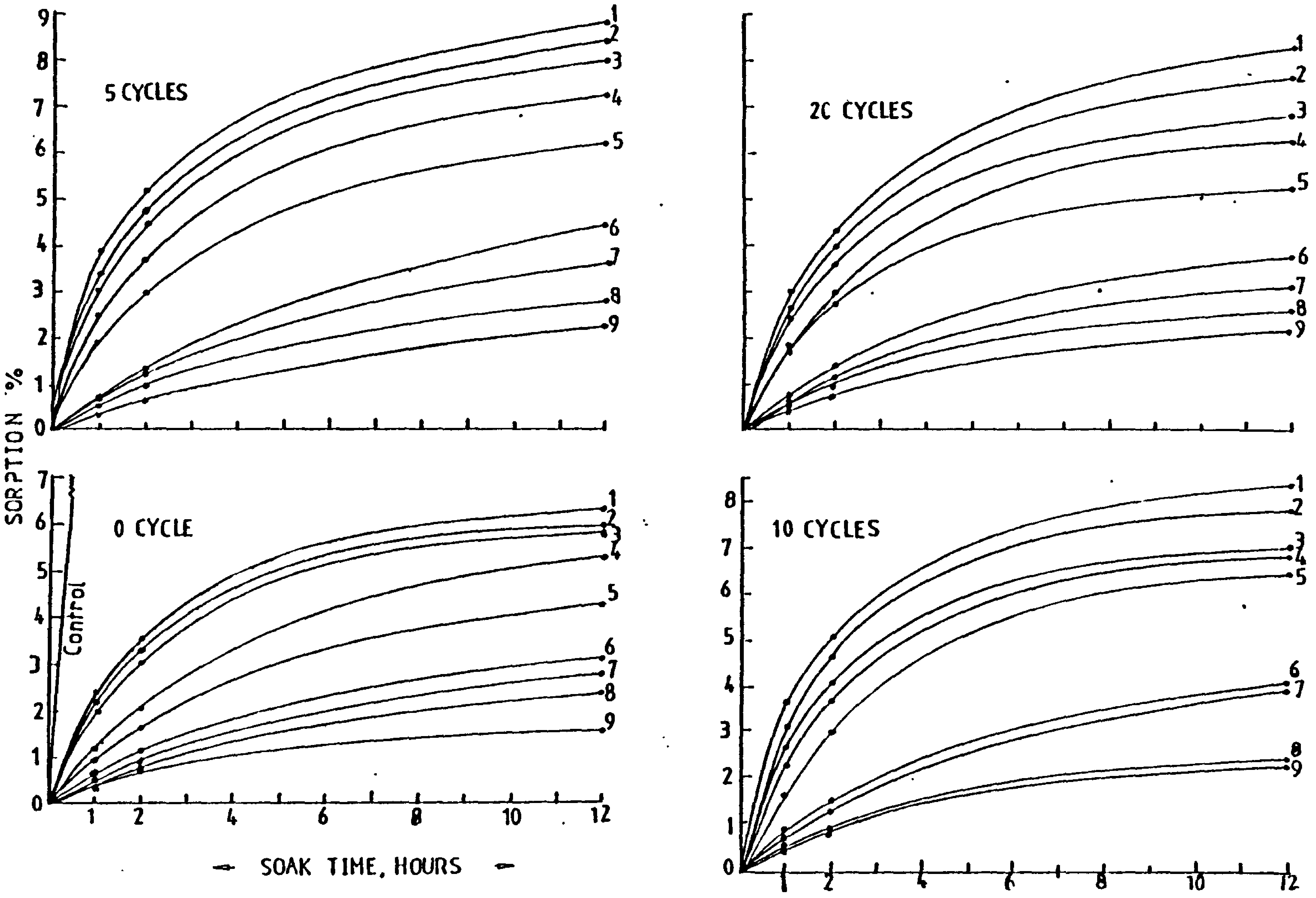


Figure 2.4 Water absorption after 12 hours soak by variously cycled pine long specimens (3 replicates). Curve nos. represent: 1 = 10% resin; 2 = 11% resin; 3 = 12% resin; 4 = 15% resin; 5 = 20% resin; 6 = 10% resin + 1% wax; 7 = 10% resin + 2% wax; 8 = 10% resin + 5% wax; 9 = 10% resin + 10% wax.

A large increase in the rate and total water absorption after 12 hours of soaking was observed to take place over this period. Thereafter, further observable wood degrade is substantially decreased, effectively diminishing any further increase in water absorption rate with continued cycling.

2.2.4.2 Water absorption data for treated long sticks

2.2.4.2.1 Water absorption by Corsican pine specimens

The rate of water absorption by Corsican pine specimens treated with various concentrations of resin and resin-wax solutions, after cyclic soaking and drying for 0,5,10 and 20 cycles is shown in Figures 2.3 and 2.4. The full data are given in Appendix I, Table 2A-D. Both resin and resin-wax solutions seem to provide water repellency in pine to a level which varies with the amount of solids present in the treated wood. However, the data suggest strongly that the degree of hydrophobicity of the solid deposit also significantly affects the level of protection afforded. It is clear from the results that by increasing the resin concentration from 10% successively to 11, 12, 15 or 20% some additional resistance to water sorption is imparted. However the improvement achieved cannot match the far superior water repellency obtained by the addition of even 1% wax. In fact, the solution containing 10% resin + 1% wax ($R_{10}W_1$) gives much better water repellency before cycling than even the 20% resin solution (R_{20}). Resin solution is thought to provide water resistance in pine specimens by depositing a coating of resin onto the walls of tracheid lumina including the bordered pit areas. Communication between adjacent tracheids being through the pit pore openings in unaspirated pits, mass flow of water will depend on the openings between margo strands and the efficiency with which these openings can be blocked by the deposited resin. The rather widely set margo strands in pine probably do not allow the formation of a coherent coating film with the 10% resin solution (Voulgaridis, 1980). With progressive increase in resin content the chances of formation of a more coherent coating increase. However, even at 20% concentration it seems that the pores are sufficiently open to allow significant water flow.

The addition of 1% wax to a 10% resin solution appreciably increases the water proofing effect in pine. With increasing wax loading the rate of moisture absorption is considerably reduced. To check further the effect of resin and wax proportions on water repellency, sets of specimens of pine and beech were treated with 11% resin plus 1% wax ($R_{11}W_1$) and 18% resin plus 2% wax ($R_{18}W_2$). Water soak tests on these specimens before cycling indicate clearly that proportion of wax in a formulation plays a much more dominant role than the resin component (Table 2.4). In the presence of wax the contact angle of water on the deposits exceeds 90^o, making water entry into the openings difficult. This hydrophobic action of wax, rather than the formation of better coating due to increased solids content is supposed to be responsible for much better water repellency obtained.

In practice, it is found that formulations containing high wax concentrations give rise to painting problems in treated wood. If water repellent efficiencies approaching, say, those of 10% resin + 2% wax and 10% resin + 10% wax could be achieved by the application of 11% resin + 1% wax and 18% resin + 2% wax respectively, then these overpainting problems might be substantially avoided. The results obtained in the probing tests with pine indicate that 11% resin + 1% wax and 18% resin + 2% wax perform similarly to 10% resin + 1% wax and 10% resin + 2% wax respectively rather than 10% resin + 2% wax and 10% resin + 10% wax as anticipated (Table 2.4). Further experimentation, thus, with these two formulations were discontinued.

After cyclic soaking and drying, the specimens treated with resin only solution showed a greater loss of effectiveness than those treated with resin-wax solutions. The observed increase in water uptake after 12 hours soaking appeared to be greater in specimens treated with solutions of lower concentration than in those treated with more concentrated ones both in the case of resin and resin-wax formulations. Rather modest but progressively increasing water repellency was obtained with the increase in treating solution concentration from 10% resin to 20% resin. Similarly, increase in water repellency was shown by specimens treated with the resin-wax solutions of increasing wax loading over the range of wax concentrations from 1 to 10%. It seems that initial cycling has the most detrimental effect on the water repellency of pine specimens. The greatest relative decrease in water repellency occurs during the first five cycles. Thereafter, on cycling for 10 or 20 cycles, very little further increase in water absorption can be seen. In some cases, a small but definite improvement in water repellency has been recorded.

Table 2.4 Water repellency in Corsican pine as affected by wax loading and total solids content in formulations (3 replicates).

Formulation	Soaking time (min) and water absorption (% of equilibrated weight at 65% RH and 20°C)							
	5	10	15	30	60	90	120	720
$R_{10}W_1$	0.14	0.18	0.24	0.32	0.52	0.78	0.96	3.11
$R_{11}W_1$	0.15	0.20	0.25	0.34	0.50	0.75	1.01	3.10
$R_{10}W_2$	0.13	0.16	0.18	0.26	0.48	0.71	0.84	2.81
$R_{18}W_2$	0.10	0.15	0.19	0.29	0.49	0.70	0.81	2.62
$R_{10}W_{10}$	0.02	0.04	0.05	0.08	0.20	0.28	0.36	1.51

This seems inconsistent with the normal behaviour of wood (see control data, Fig. 2.2). However, similar results have also been observed by other workers (Voulgaridis, 1980; Palejowski , 1980). The phenomenon has been ascribed to the between-specimen variability exhibited by the separate groups of specimens which had of necessity to be used in the reported experiments. The same explanation may also hold good in this case. However, there may be systematic reasons for these observed phenomena.

The formation of end checks and splits in wood due to drying stresses is an established occurrence. Cyclic soaking and drying is almost certain to set up this type of stress in the long specimens used in this work. In fact, end checks have been clearly observed with cycled control specimens (see Section 2.2.4.1). Similar checks and microchecks have been observed with treated specimens to a much smaller extent. It is suggested that this degrade in wood exposes untreated areas facilitating increased water entry. Further, this movement in wood may weaken the wood-resin bond and dislodge some of the coating films causing increased water entry. Once dislodged, it is extremely unlikely that re-deposition in the original locations will occur. In addition to cohesive failure, preferential wetting due to the stronger hydrogen bond forming affinity of wood for water than for resin or resin-wax is likely to contribute to coating breakdown. In the absence of wood degrade the action of water on water repellents in treated wood would probably not be so devastating. Weakening of the wood-resin bond and cohesive failure would be expected to occur much more slowly and the general deleterious effect on water repellent performance would probably be minimal except over longer periods of exposure.

On further cycling to 10 Or 20 cycles few further water entry routes are opened up by the formation of more checks or cracks (see Section 2.2.4.1). This probably accounts for the observation that further exposure beyond five cycles leads to little further loss of performance. However, usually a small improvement in water repellency was observed on cycling between 5 and 10 cycles and again further improvement between 10 and 20 cycles. This is contrary to the findings with control specimens.

The following explanations are put forward to account for the apparent anomaly observed:

i) Different groups of specimens had to be taken for various extent of cycling. Specimen variation may account for some increase in water repellency.

ii) Heating for 12 hours every day might strengthen the weakened wood-water-repellent bonds by softening the deposit and allowing slight re-distribution and re-loading to occur.

iii) Removal of last traces of carrier solvent from treated wood on extended heating may improve water repellency by leading to some increase in the value of the contact angle.

iv) There is a possibility of the formation of some furfuraldehyde by the breakdown of hemicelluloses on extended heating for long periods even at a modest temperature.

If it occurs, this may give rise to a degree of cross-linking and an accompanying reduction in water sorption. (Stamm, 1964; Shafizadeh and Chin, 1977).

Voulgaridis (1980) has reported that wetting weakened and heating persistently strengthened the wood resin bond in treated wood. He attributed the strengthening effect to fusion of the deposit with loss of final traces of retained solvent and formation of stronger deposit-cell-wall bonds on cooling. This seems to be reasonable, especially in the case of the resin-wax treated specimens, considering the low melting point of the wax used (49°C). The melting point of all organic substances is reduced on contamination. It is likely that resin-wax mixtures will melt or congeal over a range of temperature depending on the relative proportions of resin:wax and upon the presence of small quantities of entrapped carrier solvent. The oven temperature used during drying was 35±2°C. Under the circumstances the possibility of some re-distribution or rebonding of water repellents on heating cannot be excluded.

Voulgaridis (1980) has demonstrated that traces of Shellsol solvent persist in the resin "glueline" of shear test blocks, prepared using water repellent deposits as the adhesive, even after prolonged exposure to heat. Steiner and Manville (1978) found that traces of toluene solvent was present in the glueline of some elastomeric construction adhesives even after 130 days of curing by evaporation. Even a highly volatile solvent (hexane) took 10 days to evaporate from the glueline. Cockroft (1957) found benzene, toluene and xylene solvents to take 14 months and 5 to over 12 months to evaporate completely from uncoated European beech and Scots pine specimens respectively. Petroleum distillate or toluene has been shown to take a considerable time (several weeks) to evaporate completely from free surfaces of water repellent solutions (Carragher, 1980). In one of the experiments carried out during this study (concerning the contact angle of treated surfaces) it was found that water repellent treated Corsican pine and European beech long specimens, equilibrated to virtual constant weight at 20°C and 65% RH, carried a slight odour of white spirit carrier solvent on cutting up after natural weathering for a year.

Thus it seems that absolute removal of organic solvents from water repellent treated large specimens may take an inordinately long time. It seems possible, therefore, that final small traces of solvent may continue to be depleted over very long exposure periods. It is known that maximum contact angle is not fully developed until all solvent is lost and the work of Voulgaridis cited above suggests that the wood/deposit bond may not attain its full strength until removal of final traces of solvent. These factors may explain the observed slight improvement in performance observed on exposure from 5 to about 20 soak dry cycles. This fact, however, brings into focus another point which may be far more important.

If it is assumed that traces of solvents are retained in long wood specimens even after careful evaporation and equilibration, then the effect of their final removal during weathering is likely to be of lesser importance than their possible role in improvement of water repellency before removal. It has already been mentioned that heating improves the wood resin bond. The weakened wood-resin bond brought about by cyclical wetting and heating for 5 cycles is likely to get a considerable boost for rebonding if the retained solvent dissolves some of the dislodged resin and redistributes it in depleted areas. Water repellency will thus improve before the retained solvent is finally removed. It is likely that the amount of solvent retained will increase with the concentration of the treating solution, since more solids will be available to encapsulate the liquid. Furthermore, the rate of solvent loss is likely to decrease with increase in the depth of solution penetration into wood due simply to the associated increase in diffusion path length and tortuosity.

Hemicellulose, the most hygroscopic component of wood is severely degraded by heat to form furfuraldehyde, which may subsequently polymerize to form water insoluble polymers leading to reduction in the hygroscopicity and swelling of wood. This thermal decomposition takes place rapidly at 225°-325°C (Shafizadeh and Chin, 1977). However, thermal decomposition may occur slowly at temperatures below 100°C (Stamm, 1964). Heating for extended periods at 35°C as in the cyclic soak-dry exposure applied in this work may lead to slight breakdown of this type. It seems unlikely, however, that it could reach

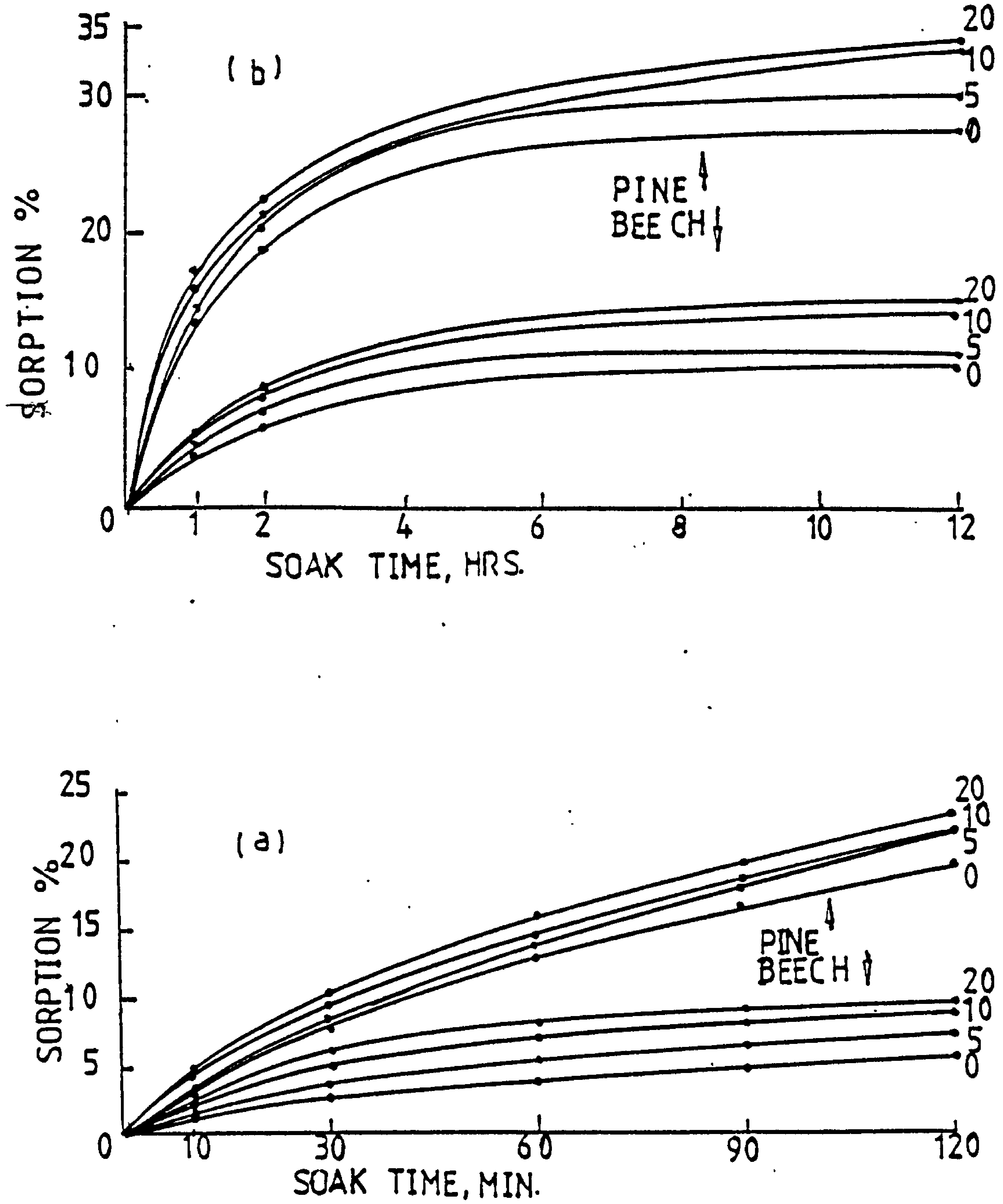


Figure 2.5 Rates of water absorption of heat treated control pine long specimens after 0, 5, 10 and 20 cycles. a = 2 hours soak; b = 12 hours soak (4 replicates).

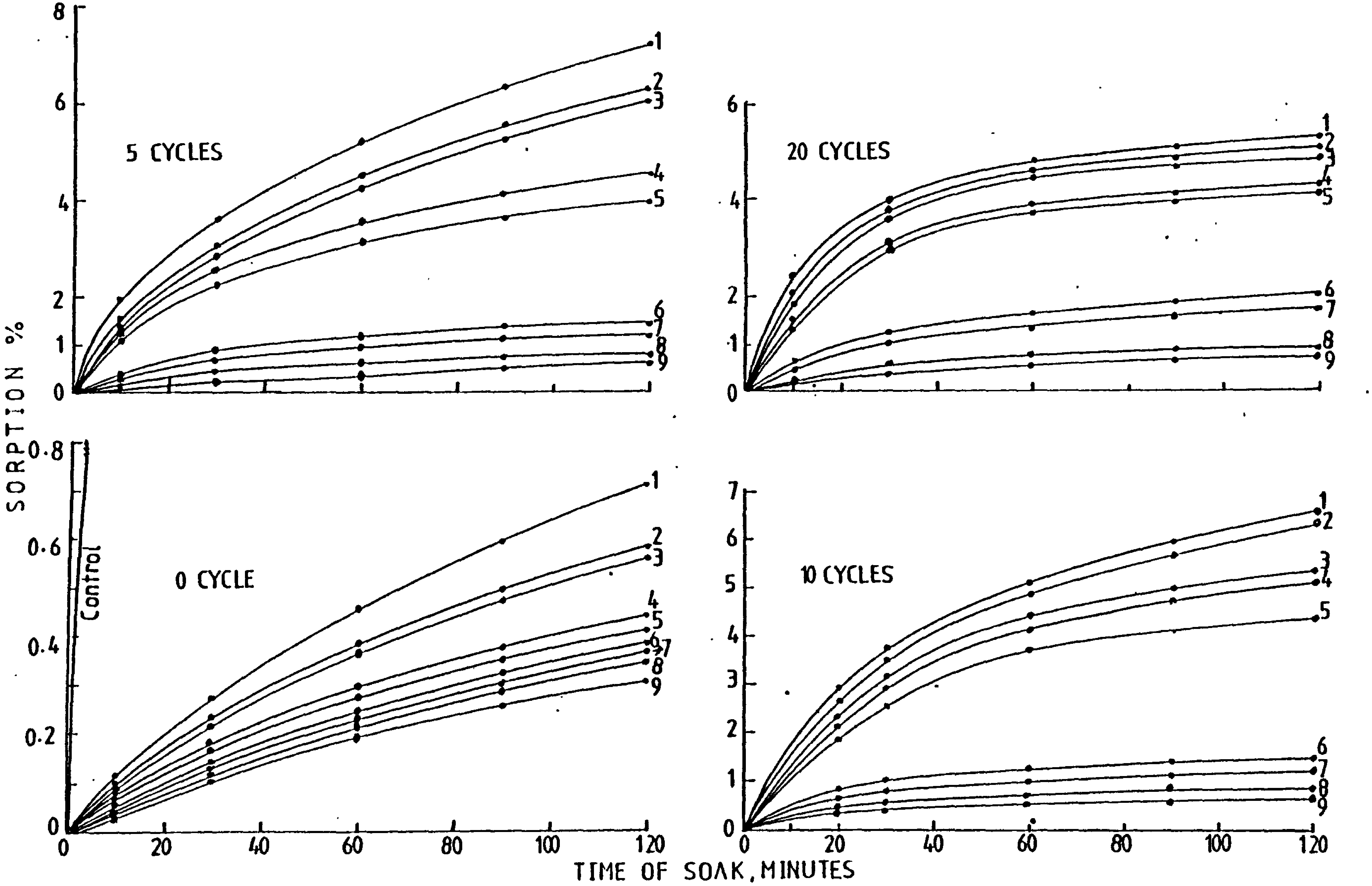


Figure 2.6 Rates of water absorption by beech long specimens after 0, 5, 10 and 20 weathering cycles (3 replicates). Curve nos. represent; 1 = 10% resin; 2 = 11% resin; 3 = 12% resin; 4 = 15% resin; 5 = 20% resin; 6 = 10% resin + 1% wax; 7 = 10% resin + 2% wax; 8 = 10% resin + 5% wax; 9 = 10% resin + 10% wax.

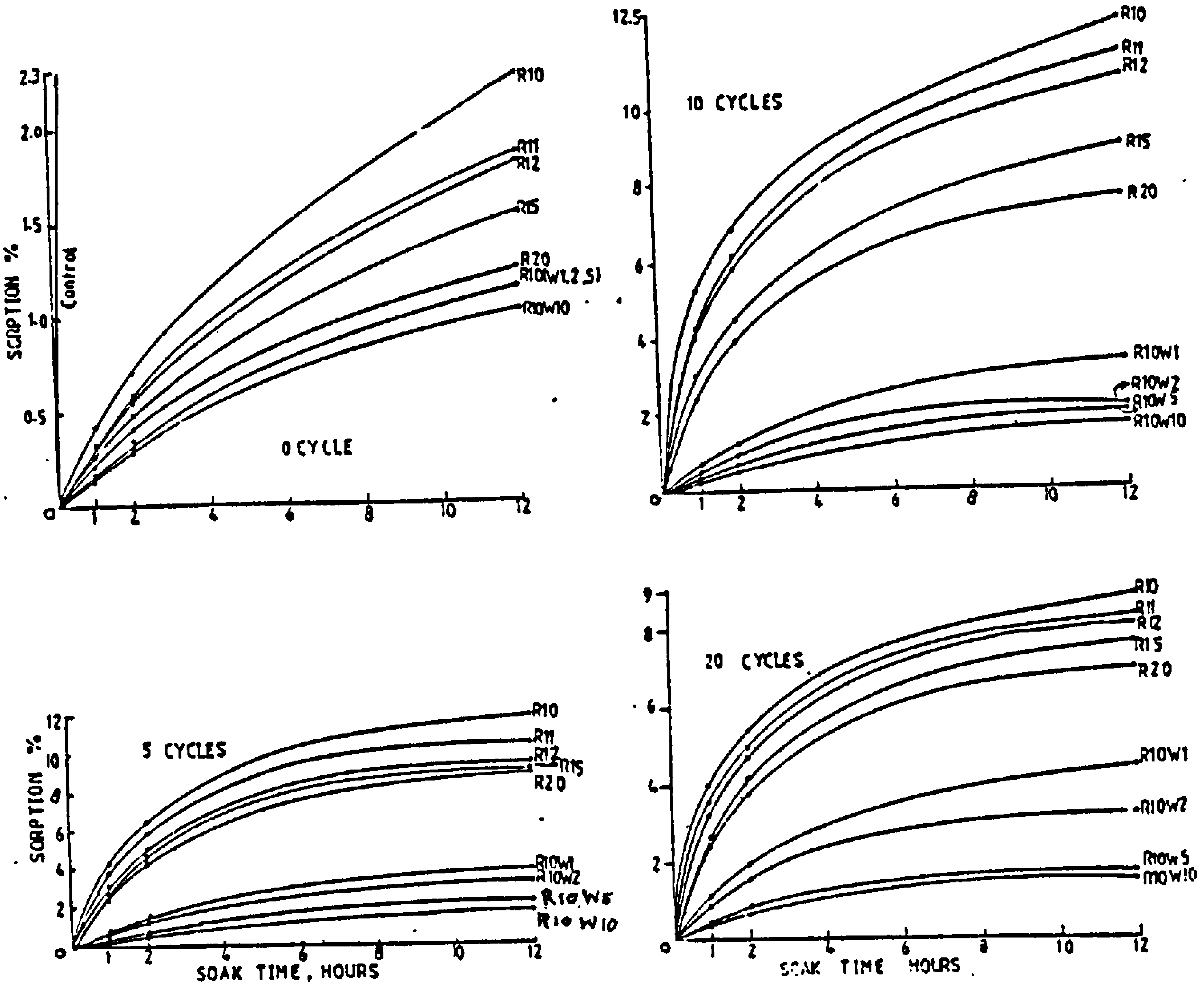


Figure 2.7 Water absorption after 12 hours soak by beech long specimens after 0, 5, 10 and 20 cycles (3 replicates). Subscripts after R and W indicate percentage of resin and wax.

significant levels under these very mild conditions.

To check on this point, a set of 15cm long, 2x2cm cross-sectional specimens coated on all sides but one transverse face was cycled for 0, 5, 10 and 20 cycles of simulated weathering and then heated for a further 7 days at 35°C. The specimens were then equilibrated to constant weight at 65% RH and 20°C and subjected to heating for 15 consecutive days at 35°C. After re-equilibrating them as described above their rate of water absorption over 12 hours of water soaking at 25°C were measured. The rate and magnitude of water absorption (Figure 2.5 and Appendix I, Table 3) is very similar to that of otherwise similarly manipulated specimens, not exposed to the final prolonged heating for 15 days (Fig. 2.2, App. I, Table 1). This probably means that even on prolonged heating at 35°C no significant pyrolytic breakdown of wood component takes place.

2.2.4.2.2 Water absorption by European beech long specimens

Treatment with various concentrations of both resin and resin-wax solutions led to much slower water sorption in beech than in similarly treated pine specimens. This may be attributed, in part at least, to the greater natural resistance to water uptake of beech wood than pine (Figure 2.2) due most probably to differences in the flow system in the two species. The various concentrations of resin solution, 10, 11, 12, 15 and 20% imparted progressively more initial water repellency. The increase observed was very small and slightly less than in the case of pine (Figure 2.6 and 2.7; Appendix I, Table 2E-H).

Addition of wax to the treating solutions led to improvement in performance beyond that achieved with the highest (20%) resin alone concentration. This indicates that in beech, as in pine, hydrophobic as well as coating qualities are desirable to achieve optimal performance from water repellent treatments. However, in contrast to pine, with beech, increase in wax concentrations beyond 1 or 2% gave little further improvement in initial water repellency.

It seems likely that this difference in initial performance between pine and beech is associated with anatomical differences between the two species. In pine, initial penetration throughout the structure is likely to involve mass flow pathways where hydrophobic action is of great importance. In beech, however, whilst initial penetration into the vessels is certain to involve mass flow processes, fibre penetration from the vessels is by way of hardwood pits with very fine membranes (Côte', 1963; Rudman, 1965) or by direct cell wall penetration. In either case, flow is likely to involve a diffusion mechanism and any protection against such flow requires a coherent coating rather than a hydrophobic action. Thus in beech, initial protection probably involves a truly water repellent effect slowing down water entry into vessels. It seems that 1-2% wax loading is sufficient to achieve this. Thereafter, further protection against fibre penetration probably depends upon an effective coherent coating over vessel lumen surfaces. The quality of this coating is likely to be improved by an increase in solids concentration irrespective of the degree of hydrophobicity.

Exposure to simulated weathering leads to very marked wood degrade in the dimensionally unstable beech. As a result, the resin treated beech wood, showing considerable water resistance before cycling, lost a great deal of water repellency after exposure to 5 soak-dry cycles. Physical degrade in the resin-wax treated specimens was observed to be not as extensive as with specimens treated with resin only solution. Decrease in water repellency was consequently less marked. This is in line with the mode of protection suggested above. Once checks occur, creating alternative water penetration pathways to the natural vessel system, internal wood surfaces not coated with any deposit are exposed to liquid water, and diffusion can occur from these areas into surrounding tissue. Where hydrophobic protection is afforded, swelling and shrinking stresses are likely to be reduced and the structure remains more intact so that the secondary diffusion routes continue to be limited to those associated with vessels, where protection by the coating effect is afforded.

Both types of formulation, however, maintained their order of water repellency in accordance with their solids concentrations throughout the soak-dry simulated weathering. Exposure beyond 5 cycles did not lead to much further increase in the rate of water absorption

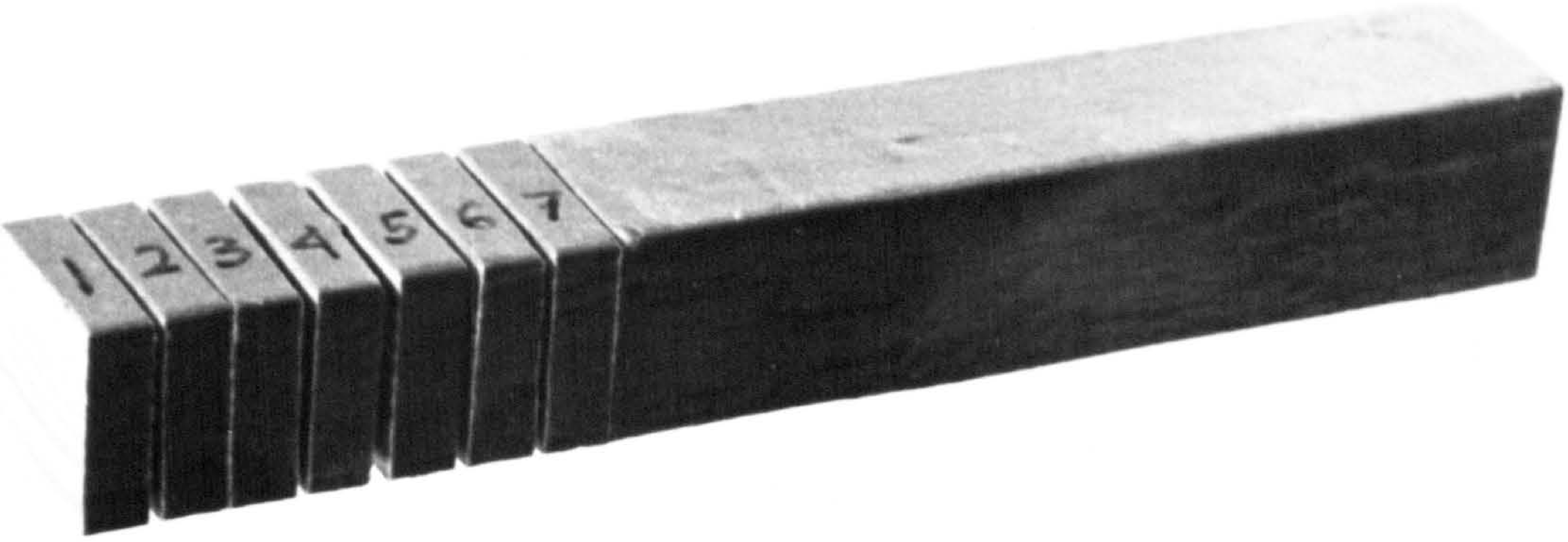


Figure 2.8. Preparation of wafer specimens from weathered long specimens.

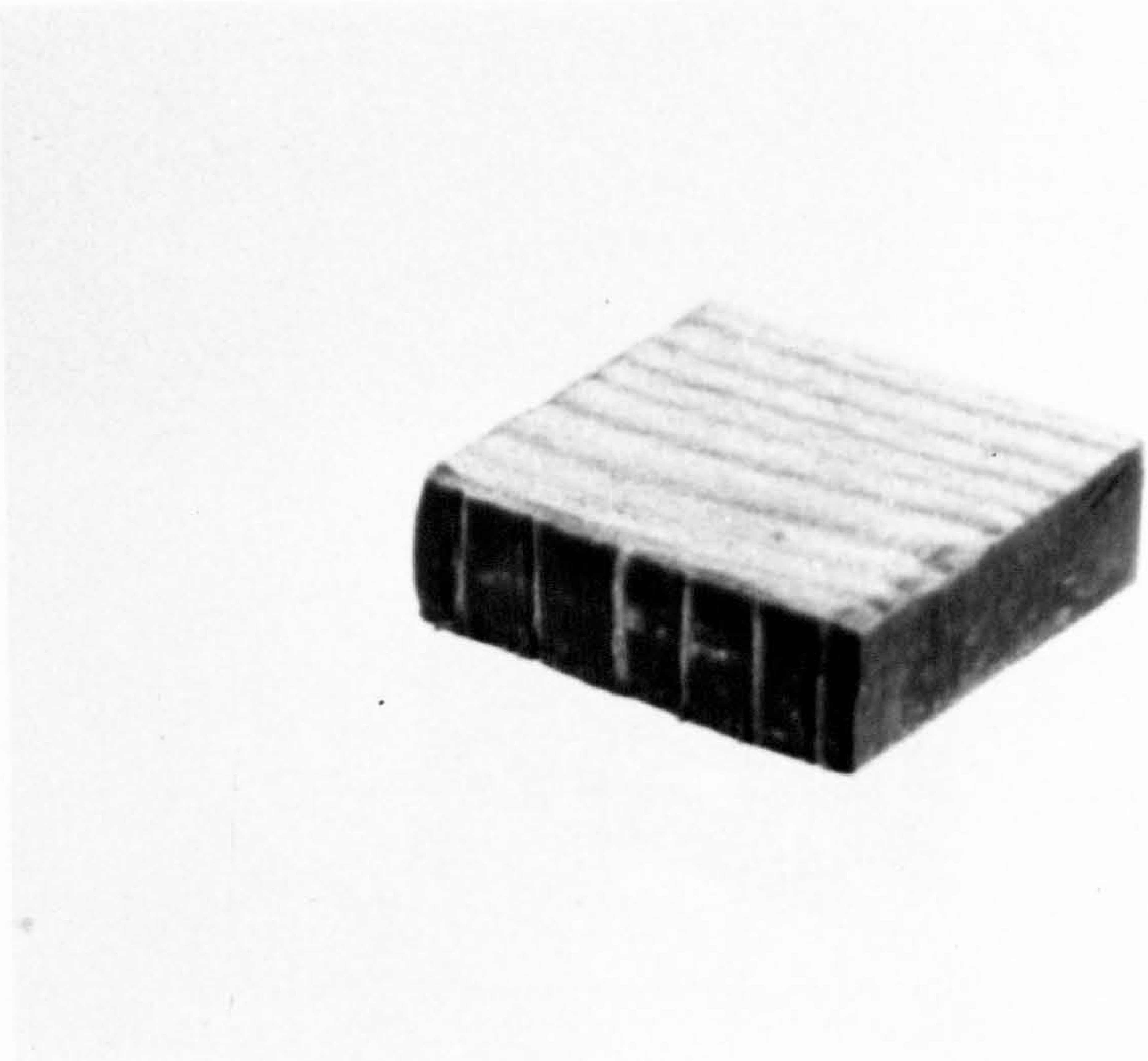


Figure 2.9. Slits cut in the styrene coating of wafer specimens.

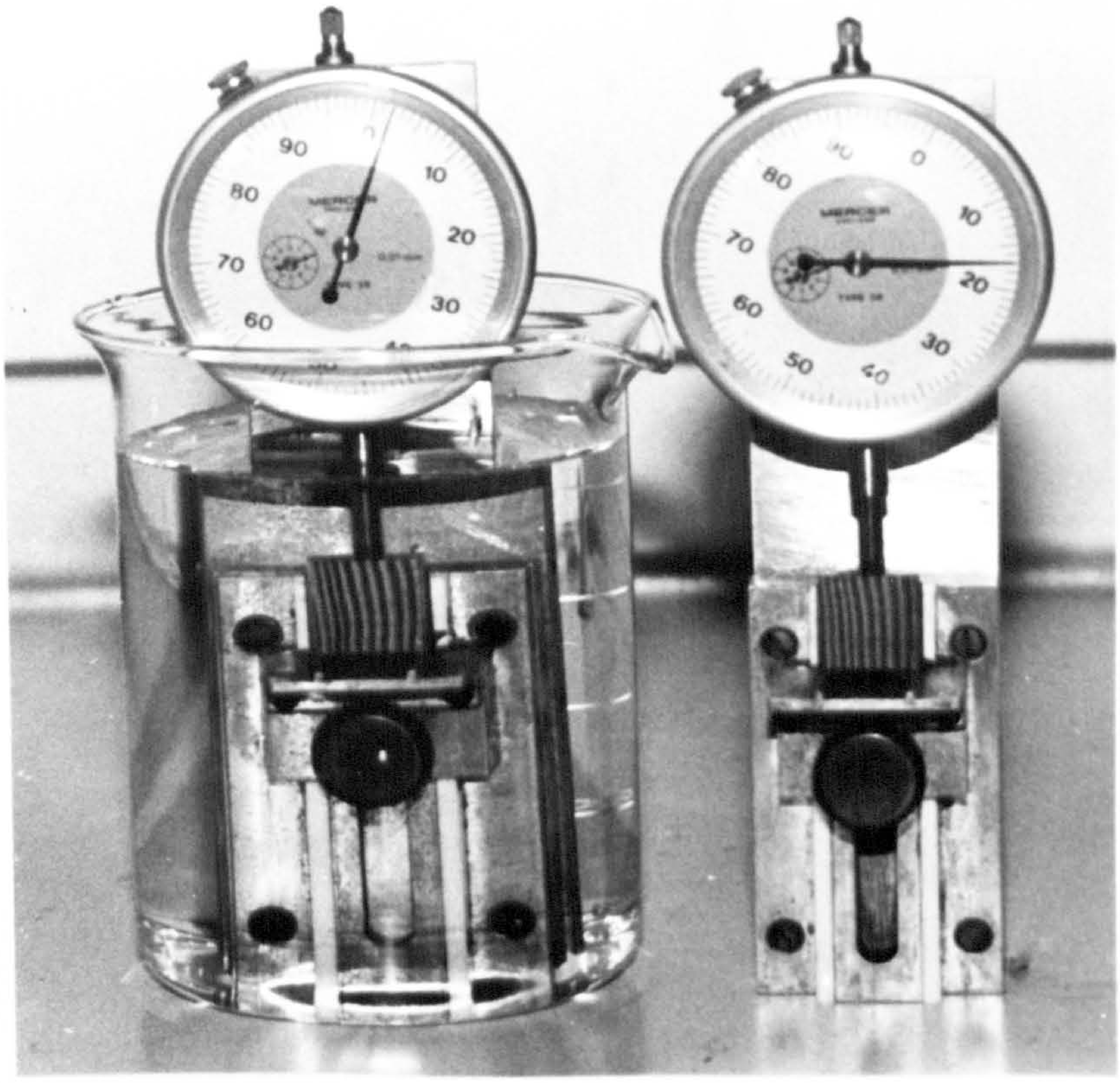


Figure 2.10. Measurement of swelling by dial gauge micrometers. Specimens held by adjustable jig.

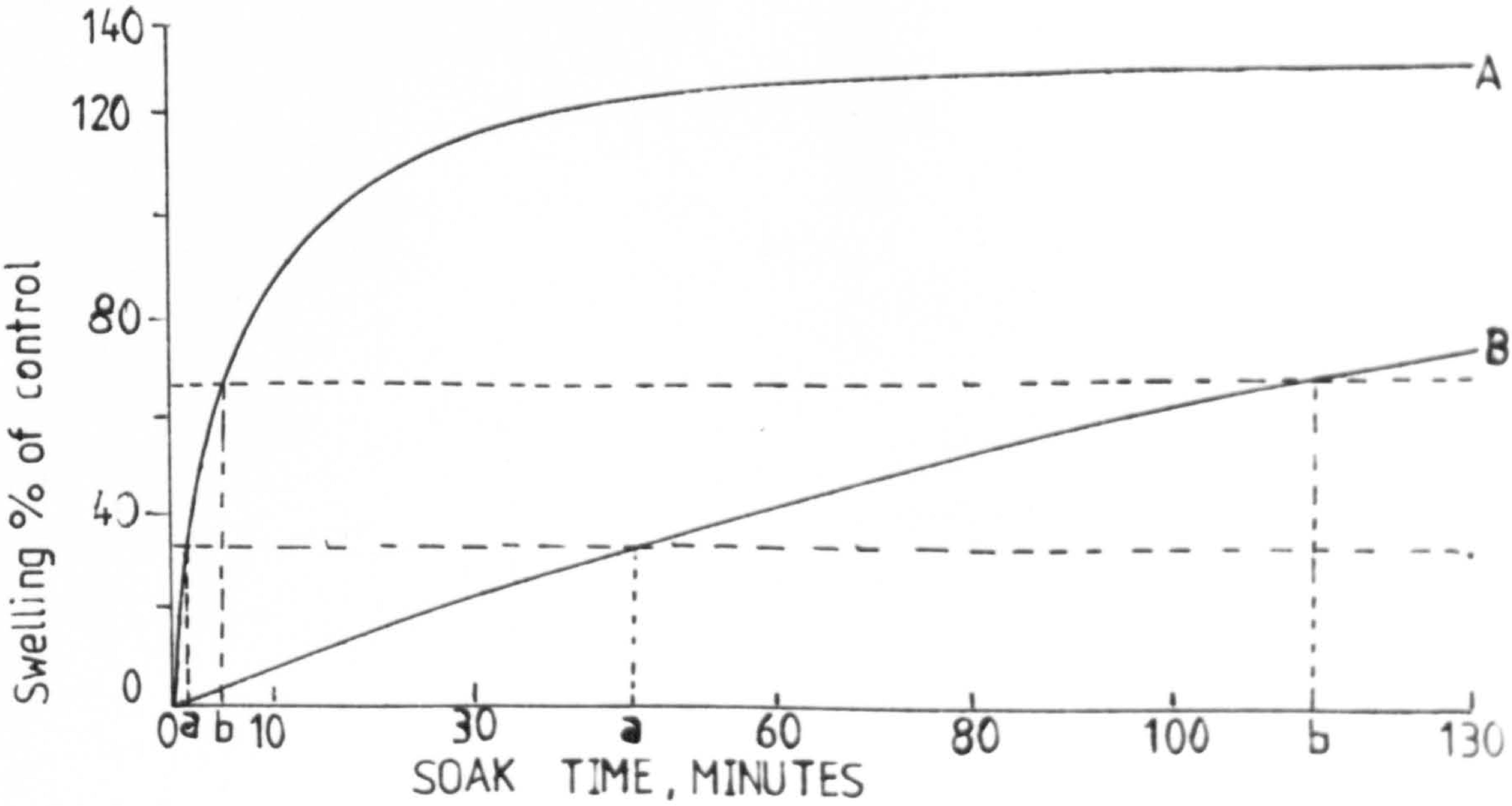


Figure 2.12. Interpolation of time to quarter (a) or half (b) maximum swell in untreated control (A) and treated (B) specimens.

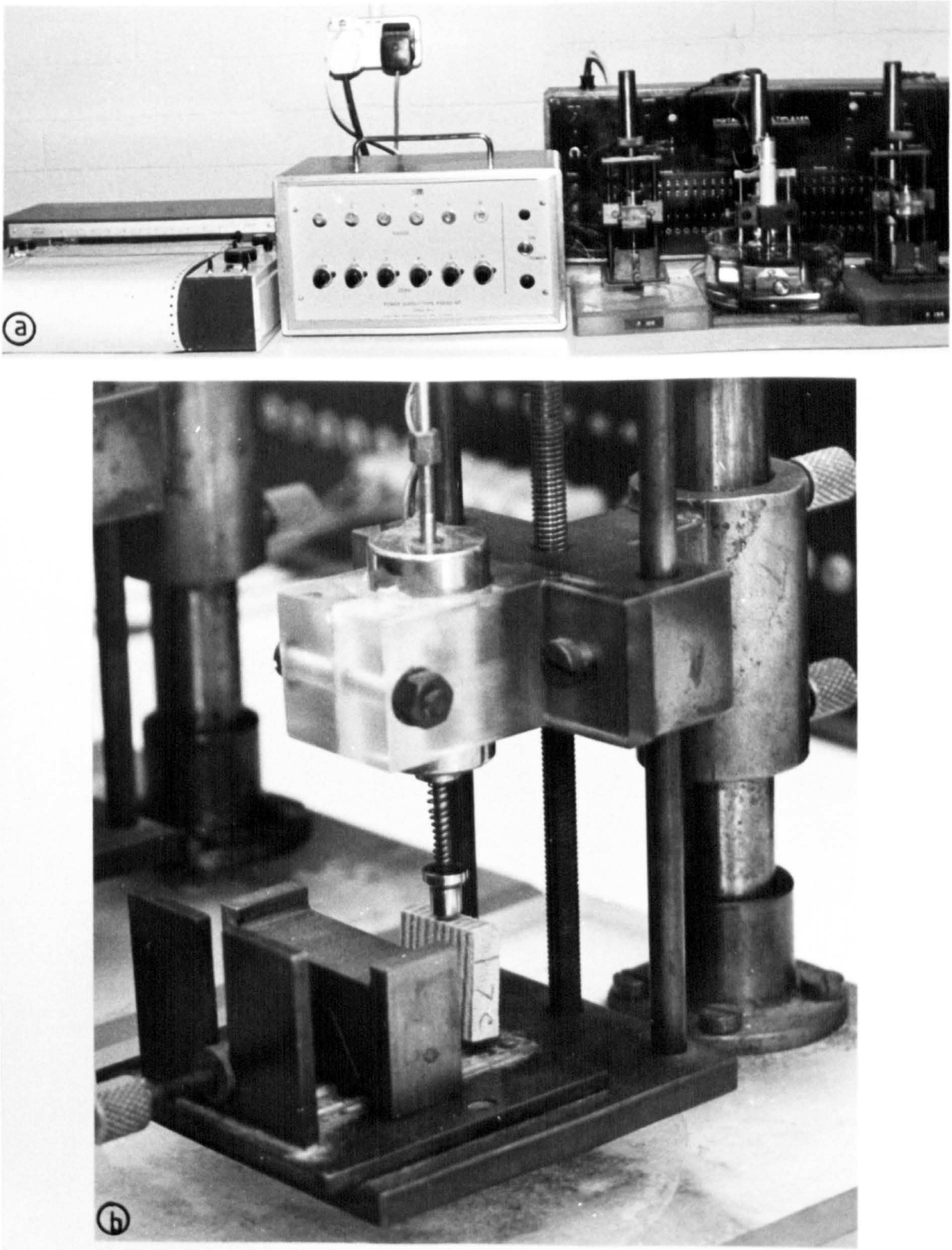


Figure 2.11. Displacement transducer.

(a) General view showing specimen holding jigs.

(b) Close up view of a specimen held in position in a jig.

due probably to similar reasons to those given in the case of pine (Section 2.2.4.2.1). Total water absorption measured after 12 hours of soaking suggests that some improvement in water repellency is obtained upon cycling resin only treated specimens through 10 and 20 cycles compared to that measured after 5 cycles. With resin-wax specimens this effect was not very clear.

It is possible to speculate about reasons for this difference in behaviour. For example, with resin only formulations, the continued heating during cycling may lead to strengthening of the wood-deposit bond (see Section 2.2.4.2.1). High wax concentration within the deposit may have a weakening effect on the bond, which coupled with differences in distribution, degree of dimensional instability and mode of protection may contribute to a fall off in performance sufficient to mask any improvement due to bond strengthening factors. Without further experimental support, however, the complexities of the system make such speculations too uncertain to be of much value.

2.3 Effect of water repellent concentration along depth of treatment

2.3.1 Assessment of water repellency using wafer specimens

The long specimens used for assessment of water absorption after 0,5,10 and 20 cycles of simulated weathering were converted to 6mm transverse wafers to examine how varying water repellent solution concentrations affect in-depth treatment. Rate of tangential swelling was adopted as the criterion for monitoring water repellent effectiveness in these wafer specimens prepared as shown in Figure 2.8. To nullify the possibility of any restraining effect of the solvent cement coating, 6 slits on each tangential face were made, taking care not to damage the wood underneath (Figure 2.9).

Swelling was measured during immersion in deionized water at 20°C using either dial gauge micrometers fitted to jigs allowing specimens to remain submerged in water during measurement (see Banks, 1971; 1973; Figure 2.10) or displacement transducers giving a potentiometric output (Figure 2.11). Results were expressed as time to attain a definite fraction of maximum swelling, time to half swell for pine ($T1/_2$) and time to quarter swell for beech ($T1/_4$).

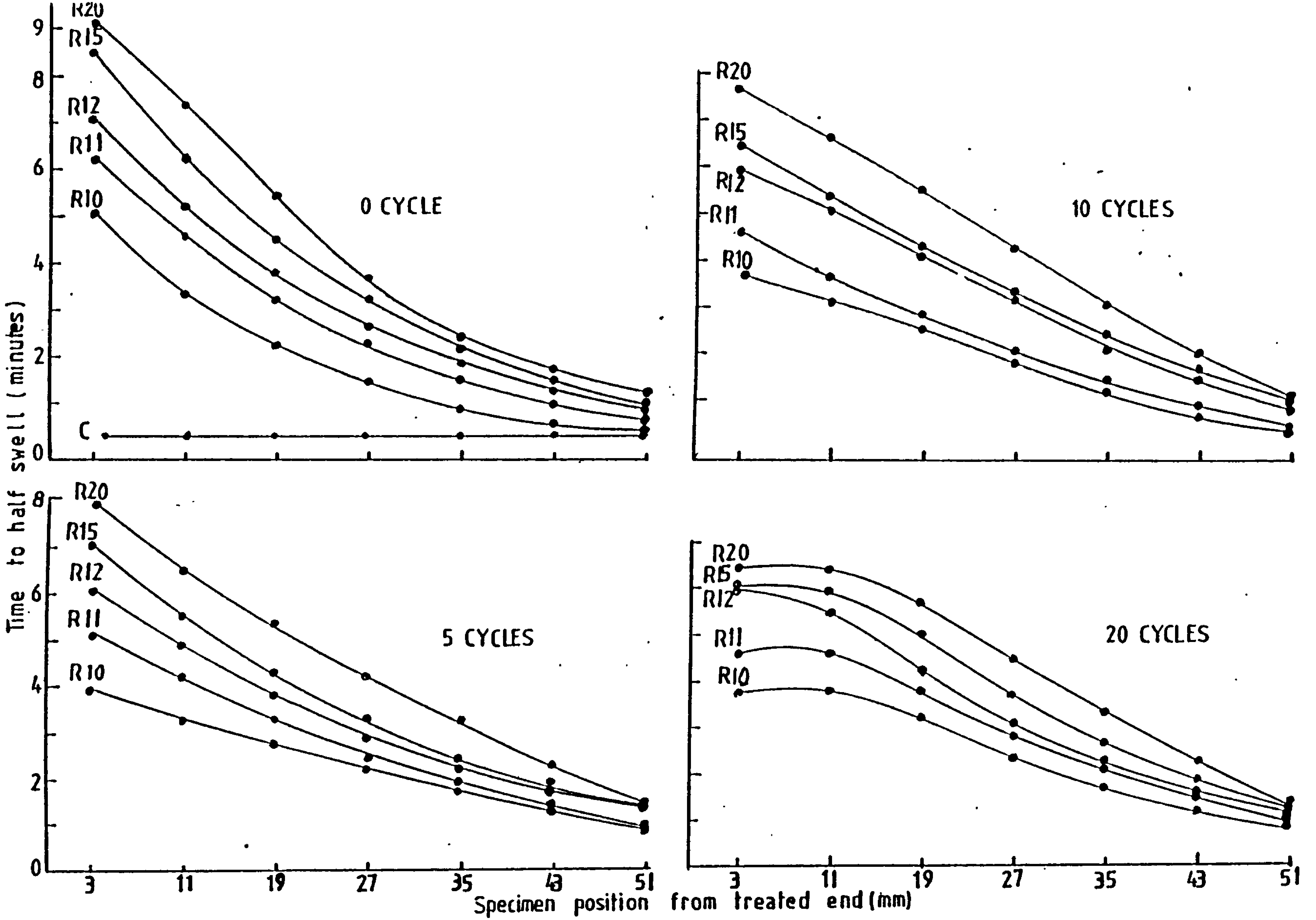


Figure 2.13 Time to half swell of pine wafer specimens cut along depth of treatment from resin-treated long sticks after 0, 5, 10 and 20 cycles (3 replicates). Subscripts after R indicate percentage of resin. C = control.

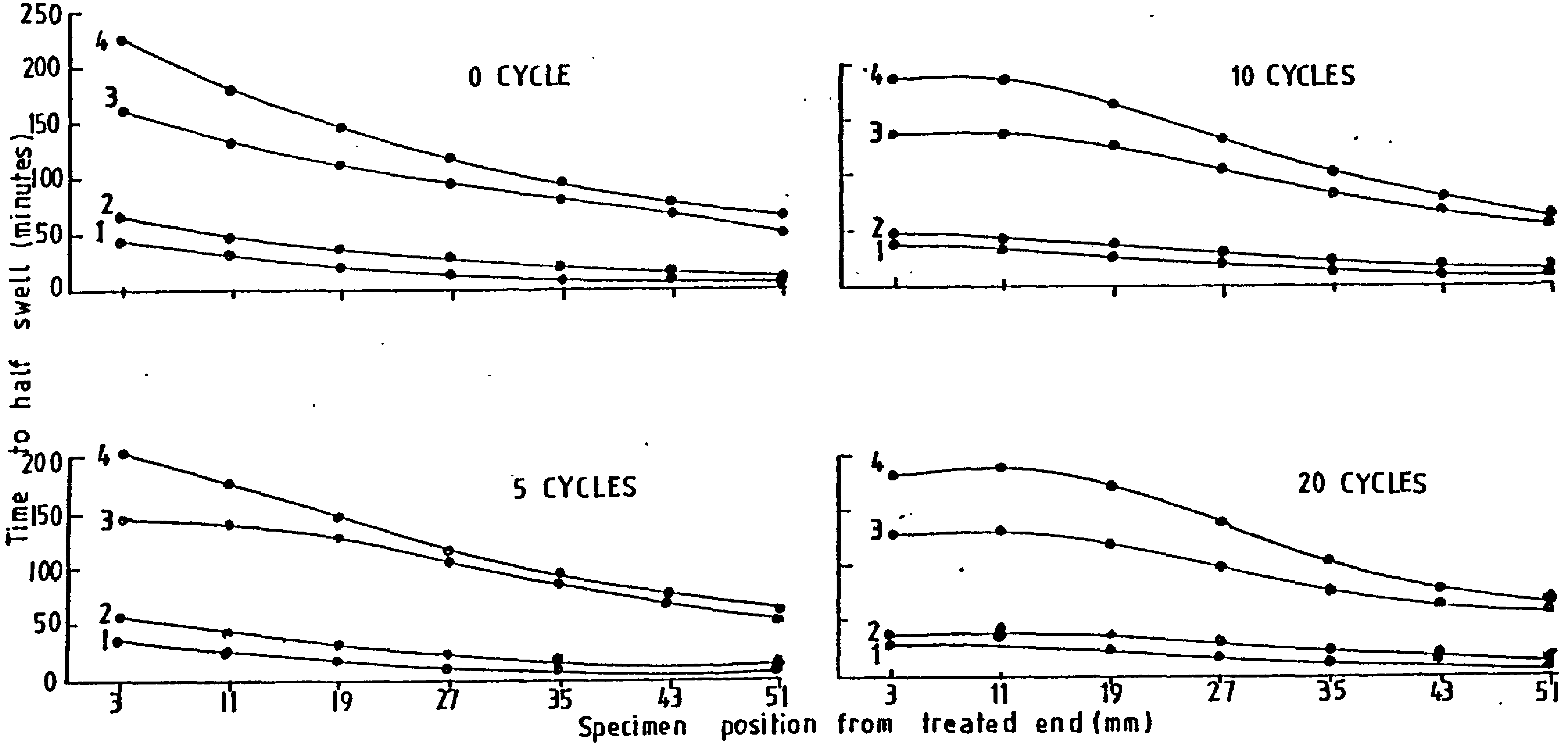


Figure 2.14 Time to half swell of pine wafer specimens cut along depth of treatment from resin-wax-treated long sticks after 0, 5, 10 and 20 cycles (3 replicates). Curve nos. represent: 1 = 10% resin + 1% wax; 2 = 10% resin + 2% wax; 3 = 10% resin + 5% wax; 4 = 10% resin + 10% wax.

With treated specimens the final stages of dimensional increase occured very slowly. Hence, the matched control specimens from the offcuts of the long specimens before treatment were used to give an estimate of equilibrium maximum swell. The time to half or quarter swell was assessed by interpolation of the record of swelling as a function of time (Figure 2.12).

2.3.2 Swelling tests for wafer specimens cut from treated long sticks; results and discussion.

2.3.2.1 Pine wafer specimens

The water repellent effectiveness of the various resin and resin-wax solutions as a function of penetration depth is shown in Figures 2.13 and 2.14 and Appendix I, Tables 1 and 4A-D. From these it appears that with both resin only and resin-wax solutions, before any weathering, the greatest effect is imparted to the outermost specimen. Also, the effectiveness falls off systematically and gradually with increasing distance from the treated end.

With resin only treatments the effect of increasing concentration seems to be relatively small, whilst, with the resin-wax treatments, increase in wax content has a very marked effect. For example, before exposure, the outermost resin only treated specimens show an increase of 50% (from 5 to 9 minutes) in time to half swell, for a corresponding increase in resin concentration from 11 to 20%. Similar increase in solids concentration (from 10% resin + 1% wax to 10% resin + 10% wax) gives rise to about 6 fold increase in time to half swell (40 to 230 minutes) in the case of resin wax solutions. An approximately similar relationship can be seen to exist between specimens treated with the various solutions and taken from positions further removed from the treated end, although the absolute time to half swell values are markedly lower for the interior specimens.

Because of the high degree of water repellency afforded by the higher concentrations of resin-wax treatments the level of resistance to water uptake even 5 or 6cm away from the treated end, remains significant, even though effectiveness is seen to decrease markedly with penetration distance. With resin only treatments, on the other hand, although time to half swell is measurably higher than that of controls, it is doubtful if the difference is of any practical

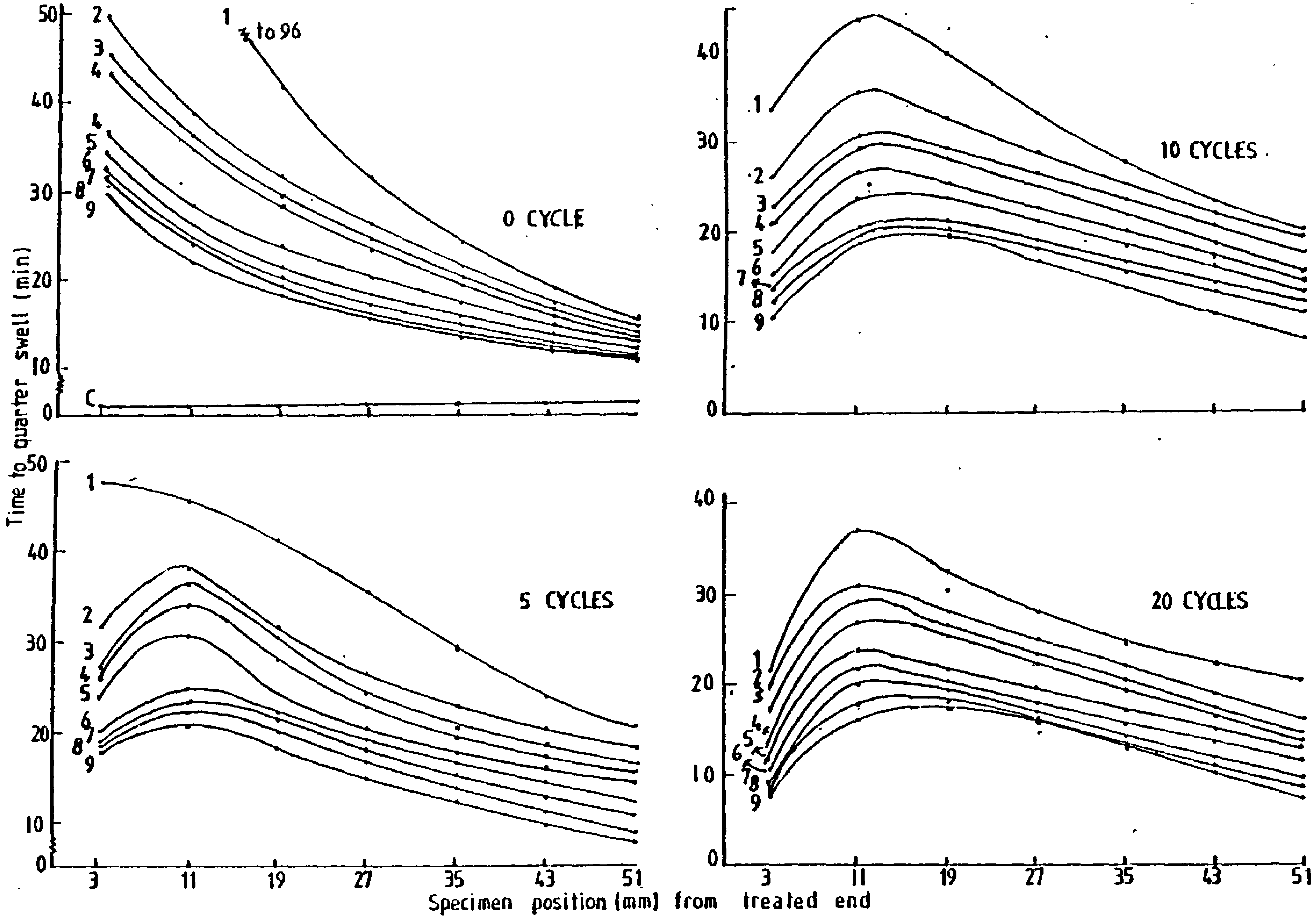


Figure 2.15 Time to quarter swell of wafer specimens cut along depth of treatment of long beech specimens after various cycles (3 replicates) Curve code: 1 = 10% resin; 2 = 11% resin; 3 = 12% resin; 4 = 15% resin; 5 = 20% resin; 6 = 10% resin + 1% wax; 7 = 10% resin + 2% wax; 8 = 10% resin + 5% wax; 9 = 10% resin + 10% wax.

significance beyond the first 2cm or so.

The effect of weathering is interesting. It can be seen that with all formulations cycling markedly reduces the time to half swell of the outermost specimens, but little loss of performance is evident in any of the other wafers even after 20 soak-dry cycles. This trend is shown clearly in Table 2.5. It has been suggested by Voulgaridis (1980) that loss of water repellent effectiveness is associated, at least in part, with wood structural degrade extending a short distance (about 1mm) from exposed end grain surfaces, rather than with significant degrade of the water repellent material itself. The results briefly discussed are not out of line with this suggestion.

Table 2.5 Loss of water repellency due to simulated weathering in the outermost specimens of pine sticks

No. of Cycles	Time to half swell (minutes)							
	Water repellent formulations and specimen numbers							
	11% resin		20% resin		10% resin+1% wax		10% resin + 10% wax	
	1	2	1	2	1	2	1	2
0	6.5	4.4	9.5	8.7	45	35	230	180
5	5.1	4.2	7.9	6.3	33	29	200	177
10	4.9	3.9	8.0	6.8	40	30	180	178
20	4.5	4.7	6.4	6.5	30	30	180	184

2.3.2.2 Beech wafer specimens

From the swelling data in Appendix I, Table 4E-H and Figure 2.15 it can be seen that much better initial resistance to water entry is observed in wafers cut from the treated zone in resin treated beech wood compared to that obtained with pine. Water repellency shows a definite gradient from the open treatment end inwards. However, unlike pine, considerable resistance to water sorption is observed in the interior specimens of beech. This probably results from the unobstructed penetration of resin solution through the vessels in beech. The effect of resin solution concentration is much less obvious in beech than in pine. There was little appreciable increase in time to quarter swell in beech wafers with the increase in solution concentration over the range 10-20%. This points to the fact that near optimal internal coating protection is probably afforded by a solution concentration of 10% or so in beech.

The contribution to overall protection afforded by the hydrophobic effect in pine long sticks has been found to be greater than in beech. A similar effect is observed with wafer specimens. In general, water repellency in beech wafers treated with resin-wax solutions, measured as time to quarter swell shows only a relatively small improvement compared with resin only solution treatment. However, although the influence of wax is very small, a progressively increasing water repellency is recorded with the progressive increase in wax concentration from 1 to 10%. This effect, as in the case of resin solution, seems to be more prominent in the first centimetre or so of the long specimen, but the gradient of water repellency decrease inwards is much less steep than in the case of pine. It is interesting to note that for all solution concentrations the time to quarter swell of specimens taken from distances greater than about 5cm from the treated end become almost identical and little greater than that of untreated control wafer specimens, suggesting that there is little water repellent deposit at or beyond this depth.

As stated above, improvement due to increase in solids concentration is, in general, very small (see Table 2.6).

Table 2.6 Time to quarter swell data for outermost uncycled resin-wax treated beech specimens

Treating Solution	Time to quarter swell (minutes)
10% resin + 1% wax	43
10% resin + 2% wax	44
10% resin + 5% wax	47
10% resin + 10% wax	96

From the above table it can be seen that increase from 1 to 5% wax concentration has an insignificant effect on time to quarter swell. This is in line with work reported by Palejowski (1980). Even at 10% wax concentration the time to quarter swell is only a little more than double that obtained with a 1% wax solution. This is in contrast to data obtained for treated pine, where similar increase in wax concentration leads to a more than 5 fold increase in time to half swell. It should, however, be mentioned here that the parameters used to express water repellency differ for the two species, i.e. $T_{\frac{1}{2}}$ for pine and $T_{\frac{1}{4}}$ for beech. Nonetheless, it appears from the shape of the swelling curves that the ratio of $T_{\frac{1}{4}} : T_{\frac{1}{2}}$ is reasonably constant so that relative changes in their values may be usefully compared with one another.

Even though the observed effect of increased wax concentration is quite small in absolute terms, the relatively large improvement in performance associated with the step from 5% to 10% wax is noteworthy. Until recently this effect was puzzling. However, evidence has recently emerged that solution properties may significantly influence deposit distribution. This is related to two factors:

1) Water repellent solids tend to migrate towards outer surfaces as solvent evaporates.

2) At relatively high wax loadings bulky gel-like deposits containing large quantities of trapped solvent tend to be formed (Carragher, 1982).

It is believed that this second factor is likely to overcome to some extent, the uneven distribution effect caused by solution migration towards the specimen open end (Factor 1). This may lead to the marked improvement in performance exhibited by wafer specimens from sticks treated with 10% wax laden solutions.

As with pine (Section 2.3.2.1), the outer specimens from treated beech sticks show marked loss of effectiveness after cycling. In fact, the effect is rather more pronounced with beech. Loss of performance at distances of a few centimetres from the treated end, as with pine, is much less marked (Table 2.7).

Table 2.7 Pronounced loss of water repellency of the outer specimens cut from cycled beech sticks

No. of cycles	$T_{1/4}$ (min), water repellent formulations and specimen nos.							
	11% resin		20% resin		10% resin + 1% wax		10% resin + 1% wax	
	1	2	1	2	1	2	1	2
0	33	24	37	26	45	34	96	56
5	18	23	24	31	26	34	48	44
10	11	19	14	27	17	30	33	44
20	7	18	11	24	12	28	20	37

Again, this fall in performance associated with the exposed wafers seems likely to be related to the loss of wood structural integrity reported by Voulgaridis (1980). As with pine, visible checks were seen to develop on exposed end grain surfaces after a few soak-dry simulated weathering cycles.

Noticeable with beech is the much less marked effect of wax in the treating solution compared to the effect with pine. Hence, with beech it seems that the coating effect may be relatively more important than the effect of increased surface contact angle. This was suggested by Banks and Voulgaridis (1980), who attributed the difference in coating efficiency in beech and pine specimens to differences in the structure of the intercellular pits. In beech the much less open fibrillar network is probably able to support a coherent coat of deposit reducing movement by the diffusion mechanisms (see Section 2.2.4.2.2), whereas, open textured pine pit membranes are incapable of doing so. Thus in pine, the provision of hydrophobic surfaces is essential for effective water resistance to develop.

Increasing the concentration of resin only solutions was seen to lead to a smaller relative improvement in performance in beech than in pine. This can be explained in terms of the contribution to water flow resistance made by the resin. It has been shown by Banks (1971a; 1973) that 'Time to half or quarter swell' is related inversely to diffusion coefficient. That is to say, it is related directly to resistance to diffusion. Now, making an electrical analogue the system can be represented as follows (see Figure 2.16).

Figure 2.16 Electrical analogue model for water diffusion through wood. R_1 = resistance due to natural cell wall properties, R_2 = resistance due to applied deposit and R_T = Total resistance = $R_1 + R_2$.

It is reasonable to assume that the resistances act in series, since water flowing from lumen into cell wall must traverse first the deposit and then the cell wall substance. It is also reasonable to assume R_2 to vary in proportion to solid content. Irrespective of solution concentration, identical cells will be impregnated, and hence the thickness of deposit on the cell wall will vary approximately in proportion to solids retention. From Figure 2.13 it can be seen that based on the above model for the outermost pine specimens, before cycling, total resistance R_T is made up of R_1 (the resistance due to the cell wall(s) + R_2 (the resistance due to the applied deposit).

Table 2.8 Increase of resistance to water penetration in pine specimens with solution concentration

Resin Concn. (approx proportional to solids content) %	R_T (Min)	R_1 (Min)	R_2 (Min)
10	5.3	0.6	4.7
11	6.5	0.6	5.9
12	7.3	0.6	6.7
15	8.8	0.6	8.2
20	9.5	0.6	8.9

Assuming R_1 to remain constant at 0.6 minute, R_2 is given by $R_2 = R_T - R_1$. These data are summarised in Table 2.8. By inspection it can be seen that R_2 does increase very approximately in proportion to solution concentration as predicted.

Similarly for beech a resistance table can be constructed (Table 2.9) from the data as given in Appendix I, Table 4 and Figure 2.15.

Table 2.9 Variation in resistance to water flow in beech specimens with solution concentration

Resin Concn. (%)	R_T (Min)	R_1 (Min)	R_2 (Min)
10	31	2.5	28.5
11	33	2.5	30.5
12	34	2.5	31.5
15	35	2.5	32.5
20	37	2.5	34.5

In this case the proportionality is not so good but the principle remains that the two species cannot be expected to respond relatively similarly to increase in thickness of deposit (indicated by increase in solids loading). The natural resistance to water uptake of the wood must also be taken into account. Failure to establish a good linear relationship between R_2 and concentration in beech, is probably due mainly to the fact that diffusion into wood is not a true steady state phenomenon. Even over a limited period, the moisture gradient falls as penetration occurs, and the profile of the gradient will vary with deposit thickness, unless the deposit has precisely the same diffusion coefficient as the wood substrate.

PART 3

DISTRIBUTION FACTOR AFFECTING THE PERFORMANCE OF WATER REPELLENTS IN WOOD

3.1 Introduction and Objectives

Most of the work done so far in the field of water repellent treatment of wood has been devoted to the study of the initial effectiveness of the treatments and the longer term performance of the treated wood. A large part of this work has involved the use of water repellents in conjunction with preservatives. Little is reported about the distribution of water repellent substances in wood, although Levi et al (1970) have published data relating to cellular distribution of waxes deposited from a wax emulsion system.

Water repellents reduce the uptake of water by forming a very thin hydrophobic layer over capillary (cell lumen) surfaces. A non-hydrophobic film coating such surfaces will not restrict the penetration of water into the pore structure. Hence it is important to be aware of the distribution of the various components (wax and resin) within the wood capillaries. Axial penetration being predominant, 10% resin and 10% resin + 10% wax solutions were allowed to penetrate longitudinally to various depths to provide a distribution gradient in the treated specimens.

The following experiments were conducted to assess distribution factors affecting water repellent performance:

i) Assessment of initial water repellent effectiveness along the treated zone of long specimens.

ii) Evaluation of long term water repellent performance using large specimens.

iii) Assessment of long term water repellent effectiveness along the treated zone.

iv) Assessment of distribution of water repellent substances within the treated zone at various stages of simulated weathering.

v) Estimation of hydrophobicity of resin-wax deposit along the treated zone at various stages of weathering.

The effectiveness of the water repellent treatments at various distances from the treated end were assessed by measuring the time to half or quarter maximum swell of wafer specimens cut from the treated zone of the long sticks. Water sorption rate was measured on control and treated long specimens after 0, 5, 10 and 20 cycles of simulated weathering.

3.2 Distribution of Water Repellent Effect Along End Treated Specimens

3.2.1 Preparation of Wood Specimens and Water Repellent Solutions

Wood specimens, 15 cm long and 2 x 2 cms in cross section, were prepared from Corsican pine and European beech wood in a similar manner to that described in Section 2.2.1. Again, care was taken to select wood with straight grain and of even growth rate of about 4 annual rings per cm. Control 6 mm thick transverse wafer specimens were also taken from the off-cuts of the long specimens and monitored for maximum tangential swelling in the manner described in Section 2.3.1. The long specimens were equilibrated to constant weight at 65% RH and 20°C before being coated on all faces except one transverse face with a styrene resin (see Section 2.2.2). When the styrene solvent cement had completely dried the specimens were again equilibrated at 65% RH and 20°C.

It has been shown in Part 2 that the hydrophobe and the dispersant in a water repellent solution both contribute to reducing water uptake rate but by different mechanisms. It has also been seen that water repellent effectiveness varies, more or less, directly with the solids concentration of the formulation. In the light of the above findings only the two extreme concentrations, namely, 10% resin (R_{10}) and 10% resin + 10% wax ($R_{10}W_{10}$) were used in this experiment.

Resin solution was prepared by dissolving 10% of resin in white spirit on a weight to volume basis. Resin-wax solution was prepared in the same way adding 10% by weight of each of resin and wax to the white spirit solvent. The volume was adjusted after cooling to 20°C and the solutions were stored at that temperature.

3.2.2 Treatment of Wood Specimens with Water Repellent Solutions

The amount of water repellent absorbed during treatment depends mainly on 3 factors:

a) permeability of the wood specimens,
b) the properties of the treating solutions,
c) the time that the solutions remain in contact with the wood specimens (Morgan and Purslow, 1973).

To study the effect of distribution on water repellent performance, matched specimens were selected from pine and beech wood. Resin and resin-wax solution properties remaining constant, variation in the period of treatment was expected to effect penetration of water repellents to various depths in the specimens, bearing in mind that liquid flow was restricted to the longitudinal direction only.

Sets of specimens, each of 12 replicates, were impregnated with the relevant solution according to the following schedules.

Specimen Set 1 - Simple immersion treatment for 30 seconds.

The remaining sets were treated by vacuum impregnation. Using a vacuum desiccator, a vacuum of 200 mm Hg was drawn and maintained for about 2 minutes. Solution was then admitted to immerse the specimens and atmospheric pressure was restored. Sets of specimens were kept immersed at this pressure for the following periods of time:

Specimen Set	Immersion Time (min.)
2	½
3	1
4	3
5	5
6	10

After removing the specimens from the treating solution, they were wiped clean of surface solution and weighed to assess water repellent absorption. The specimens were then dried and equilibrated in the same manner, as described earlier (Section 2.2.2), to a constant weight.

It was observed that considerable variation in water repellent absorption was obtained with pine specimens depending upon the time they were in contact with the water repellent solutions. In beech, however, absorption of treating solutions was similar for both resin and resin-wax solutions and did not vary with the period of treatment to any appreciable degree. Because the vacuum impregnation method of treatment did not allow significantly differing loadings to be introduced into beech specimens, the following method of introducing monitored doses of water repellent solutions was adopted.

Beech specimens, 15 cm long and 2 x 2 cm in cross-section, were coated on lateral faces with solvent cement keeping both transverse faces open. The dried, equilibrated and weighed specimens were snuggly fitted on one transverse end with rubber collars sealed with silicone rubber sealant. Measured quantities (1, 2, 3 or 5 ml) of water repellent

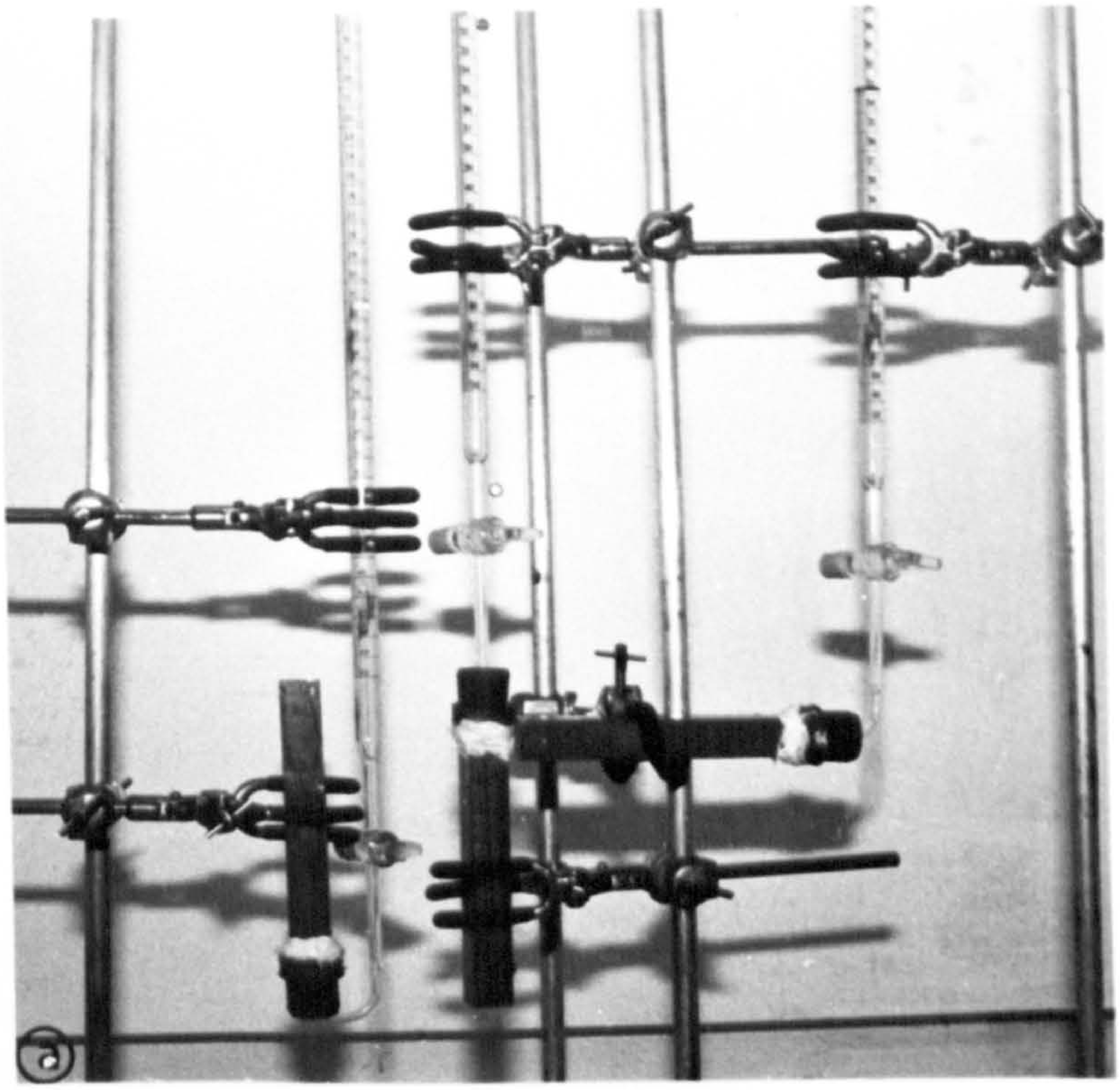


Figure 3.1. (a) Introduction of monitored doses of treating solution by gravity penetration.
(b) Specimen with rubber collar.

solution were allowed to flow into the specimens from a burette, connected to the rubber collar (see Figure 3.1). Due to the almost uninterrupted nature of vessel passageways in beech, some of the solution, especially at the higher dose levels, emerged from the opposite end when liquid was introduced at the top of the specimens. To avoid this problem, the amount of solution to be introduced was limited to a maximum of 5 ml and the penetration was effected in all cases from the bottom upwards (Figure 3.1). After treatment, the collar and silicone rubber sealants were removed and the specimens were conditioned for 10 days at 20°C and 65% RH. The untreated transverse faces of the specimens were then sealed with the styrene resin and the specimens were manipulated in the same way as the vacuum impregnated specimens. Separate batches of matched specimens were used as untreated controls.

3.2.2.1 Solution Absorption Data and Discussion

The solution absorption data for pine are given in Table 3.1. For 1, 2, 3 and 5 ml of solution impregnation in beech the calculated solids retention is 0.1, 0.2, 0.3 and 0.5 gm of resin and double these quantities of resin-wax respectively.

Table 3.1 Water Repellent Solution Absorption by End Treated Corsican Pine Specimens

Water Repellent Solution	Period and method of treatment	Solvent absorption in gms. Mean of 12 specimens.	(1 standard deviation)	Calculated water repellent solids content. Mean of 12 specimens (gms)
10% Resin (R_{10})	0.5 min (dip)	0.6	(0.01)	0.06
	0.5 min (vac)	2.3	(0.30)	0.23
	1 min (vac)	3.2	(0.30)	0.32
	3 min (vac	4.2	(0.70)	0.42
	5 min (vac)	4.8	(0.70)	0.48
	10 min (vac)	5.1	(0.60)	0.51
10% Resin + 10% Wax ($R_{10}W_{10}$)	0.5 min (dip)	0.7	(0.10)	0.14
	0.5 min (vac)	1.3	(0.20)	0.26
	1 min (vac)	2.4	(0.40)	0.48
	3 min (vac)	4.1	(0.40)	0.82
	5 min (vac)	5.6	(0.60)	1.12
	10 min (vac)	7.1	(0.60)	1.42

The pore volume filled by the solution may be estimated if the wood density, specimen volume and solution uptake are known. The density values for pine and beech are assumed to be ∿500 and ∿750 Kg/m^3 respectively. Dry wood substance density is taken as 1500 Kg/m^3 (Stamm, 1964). Available pore space is calculated to be approximately 67 and 50% of the bulk volume for pine and beech respectively. The solution specific gravity is approximately 0.9. Therefore, complete saturation would give a weight increase of 60 — >100%. Hence, it is evident that only a fraction of the pore space was filled by water repellent solutions under the mild vacuum treatments used.

In the case of pine, solution absorption formed a clear gradient with time of impregnation. There was also a difference between the absorption of resin and resin-wax solutions by pine specimens.

From the non-steady state form of Darcy's Law:

$$V = \left(\frac{2Kt}{\eta}\right)^{\frac{1}{2}} A$$

where V = volume absorbed in time 't',
K = permeability,
η = liquid viscosity,
A = specimen cross-sectional area normal to the flow direction,

it can be seen that volume (or mass) absorbed will vary directly with the square root of $\frac{t}{\eta}$. For simple solutions, viscosity increases with some function of concentration. Hence, the pattern of uptake observed is in line with Darcian prediction.

3.2.3 Water Repellent Assessment Using Whole Specimens

The 15 cm long specimens were equilibrated to constant weight at 20°C and 65% RH. Each set of 12 similarly treated specimens was divided into 4 sub-sets each containing 3 specimens each. These sub-sets were exposed to 0 (control), 5, 10 or 20 artificial weathering cycles in the manner described in Section 2.2.3. They were then dried and equilibrated to constant weight before soaking in deionized water to monitor the rate of water absorption (see Section 2.2.4).

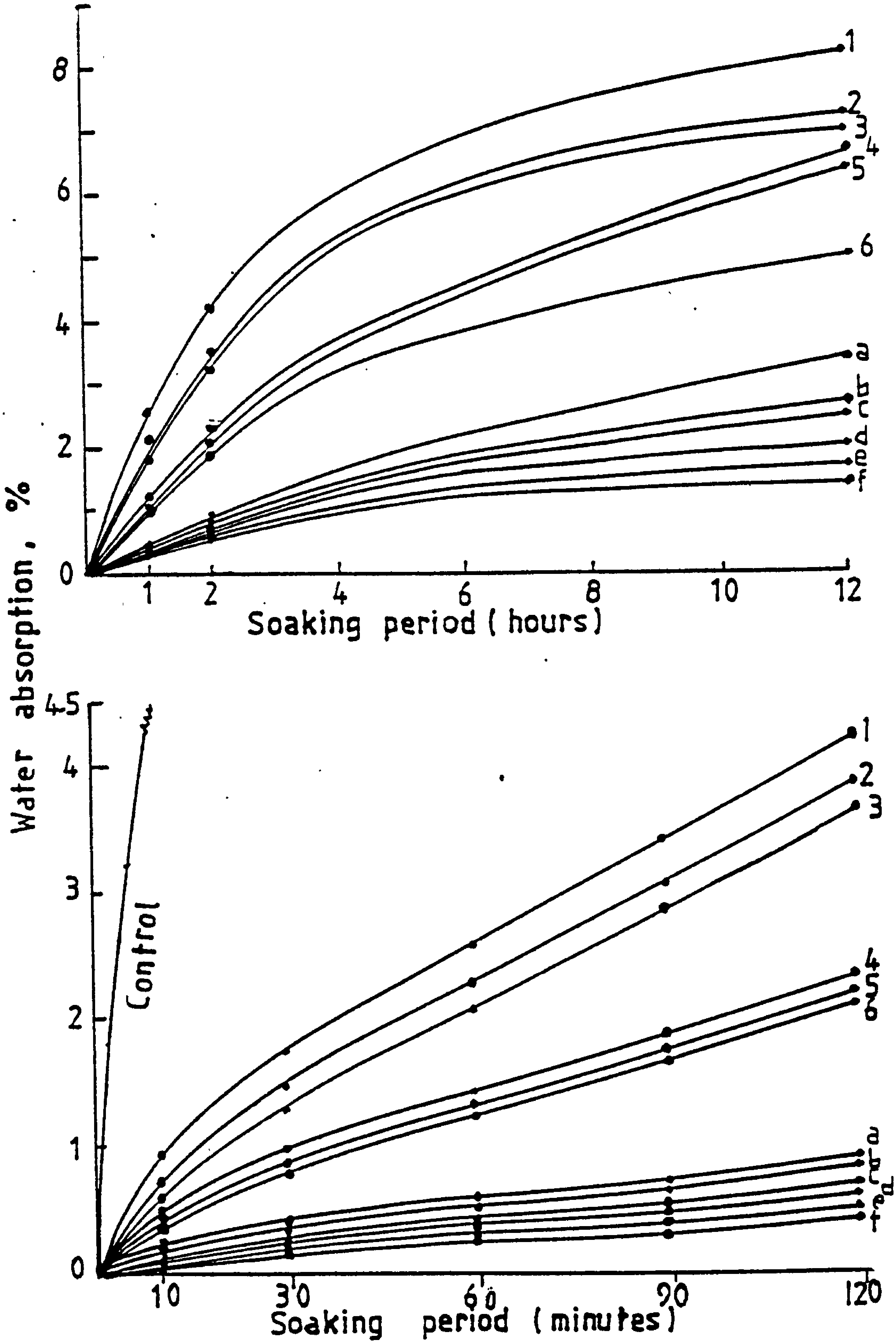


Figure 3.2 Rates of water absorption of long pine specimens before cycling (each point is mean of 3 specimens). Curve code: 1-6 resin and a-f resin-wax treatment. 1, a = ½ min (dip); 2, b = ½ min (vac); 3, c = 1 min (vac); 4, d = 3 min (vac); 5, e = 5 min (vac); 6, f = 10 min (vac).

3.2.3.1 Sorption Data for Long Specimens and Discussion of Results

3.2.3.1.1 Corsican Pine Specimens Before Cycling

Water absorption data for treated long specimens before cycling are shown in Figure 3.2 and Appendix II, Table 1. From the figure it can be seen that absorption rate varies greatly between the resin only and resin/wax treatments. With pine it has been shown that resin-wax treatment provides a many-fold improvement in water repellency of wafer specimens cut from the long specimens compared to that provided by resin only treatment (see Section 2.2.4.2.1). Over the test period (up to 12 hours), it can be seen that water uptake at any time by specimens treated with resin only solutions is 2.5 to 4 times greater than that by specimens treated with resin-wax solutions. This is in agreement with observations made by Voulgaridis and Banks (1979) using wafer specimens. Water absorption by resin and resin-wax treated large specimens decreases as solution uptake is increased. This is reflected as a decrease in sorption rate with increasing severity of treatment (Figure 3.2; Appendix II, Table 1).

Treatment by 30 seconds immersion in water repellent solution without the application of any vacuum, led to very small water repellent absorption. Much greater uptake is achieved when a vacuum is applied prior to soaking for an identical period. Although increasing solids content can be seen to reduce water sorption rate quite markedly, it is also noteworthy that the lowest level of treatment seems initially to reduce water sorption rate quite significantly compared to the untreated controls (Figure 3.2; Appendix I, Table 1). It seems possible that the small quantity of water repellent introduced into immersion treated specimens is concentrated mainly in the surface zone. Resistance to an advancing water front probably depends initially to a great extent upon the efficiency with which the surface is protected. The concentration of water repellent at the open transverse end, in spite of its sparse distribution in the interior of the specimens, may make initial water entry as difficult as in more heavily treated specimens, until the breakdown of deposits or wood structure takes place at the exposed end.

With solutions containing resin only, a decreased rate of water sorption is observed systematically with increase in severity of treatment, throughout the range of treatments used. The rate of water uptake is

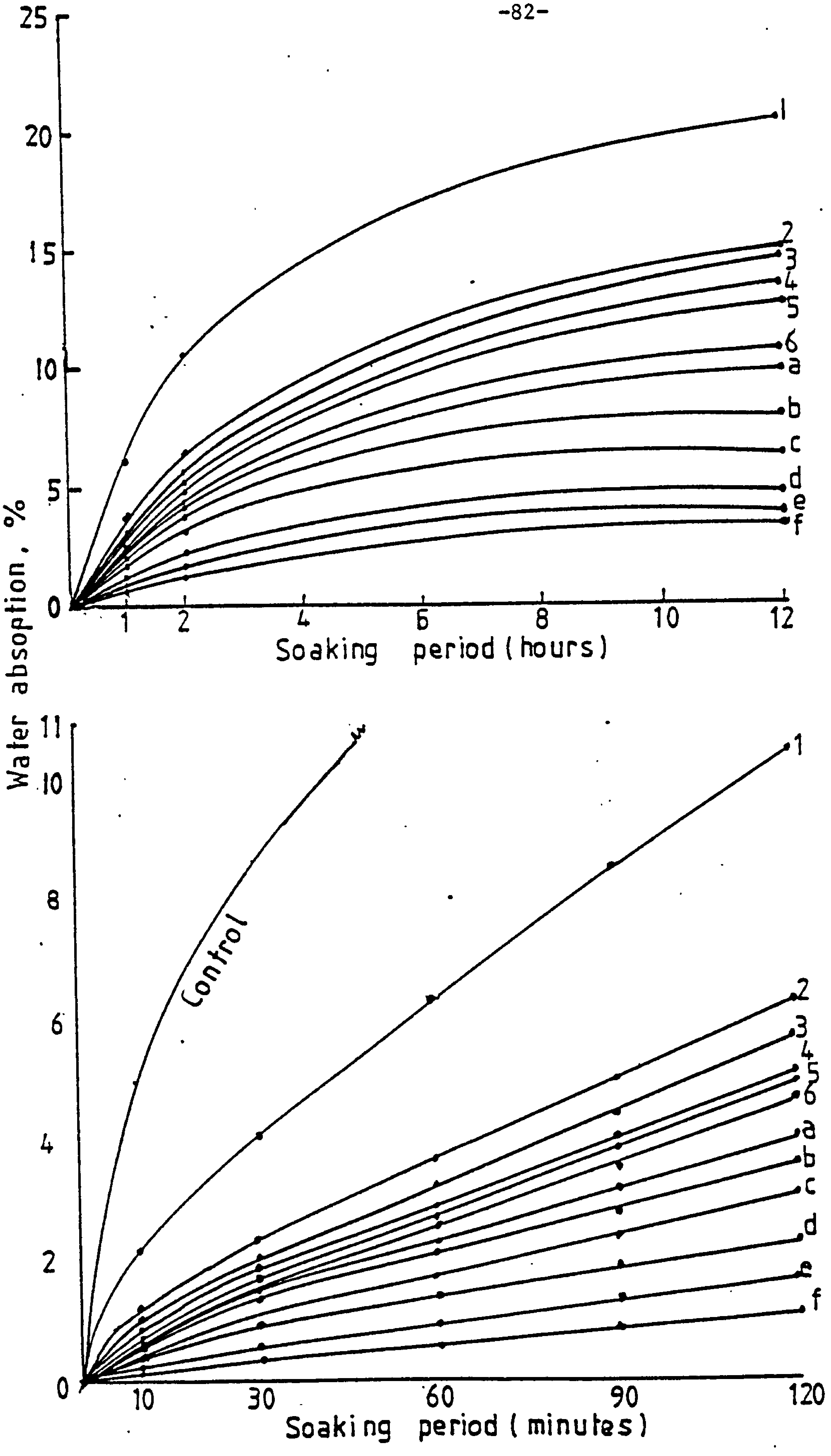


Figure 3.3 Rates of water absorption by long pine specimens after 5 cycles (3 replicates). Curve code: 1-6 resin and a-f resin-wax treatments. 1, a = ½ min (dip); 2, b = ½ min (vac); 3, c = 1 min (vac); 4, d = 3 min (vac); 5, e = 5 min (vac); 6, f = 10 min (vac).

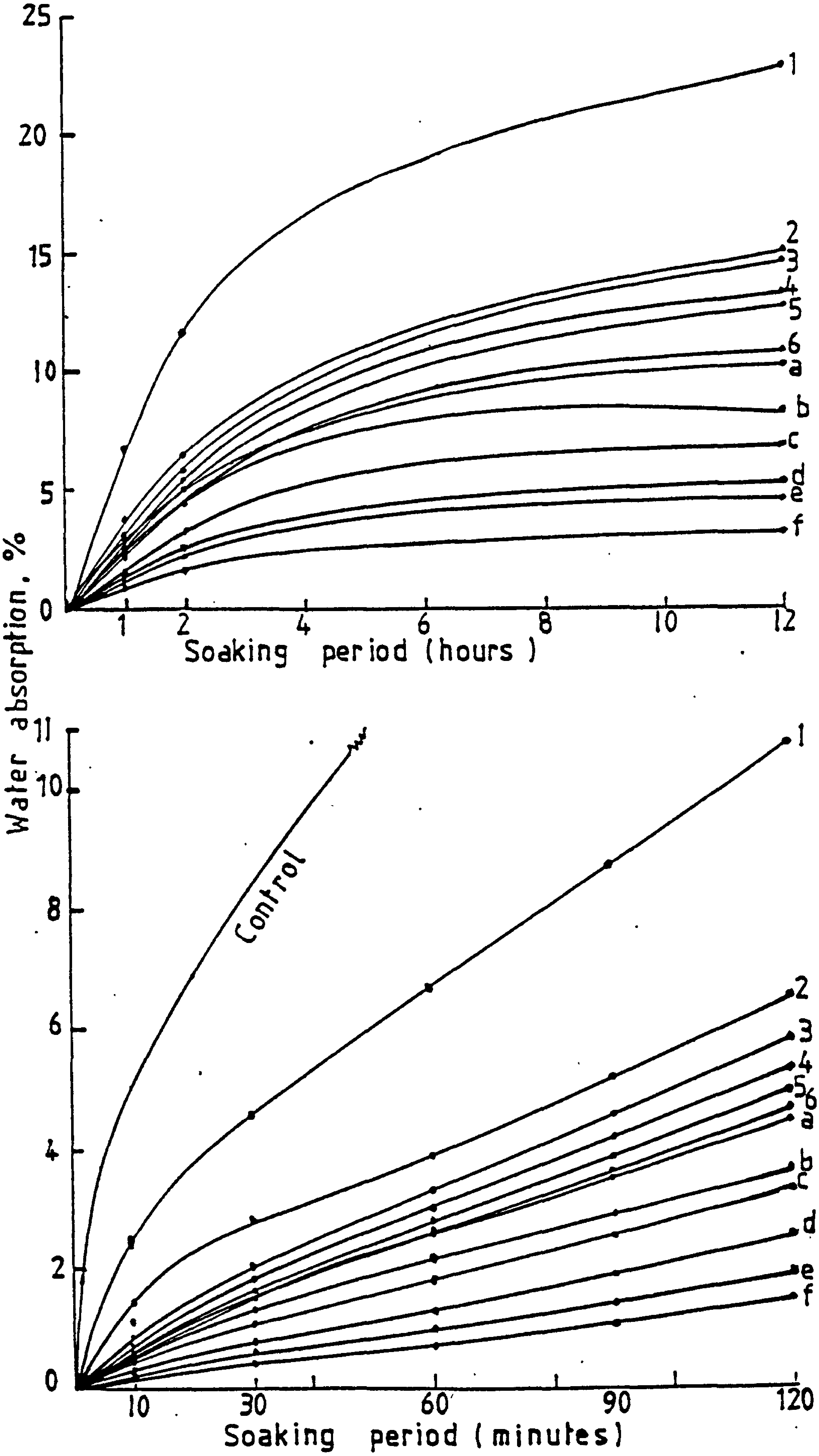


Figure 3.4 Rates of water absorption by long pine specimens after 10 cycles (3 replicates). Curve code: 1-6 resin and a-f resin-wax treatment. 1, a = ½ min (dip); 2, b = ½ min (vac); 3, c = 1 min (vac); 4, d = 3 min (vac); 5, e = 5 min (vac); 6, f = 10 min (vac).

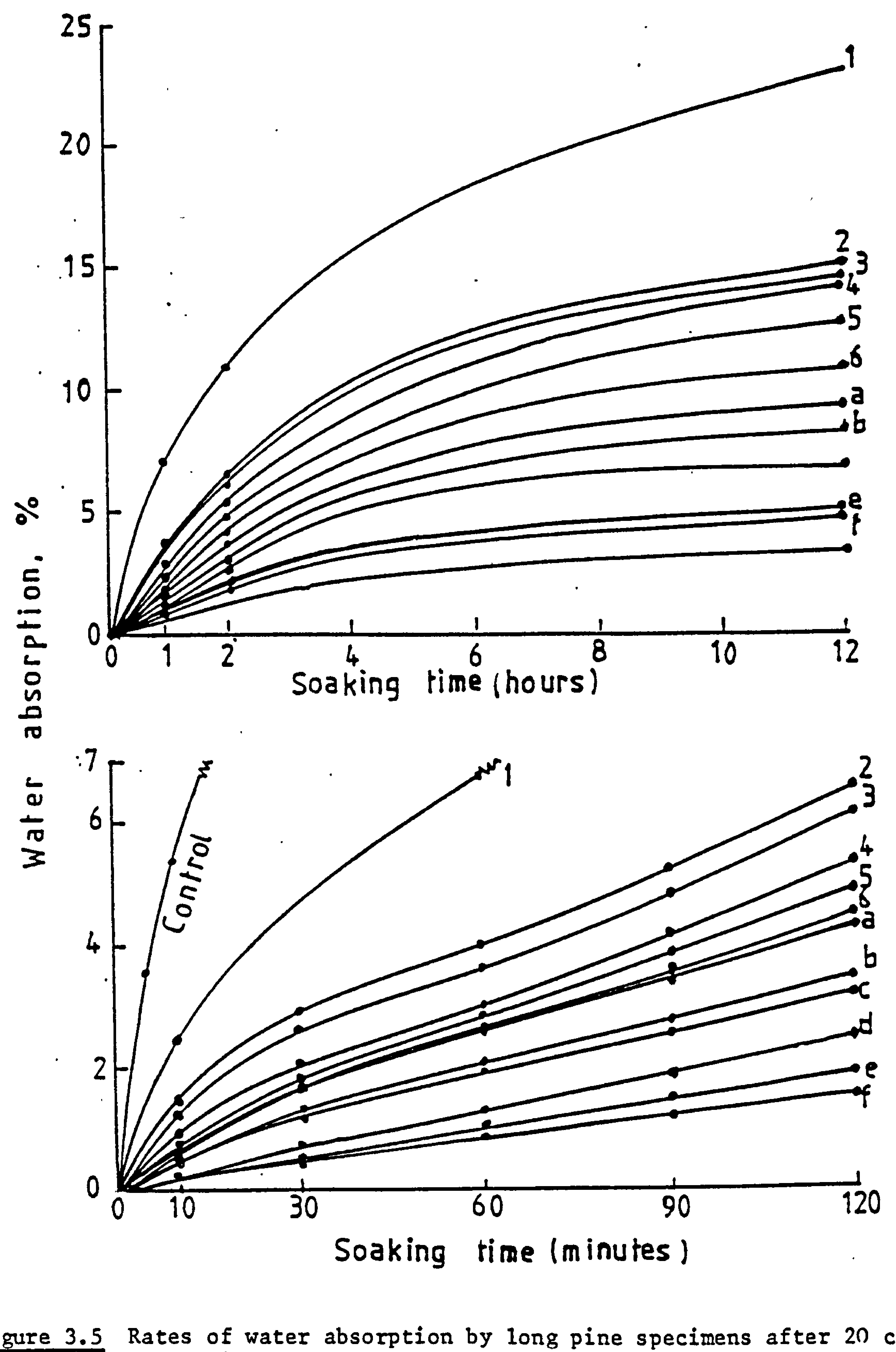


Figure 3.5 Rates of water absorption by long pine specimens after 20 cycles (3 replicates). Curve code: 1-6 resin and a-f resin-wax treatment. 1, a = ½ min (dip); 2, b = ½ min (vac); 3, c = 1 min (vac); 4, d = 3 min (vac); 5, e = 5 min (vac); 6, f = 10 min (vac).

fastest during the first part of the water soak. Thereafter the rate is observed to decrease throughout the immersion period. This is due to the increased flow path length as water is absorbed, coupled with a decrease in permeability associated with this increase in path length (Banks, 1971a and 1981; Bramhall, 1971).

Very effective resistance to water uptake is afforded to specimens treated with resin-wax solutions (Figure 3.2 and Appendix II, Table 1). Although increasing wax concentration shows systematic improvement in performance, this improvement seems to be quite small, compared to the resin concentration effect. It is believed that this is probably associated with the mechanism of protection afforded by paraffin wax. Hydrophobic surfaces are produced by the deposition of even a single monolayer of hydrophobe onto capillary surfaces. Once such a layer is present, addition of further hydrophobe will not further increase contact angle. Furthermore, effective protection will be afforded by the deposition of hydrophobe onto certain areas within the specimen, even if much of the capillary porous surface remains deplete of deposit. For example, provided that cut ends of exposed capillaries, membranes of unaspirated bordered pits and other key structures involved in water conduction are coated with wax, effective protection will be achieved, even if a large part of the structure (e.g. lumen surfaces of tracheids in the specimen interior) have no water repellent deposit.

3.2.3.1.2 Water Absorption by Corsican Pine After Cycling

Water repellents introduced into end-sealed specimens are deposited in the lumen surface. The solution passes rapidly through some of the rays and into adjacent tracheids (Levi et al., 1970). The water repellent appears to be concentrated in the rays and tracheids, especially in the summer-wood, the tissues most vulnerable to degradation in untreated wood (Levi et al., 1970; Carragher, 1982). The excellent water repellent action, manifested by treated pine specimens initially, slowly deteriorates with simulated weathering.

Resin treated specimens lose a significant amount of their water resistance over the first few artificial weathering cycles. Thereafter, further cycling leads to little further loss of effectiveness (Figure 3.3 - 3.5; Appendix II, Table 1). This effect is illustrated clearly in Table 3.2 which gives water uptake data for various specimens after 60 minutes water soak. The 't'-test data on the water soaking results of pine specimens after 60 minutes immersion show significant differences between controls on the one hand and all other treatments at the other (Table 3.3). Even the differences between simple immersion treatments and vacuum treatment for 3 minutes or more and between vacuum treatments of short and longer durations are significant at95% confidence level. Differences in sorption between weathered and unweathered resin only and resin-wax treated specimens are significant at95 and99% confidence level respectively.

Table 3.2 Water Uptake Data of Resin and Resin-Wax Treated Cycled Pine Specimens After 60 Minutes Soak

Treating Solution	Treatment time and mode	Water absorption after 60 minutes soak (%) and no. of cycles			
		0	5	10	20
10% Resin	½m (dip)	2.6	6.2	6.6	6.7
	½m (vac)	2.2	3.7	3.6	3.6
	1m (vac)	1.9	3.2	3.3	3.6
	3m (vac)	1.3	3.0	3.0	2.5
	5m (vac)	1.2	2.6	2.7	2.4
	10m (vac)	1.2	2.2	2.4	2.3
10% Resin + 10% Wax	½m (dip)	0.6	2.3	2.9	3.0
	½m (vac)	0.5	2.0	2.3	2.1
	1m (vac)	0.5	1.8	2.1	2.0
	3m (vac)	0.4	1.2	1.2	1.2
	5m (ac)	0.4	0.9	1.0	1.0
	10m (vac)	0.3	0.5	0.7	0.7
Control	-	8.7	9.2	11.2	11.9

The observed loss in water repellency may be caused by several factors acting in isolation or in combination. Weakening of the wood-water repellent bond (Voulgaridis, 1980), physical dislodgement of deposits culminating in the removal and some redistribution of water repellents are often held to be responsible for the loss of effectiveness in water repellent treated wood.

Table 3.3 Students 't' test Data for Water Absorption Values at 60 Minutes Soak Between Cycles and Between Treatments of Corsican Pine

Difference Between Treatments[1]		Difference Between Cycles	
Treatments compared (resin treated end sp)	t-value and significance	Cycles compared	t-value and significance
Control - ½m dip	27.90^{**}	Resin 0-5	2.87^{*}
Control - ½m vac	29.00^{**}	Resin 0-10	2.80^{*}
Control - 1m vac	30.03^{**}	Resin 0-20	2.54^{*}
Control - 3m vac	31.74^{**}	Resin-Wax 0-5	3.65^{**}
Control - 5m vac	31.92^{**}	Resin-Wax 0-10	3.60^{**}
Control - 10m vac	32.05^{**}	Resin-Wax 0-20	3.50^{**}
½m dip - 3m vac	4.04^{**}	All others	n.s.
½m dip - 5m vac	4.35^{**}		
½m dip - 10m vac	4.35^{**}		
½m vac - 5m vac	3.10^{*}		
½m vac - 10m vac	3.10^{*}		
Others	n.s.		

$^{*}p = 0.05$, $^{**}p = 0.01$, n.s. = Not Significant

[1] Mean square value obtained from analysis of variance between means of replicates were used for 't' calculation.

If loss of bond strength, deleterious effect of moisture on deposits and inequitable distribution generally throughout the specimens were responsible for the increased rate of water sorption, it is likely that progressive weathering would lead to a cumulative adverse effect on performance. From the data presented (Figures 3.3 - 3.5 and Appendix II, Table 1) it can be seen that this is not the case. The reason for the observed rapid initial loss of performance followed by a period of stability is believed to be associated with the following mechanism. During initial stages of weathering, significant wood degrade of exposed surfaces occurs (Voulgaridis, 1980). This is in the form of microchecks, checks and end splits. This checking and splitting is thought to be largely due to stresses set up by the repeated swelling and shrinking occuring during weathering. By this process new water entry routes into the wood structure are provided. As importantly, perhaps, these splits and checks may severely damage the bond between wood and water repellent deposit, which is likely to give rise to physical removal of some of the deposit from the treated area. It has been shown (see Section 3.2.2.1) that water repellent material is heavily concentrated in the treated surface zone. Thus the degradation to wood structure and the wood-deposit bond described, also being most marked at the exposed surface can be expected to lead to the early loss of a significant part of the initial protection afforded by water repellent treatment.

The mechanism of loss of water repellency discussed above explains the greatly increased water absorption rate of immersion treated specimens. The specimens treated with resin only by 30 seconds immersion were probably penetrated only to a depth of a centimetre or so. When the surface zone in such specimens is opened up due to the wood degrade and general loss of water repellent coating action discussed, there is little or no deposit in the interior to give continued water resistance. Specimens treated under a vacuum have much deeper penetration (see Section 3.5.1). In this case, when the surface zone is degraded, a large fall in performance is observed, but the interior zone, having significant deposit, continues to afford protection against water entry, thus providing a second line of defence. The relative effectiveness of the various treatments was maintained throughout the 20 cycles of simulated weathering. This is reflected both in the rate of absorption and total water uptake after 12 hours soaking (Figures 3.3 - 3.5).

As stated above, little further loss of performance beyond that observed after 5 cycles is seen to occur with further cycling up to 10 or 20 cycles. It is possible that the stresses set up in the wood specimens due to rapid dimensional changes on weathering are lessened to a considerable extent on the formation of the initial checks and splits. As a result, not many more or deeper checks and splits are formed after about 5 cycles. As a consequence little further degrade is caused to the bond formed between the cell wall and the deposit. This may account for the apparently stable performance observed over the longer cycling period. Some of the dislodged resin may even become re-bonded during the drying parts of the cycling and testing procedure (Figure 3.6).

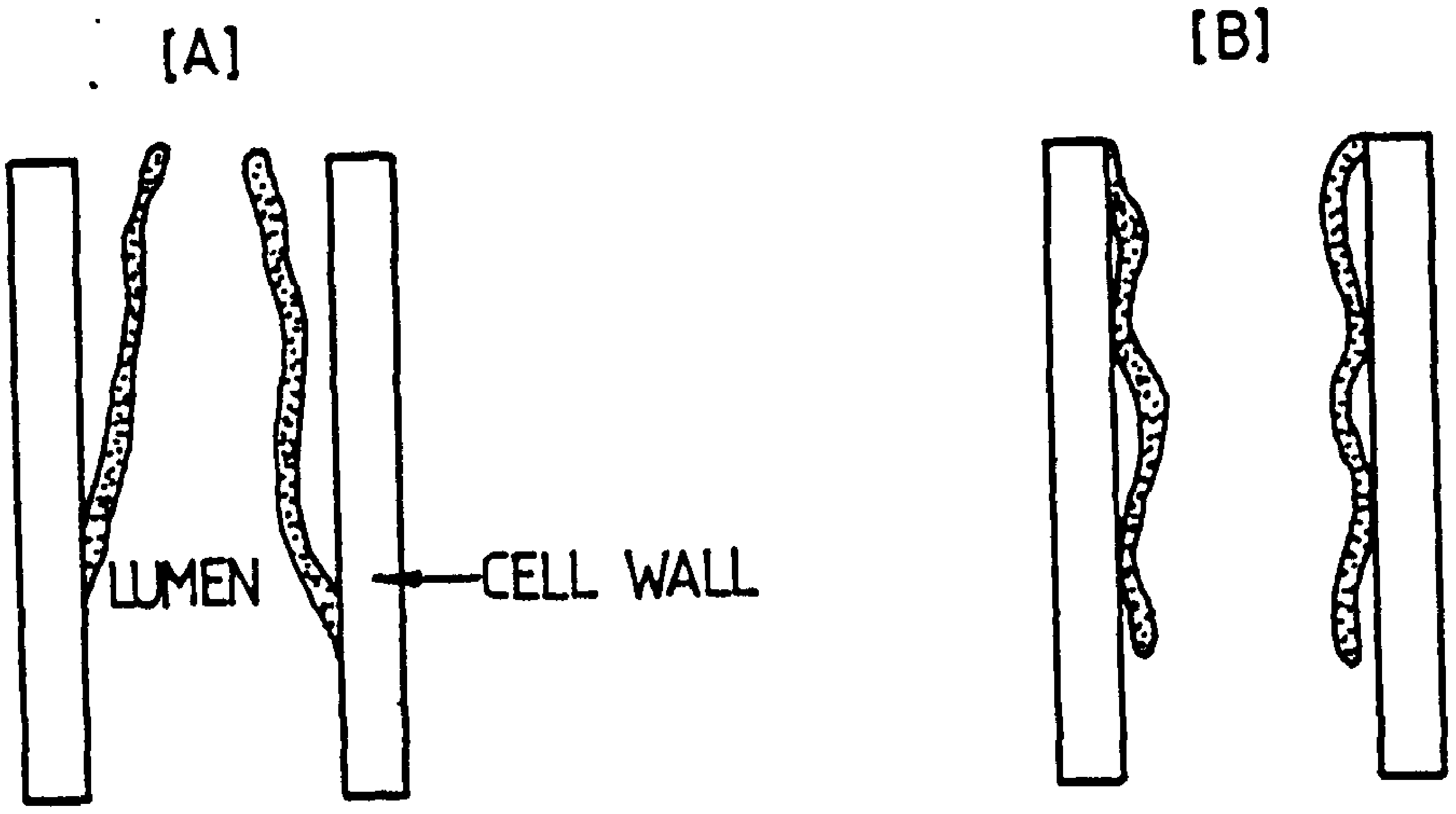


Figure 3.6 Dislodged resin deposit (A) may be re-bonded onto the wood surface on heating (B)

As evident from the swelling tests (see Section 2.3.2) much better water repellency and thus much reduced water uptake rate was obtained with resin-wax treatment than with resin treatment alone. This trend remained unchanged even after cycling. As noted above, immersion treated specimens were protected to only a relatively shallow depth. After simulated weathering for 20 cycles these specimens gave somewhat higher water absorption than the best resin-treated specimens during the early parts of the soak test (Figure 3.5). As explained above with respect to the resin-treated specimens, wood degrade in the surface zone, which may be the only part of dip treated specimens having any significant water repellent deposit, drastically reduces water repellent effectiveness. Generally, however, the treatments based on a hydrophobe (paraffin wax) perform better than the resin only treatments, throughout the exposure period.

As with resin treated specimens, those treated with resin-wax mixtures also show most deterioration during the first few cycles of artificial weathering. Between 5 and 20 cycles of weathering there was no substantial change in water absorption during the soak test. Stabilization of performance to a relatively constant level after the initial loss over the first 5 cycles of artificial weathering is probably due to similar reasons to those described above with respect to the resin only treatment.

Because the full evaluation of performance involved destructive testing (see Section 3.4 and 3.5), different specimens were used for the various periods of artificial weathering. There was noticeable between-specimen variability in water repellent solution absorption and water uptake during soak testing exhibited by variously cycled specimens (Table 3.4). However, this variability does not appear to obscure the general trends reported.

Table 3.4 Between Specimen Variability of Water Repellent Solution Absorption and Water Absorption on 12 Hours Soaking of Vacuum Treated (3 minutes) Pine Specimens

Water repellent solution absorption (gms/stick)					Water Absorption (%)			
10% Resin	Mean	10% Resin + 10% Wax	Mean	No. of Cycles	Resin treated	Mean	Resin-Wax treated	Mean
3.35		3.54			6.25		1.54	
4.20	4.1	4.43	4.1	0	6.62	6.7	2.12	2.0
4.80		4.49			7.08		2.47	
3.61		3.65			13.48		4.32	
4.95	4.3	3.53	3.8	5	12.67	13.5	4.58	4.6
4.20		4.25			14.20		4.96	
3.68		4.42			12.04		4.32	
4.60	3.9	4.10	4.0	10	14.68	13.4	4.79	4.8
3.31		3.55			13.40		5.35	
5.05		4.48			13.84		4.49	
3.30	4.5	4.20	4.4	20	13.02	13.9	4.87	4.9
5.10		4.62			14.69		5.51	

Students 't' tests carried out on the data of table 3.4 suggest that for both resin only and resin-wax treatments water absorption after 5, 10 and 20 weathering cycles is significantly different than that before cycling (Table 3.5). Between 5, 10 and 20 weathering cycles, however, there is no significant difference in water sorption. It must be recognized that the sample size (3 specimens per set) is too small to give more than a little extra confidence to what is visually apparent.

Table 3.5 Result of 't' test on Data for Water Sorption in Table 3.4

	Difference Between Means of Sorption		
Treatment	Comparison	't' Value and Significance	
Resin 10%	0-5 cycles	13.6	Significant at 0.1%(P)
	0-10 cycles	8.4	
	0-20 cycles	13.4	
	Others	Not Significant	
Resin 10% + Wax 10%	0-5 cycles	7.8	Significant at 1%(P)
	0-10 cycles	6.9	
	0-20 cycles	7.2	
	Others	Not Significant	

Vacuum impregnation treatments appear to be more effective than simple immersion treatments in long term performance. Within the range of vacuum treatments examined, effectiveness was seen to improve with the length of the impregnation period and hence with the amount of water repellent absorbed.

As stated above (Section 3.2.3.1.1) with respect to initial performance, the improvement in water resistance associated with increased loading, whilst unequivocally evident, is of small magnitude. This is probably because of the mode of hydrophobic action described above (Section 3.2.3.1.1). Small though the effect is, it was, nevertheless seen to persist throughout the artificial weathering period.

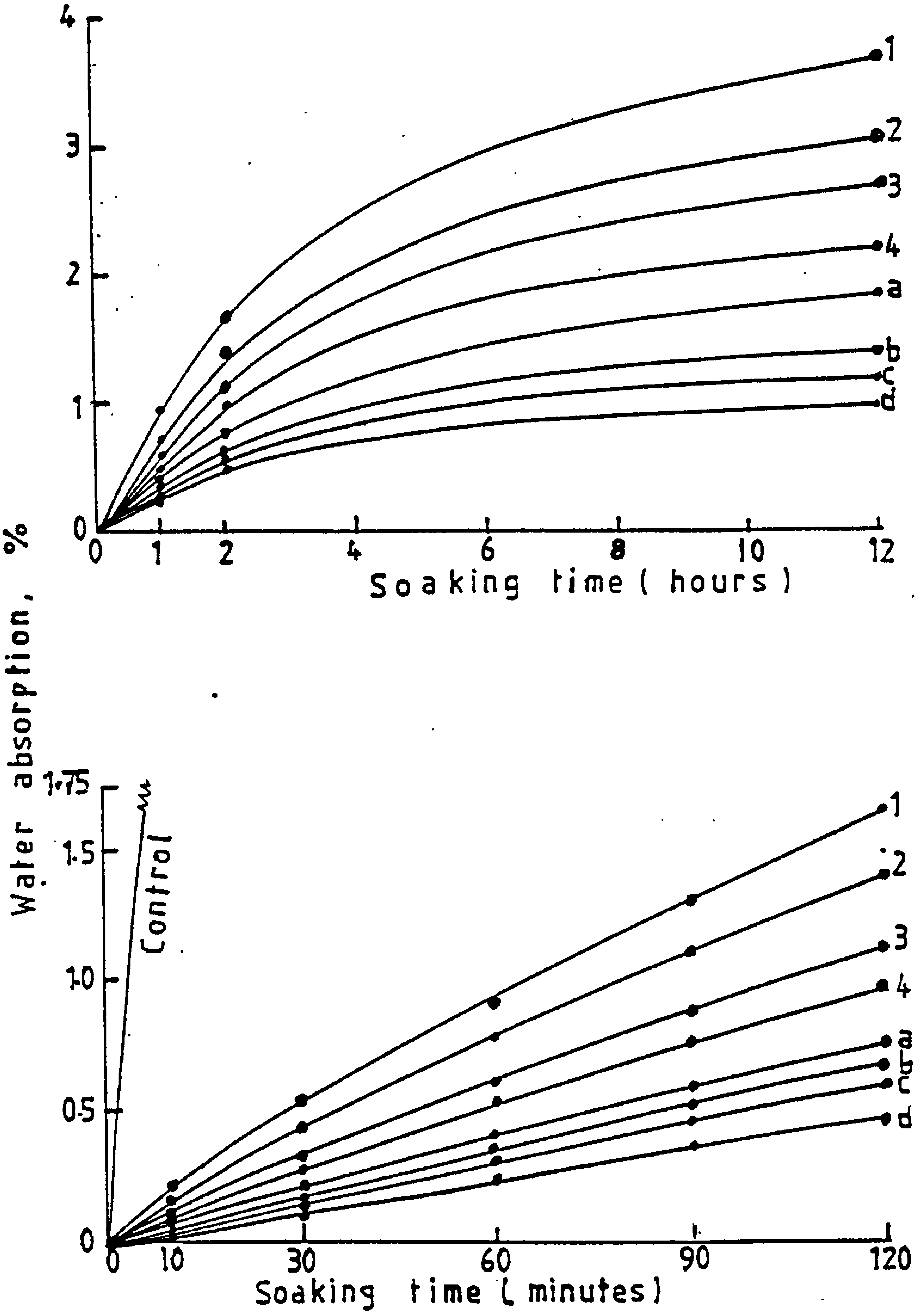


Figure 3.7 Rates of water absorption by long beech specimens before cycling (4 replicates). Curve code: 1-4 resin and a-d resin-wax treatment. 1, a = 1 ml; 2, b = 2 ml; 3, c = 3 ml; 4, d = 5 ml. C = control

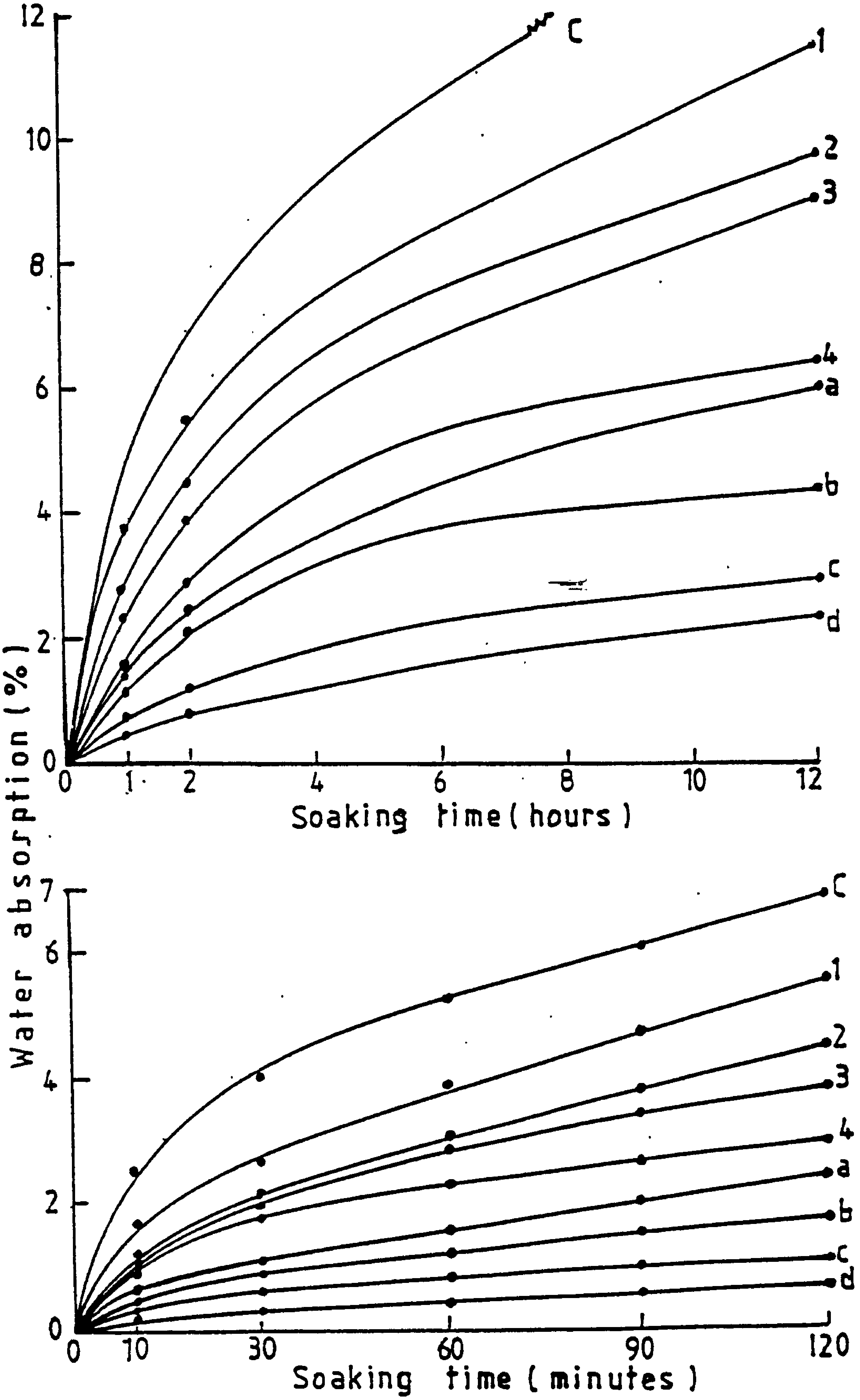


Figure 3.8 Rates of water absorption by long beech specimens after 5 cycles (4 replicates). Curve code: 1-4 resin and a-d resin-wax treatment. 1, a = 1 ml; 2, b = 2 ml; 3, c = 3 ml; 4, d = 5 ml. C = Control.

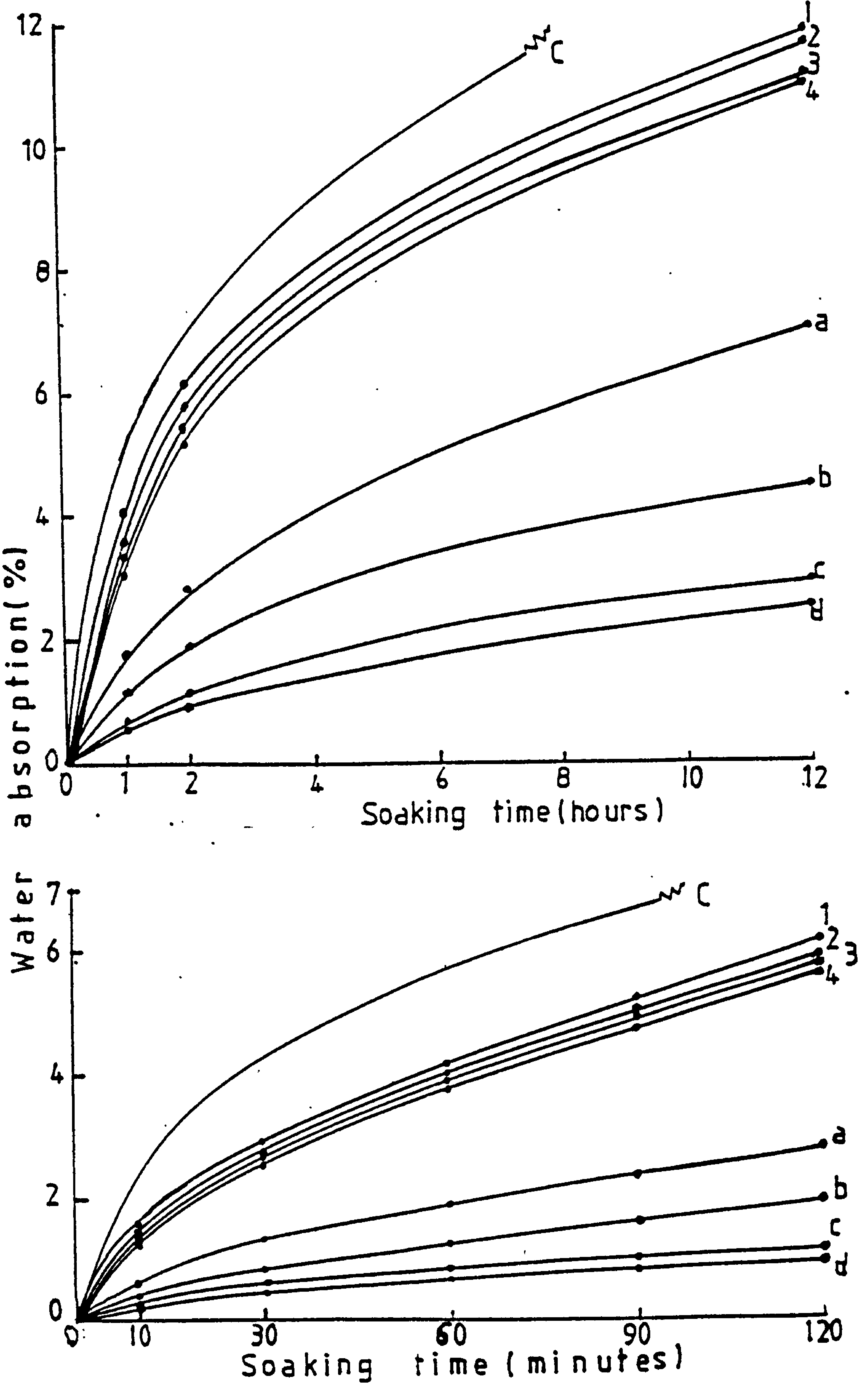


Figure 3.9 Rates of water absorption by long beech specimens after 10 cycles (4 replicates). Curve code: 1-4 resin and a-d resin-wax treatment. 1, a = 1 ml; 2, b = 2 ml; 3, c = 3 ml; 4, d = 5 ml. C = control.

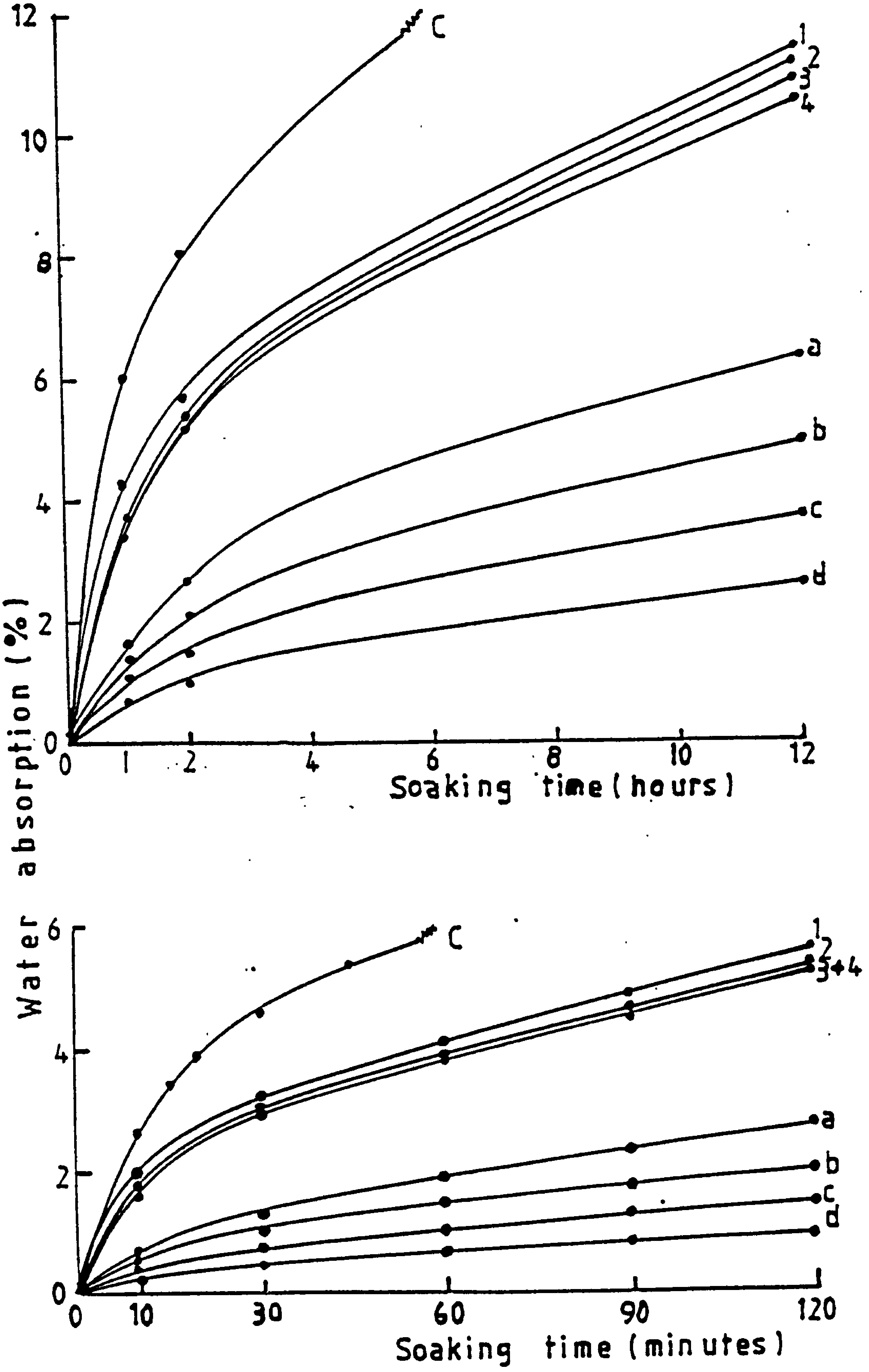


Figure 3.10 Rates of water absorption by long beech specimens after 10 cycles (4 replicates). Curve code: 1-4 resin and a-d resin-wax treatment. 1, a = 1 ml; 2, b = 2 ml; 3, c = 3 ml; 4, d = 5 ml. C = control.

3.2.3.1.3. Water Absorption by Water Repellent Treated European Beech Long Specimens Before and After Cycling

When carrier solvent is removed from treated beech wood by evaporation, water repellents are likely to be deposited on the vessel walls, including the pit areas, coating the fluid flow paths, more or less effectively. Because of the fine microfibrillar mesh in the pit membrane any coating of this structure is likely to be more coherent in beech than in pine. This, coupled with the natural water resistance of beech probably accounts for the much lower water absorption of beech specimens treated with resin solution compared to those of similarly treated pine specimens.

As with the treatments described in Section 2.2.4.2.2, formulations containing paraffin wax perform somewhat better than those based only on resin. Again, as observed and discussed fully in Section 2.2.4.2.2 the effect of wax is rather less marked in the case of beech treatment, than it is with pine (Appendix II, Table 2 and Figures 3.7 - 3.10). From Figure 3.7 it can be seen that a much reduced rate of water absorption over a 12 hour soak period was obtained with both resin and resin-wax treatment compared to that of controls.

The difference in performance after exposure to simulated weathering of the resin only and resin-wax treatments is interesting. Comparing Figures 3.7 and 3.10 it can be seen that:

1) Before exposure (Figure 3.7), after 12 hours water soak, the specimens treated with 1 ml of resin solution absorbed 3.7% of water while those treated with 5 ml of resin solution absorbed 2.2% (a range of 1.5% difference). For the resin-wax treatments, the corresponding water sorption values are 1.8 and 1% respectively (a range of 0.8%).

2) After 20 cycles exposure (Figure 3.10) corresponding water sorption data are as follows:

Resin only solution absorption	Water sorption
1 ml	11.4
5 ml	10.5

(Water sorption range 0.9%)

Resin-wax solution absorption	Water sorption
1 ml	6.3
5 ml	2.6

(Water sorption range 3.7%)

In the case of resin-wax hydrophobic treatments after exposure to artificial weathering, the range of water sorption associated with the severity of treatment (amount of solution absorbed) is increased. This is in line with the idea that loss of performance is strongly associated with degradation from the exposed end. As depth of treatment is increased, an increasingly long treated zone is provided, giving significant protection after exposed end degradation (Figure 3.11). With a hydrophobic deposit, liquid water can penetrate only as far as the hydrophobic barrier is broken down. Thus, deposit degrade may be expected to occur progressively from the exposed surface inwards and hence deeply penetrated wood might offer significant protection for longer periods of exposure than that penetrated only to a shallow depth.

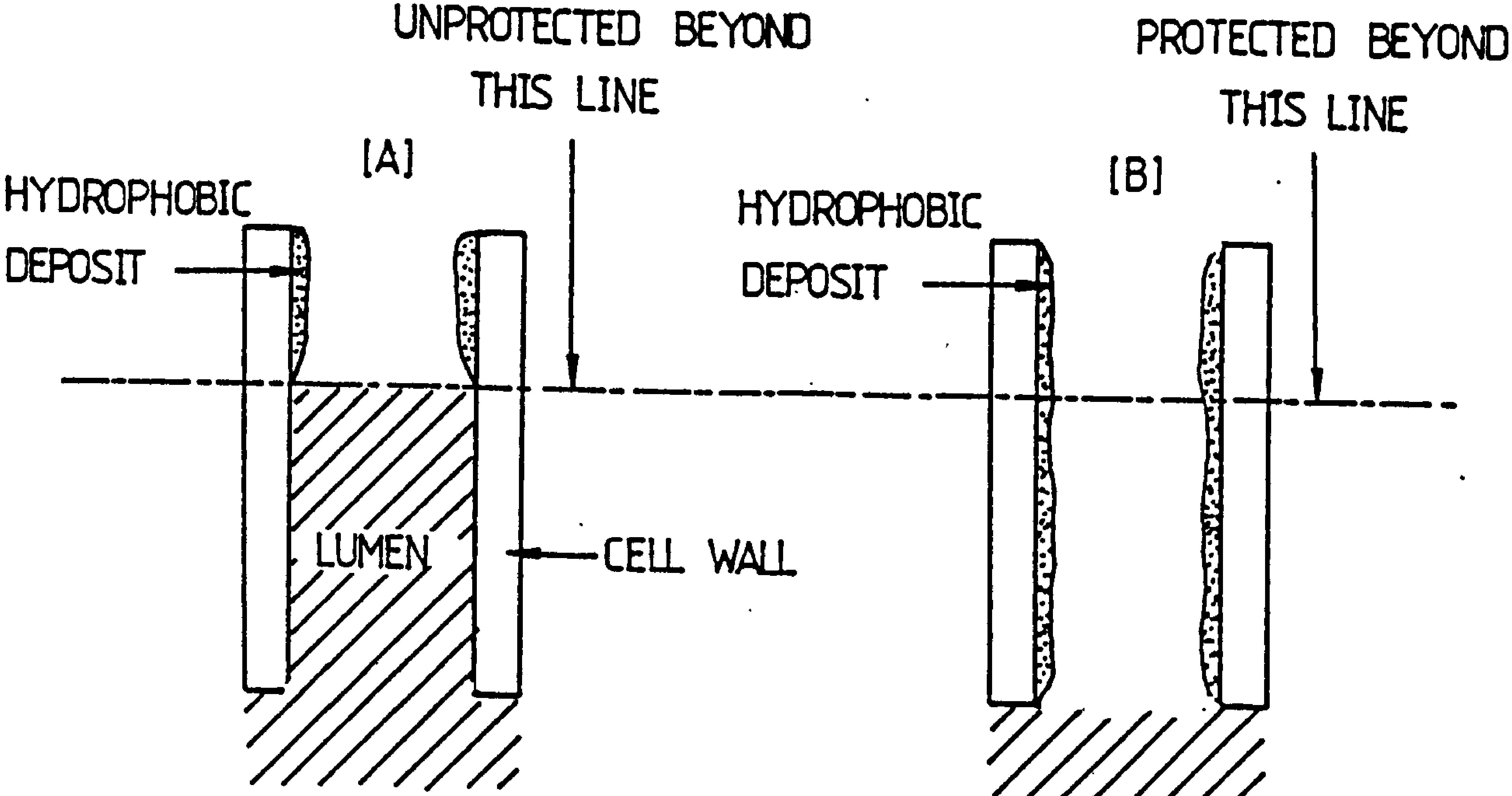


Figure 3.11 Depth of hydrophobic penetration affecting performance in beech. (A) Shallow deposit, (B) Deep deposit

With resin only treatments, the range of water sorption associated with severity of treatment remains fairly constant irrespective of degree of exposure. This suggests that with resin treatments degradation of the deposit might be occuring fairly evenly throughout the treated zone. This is in the line with the behaviour of a non-hydrophobic deposit (Figure 3.12). In both situations illustrated, liquid water can enter the capillary structure, irrespective of the depth of deposit. Hence, the deposit may be expected to degrade at a fairly uniform rate irrespective of distance from the exposed surface.

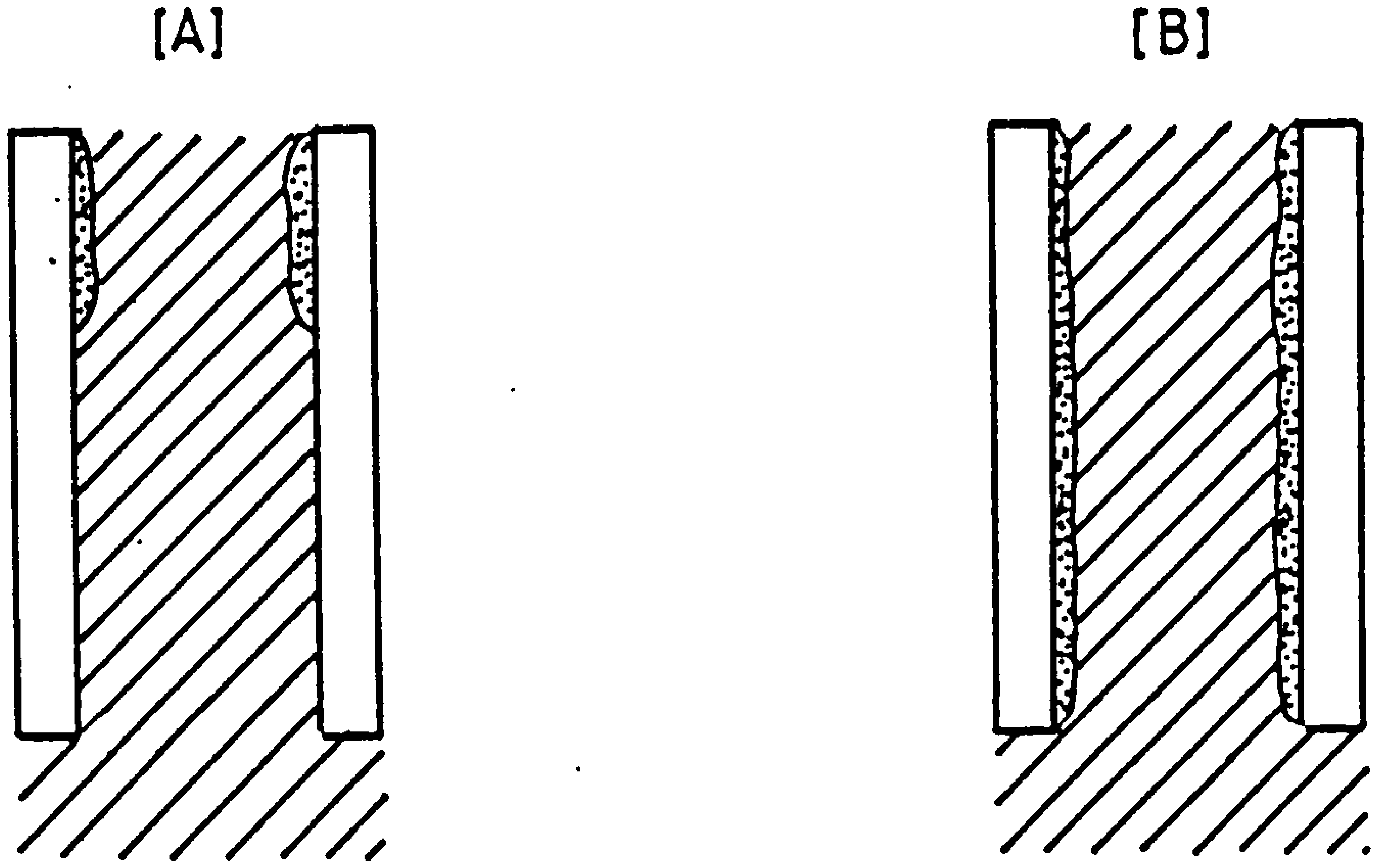


Figure 3.12 Water penetration unaffected by non-hydrophobic deposit (A) Shallow deposit, (B) Deep deposit

As with pine specimens, 't' tests have been carried out on water sorption data after 60 minutes water soaking of beech long specimens to give an indication of where differences in water sorption between sets of specimens are significant (Table 3.6). From this table it is clear that the significant change in performance occurs during the first few cycles. Thereafter any further loss of performance has not been shown to be significant with the small sample size used (3 samples per set).

3.3 Assessment of Water Repellent Efficiency

To allow comparison of the effectiveness of water repellent treatments applied to beech and pine, the water absorption data have been converted to water repellent efficiency (WRE) values using the formula,

$$\mathrm{WRE} = \frac{S_u - S_t}{S_u} \times 100$$

WRE has no fundamental significance. It will vary with soaking period and soaking temperature as well as with basic differences in efficiency of treatment. Nonetheless, it provides a useful guide to comparative effectiveness of various water repellent treatments. The calculations for treated specimens were based on the absorption of water by pine and beech control specimens after 12 hours soaking (Appendix I, Table 1). It is interesting to note that water absorption by beech during the 12 hour soak was only about 45% that by pine. This is presumed to be due to the difficulty encountered by water in flowing from vessel into fibre tissue in beech. This comparative resistance to penetrating moisture in beech is maintained after water repellent treatment and appears to act additively with the protection afforded by treatment.

Table 3.6 Between Cycles Variability of Water Sorption at 60 Minutes Immersion of Treated Beech Sticks

Treatment	Difference Between Means (t-test) Cycles Compared	Value of 't' and Significance
10% Resin	0-5	5.73^{**}
	0-10	21.30^{***}
	0-20	22.37^{***}
	5-10	2.67^{*}
	5-20	2.53^{*}
	10-20	n.s.
10% Resin + 10% Wax	0-5	2.69^{*}
	0-10	3.17^{*}
	0-20	3.90^{**}
	Others	n.s.

*p = 0.05, **p = 0.01, ***p = 0.001, n.s. = Not Significant

3.3.1 Comparison of Performance of Water Repellent Treated Pine and Beech Long Specimens

Approximately 28 and 13% water absorption was recorded for control pine and beech long specimens respectively after 12 hours of soaking. Before cycling the water repellent efficiency (WRE) of resin-treated long pine specimens was found to vary from 70 to 82% depending on the severity of treatment (Table 3.7). At the end of cyclic soaking and drying for 5 cycles a considerable fall in WRE was observed. Loss of efficiency was, however, more pronounced in specimens treated by immersion or by mild vacuum schedules than in those treated by the more severe vacuum schedules. Between 5 and 10, and 10 and 20 cycles WRE changed

Table 3.7 WRE of Pine and Beech After 12 Hours Soak

Treatment	WRE (%) at various cycles			
	0	5	10	20
Pine: R_{10}				
½ min (dip)	70	22	18	18
½ min (vac)	74	46	46	46
1 min (vac)	75	48	48	47
3 min (vac)	76	52	52	50
5 min (vac)	77	55	55	60
10 min (vac)	82	62	61	61
Pine: $R_{10}W_{10}$				
½ min (dip)	88	65	63	63
½ min (vac)	90	71	70	71
1 min (vac)	91	77	76	76
3 min (vac)	93	83	83	83
5 min (vac)	94	86	84	83
10 min (vac)	95	89	88	87
Beech: R_{10}				
1 ml	72	10	7	11
2 ml	76	25	9	13
3 ml	79	30	13	15
5 ml	83	50	15	18
Beech: $R_{10}W_{10}$				
1 ml	86	53	45	52
2 ml	89	67	65	62
3 ml	91	78	77	72
5 ml	92	83	80	80

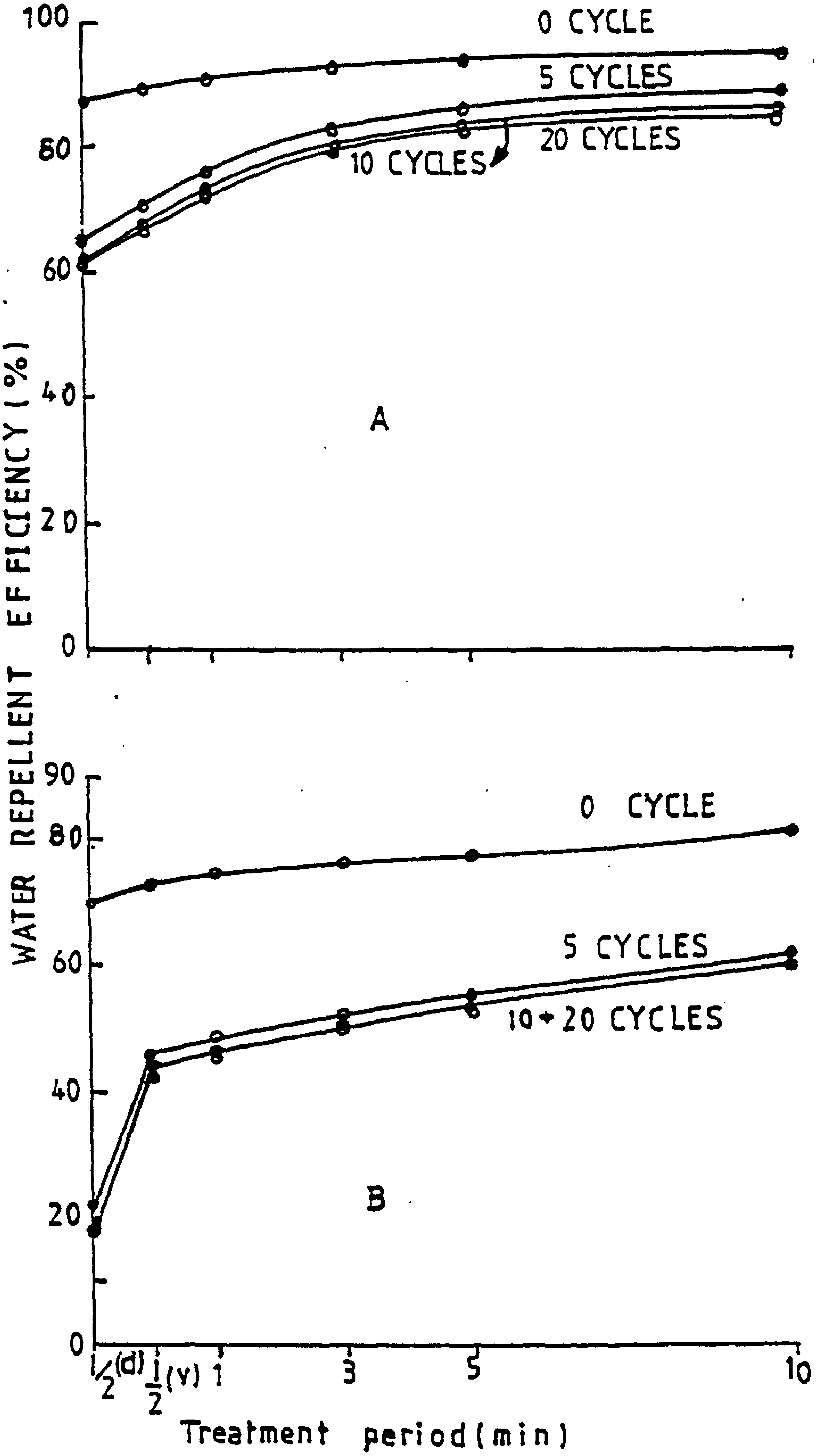


Figure 3.13 Water repellent efficiency varying with severity of treatment with resin-wax (A) and resin (B) after 0, 5, 10 and 20 weathering cycles.

insignificantly (Table 3.8 and Figure 3.13). The sample size is very small (3 replicates per set), hence 't' tests are offered as a guide rather than as a strict statistical estimate of significance. With resin-wax treatments higher initial WRE values are achieved and the effect appears to be more resistant to the effects of simulated weathering (Table 3.7 and Figure 3.13).

Table 3.8 Between Cycles Variability of Water Repellent Efficiency After 12 Hours Soak of Treated Pine and Beech Specimens

Student's 't' test difference between means							
PINE SPECIMENS				BEECH SPECIMENS			
Resin Treatment		Resin - Wax Treatment		Resin Treatment		Resin - Wax Treatment	
Cycles compared	Value of 't'	Cycles compared	Value of 't'	Cycles compared	Value of 't'	Cycles compared	Value of 't'
0-5	4.84^{+++}	0-5	3.40^{++}	0-5	5.68^{++}	0-5	2.84^{+}
0-10	4.60^{+++}	0-10	3.60^{++}	0-10	22.48^{+++}	0-10	2.83^{+}
0-20	4.40^{+++}	0-20	3.83^{++}	0-20	22.87^{+++}	0-20	3.70^{+}
5-10	Not Significant	5-10	Not Significant	Others	n.s.	Others	n.s.
10-20		10-20					
5-20		5-20					

Significance: +++ p = 0.001, ++ p = 0.01, + p = 0.05,
n.s. = Not Significant.

The difference in the WRE between resin and resin-wax treated beech specimens before cycling was less pronounced than in the case of pine. Initial weathering for 5 cycles was found to cause greater loss of water repellency in resin treated beech specimens than in resin-wax treated ones (Table 3.7; Figure 3.13). It is likely that this greater resistance to weathering of the hydrophobic treatments applied to both pine and beech is associated with factors described earlier with respect specifically to the beech data (Section 3.2.3.1.3). That is, with resin only (non-hydrophobic) treatments, water has immediate access to all structurally available pores and hence degradation of the deposit at the deposit/wood interface may proceed simultaneously throughout the treated zone. In the case of resin-wax (hydrophobic) treatments, on the other hand, the liquid water front may advance only as the deposit or deposit/wood interface is degraded (Figure 3.11, Section 3.2.3.1.3), and hence only a small part of the treated zone is degraded at a time.

Significant differences between the means of WRE measured at 0 and 5, 10 and 20 cycles were obtained from all specimens. With resin treatments highly significant differences occurred (Table 3.8) with both pine and beech. Resin-wax treated pine specimens gave 't' values significant at the 1% level, while those for beech were significant only at the 5% level. Differences between means measured at 5 and 10, 5 and 20 and 10 and 20 cycles were non-significant in all cases. Again it must be emphasized that the data are for very small samples (3 replicates per set).

3.4 Assessment of Water Repellency of Successive Wafers Along the Depth of Treatment

The Corsican pine and European beech long (15cm) specimens after cycling and water absorption testing (Section 3.2.3) were dried for 7 days at 35°C and equilibrated to constant weight at 20°C and 65% RH. From each stick seven transverse wafer specimens of thickness 0.6cm were cut and manipulated in the same way as described in Section 2.3.1. The kerf for each cut was about 2mm, hence, the centres of the wafer specimens were 3, 11, 19, 27, 35, 43 and 51mm from the treated end (Figure 2.8). In the case of Corsican pine specimens treated with each of the two treating solutions there were six treatment levels and 3 replicates for each of these levels of treatment. With European beech, specimens treated by the gravity method (Figure 3.1), there were 5 treatment levels initially and 4 levels after weathering.

Since there is no fundamental difference in the trends observed using rate of swelling and rate of water absorption as the test parameter (Stamm,1964), for convenience, rate of swelling was adopted as the criterion for monitoring the water repellent effectiveness. Wood shrinks and swells to the greatest extent in the tangential direction. For this reason, the rate of swelling of the 6mm wafer specimens were measured in this direction during immersion in water. With treated specimens, the final stages of dimensional increase occurredvery slowly. Hence, the matched control specimens were used to give an estimate of equilibrium maximum swell.

Table 3.9 Time to Half Swell ($T_{1/2}$) for Pine Wafers Cut Along Depth of Treatment from Treated Long Specimens After Cyclic Soaking and Drying

10% Resin treatment time (min)	No. of Cycles	Specimen nos. and mid-distance from treated end (mm) and $T_{1/2}$ ± standard deviation, minutes (3 replicates)						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
Untreated controls	0	1.1 (0.1)	1.1 (0.1)	1.1 (0.1)	1.1 (0.1)	1.1 (0.1)	1.1 (0.1)	1.1 (0.1)
½ (dip)		8.8 (0.8)	5.2 (0.4)	2.8 (0.4)	1.6 (0.2)	0.6 (0.1)	0.6 (0.1)	0.6 (0.1)
½ (vac)		12.8 (1.6)	10.0 (0.6)	7.2 (0.6)	6.4 (0.4)	5.2 (0.5)	5.2 (0.4)	5.0 (0.6)
1 (vac)		13.4 (2.0)	10.4 (0.8)	8.0 (0.6)	7.2 (0.6)	7.0 (0.4)	6.6 (0.6)	6.0 (0.6)
3 (vac)		14.2 (1.0)	11.1 (1.6)	10.0 (1.2)	8.5 (1.4)	8.0 (0.6)	7.2 (0.8)	7.4 (1.6)
5 (vac)		16.5 (1.5)	13.2 (1.2)	11.0 (1.2)	10.6 (0.8)	10.9 (1.0)	9.0 (0.8)	9.0 (1.0)
10 (vac)		18.6 (2.1)	14.4 (1.8)	12.6 (1.6)	12.0 (0.8)	11.0 (1.2)	10.4 (1.0)	10.0 (0.8)
Control	5	0.6 (0.1)	0.9 (0.1)	0.9 (0.1)	0.9 (0.1)	0.9 (0.1)	0.9 (0.1)	0.9 (0.1)
½ (dip)		5.6 (2.0)	3.3 (0.4)	2.0 (0.5)	1.1 (0.2)	0.5 (0.1)	0.5 (0.1)	0.5 (0.1)
½ (vac)		10.6 (2.4)	10.8 (1.1)	6.9 (1.0)	5.3 (0.6)	5.0 (0.5)	5.2 (0.3)	4.8 (0.4)
1 (vac)		12.2 (0.7)	11.8 (1.0)	7.6 (0.8)	6.8 (0.6)	6.2 (0.4)	5.6 (0.5)	5.2 (0.4)
3 (vac)		13.8 (1.2)	11.9 (1.0)	9.8 (0.5)	8.2 (0.5)	6.5 (0.3)	6.3 (0.2)	6.6 (0.6)
5 (vac)		14.8 (1.5)	12.3 (1.1)	10.0 (1.0)	9.0 (0.8)	9.0 (0.5)	8.6 (0.8)	8.4 (0.6)
10 (vac)		15.7 (1.6)	12.9 (1.2)	10.6 (1.0)	9.8 (0.8)	9.4 (0.6)	9.3 (0.8)	9.4 (0.5)

Table 3.9 continued:-

10% Resin treatment time (min)	No. of Cycles	Specimen nos. and mid-distance from treated end (mm) and T½ ± standard deviation, minutes (3 replicates)						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
Control	10	0.5 (0.1)	0.8 (0.1)	0.8 (0.1)	0.8 (0.1)	0.8 (0.1)	0.8 (0.1)	0.8 (0.1)
½ (dip)		4.8 (0.5)	1.7 (0.2)	1.3 (0.1)	0.5 (0.0)	0.5 (0.0)	0.5 (0.0)	0.5 (0.0)
½ (vac)		9.3 (0.7)	10.0 (0.8)	6.2 (0.5)	5.0 (0.5)	5.2 (0.6)	4.5 (0.2)	4.0 (0.3)
1 (vac)		10.6 (0.8)	11.0 (0.4)	7.6 (0.5)	6.1 (0.4)	5.0 (0.5)	5.0 (0.4)	5.1 (0.2)
3 (vac)		10.8 (1.8)	11.2 (0.8)	9.4 (0.4)	8.0 (0.2)	6.3 (0.4)	5.8 (0.2)	5.8 (0.3)
5 (vac)		10.8 (0.7)	11.8 (0.6)	10.0 (0.8)	8.8 (0.5)	8.9 (0.5)	7.9 (0.4)	7.8 (0.5)
10 (vac)		11.4 (0.5)	12.9 (0.7)	10.5 (0.8)	10.0 (1.2)	9.1 (0.7)	8.7 (0.5)	8.8 (0.3)
Control	20	0.4 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)
½ (dip)		4.3 (0.2)	1.8 (0.1)	1.5 (0.1)	0.6 (0.0)	0.6 (0.0)	0.5 (0.0)	0.5 (0.0)
½ (vac)		8.6 (0.6)	10.1 (0.3)	6.0 (0.5)	5.6 (0.4)	5.0 (0.5)	4.7 (0.2)	5.0 (0.4)
1 (vac)		9.2 (0.8)	11.1 (0.4)	8.0 (0.5)	6.7 (0.3)	6.5 (0.2)	5.8 (0.4)	5.2 (0.2)
3 (vac)		9.8 (1.3)	11.2 (1.2)	9.1 (0.6)	8.0 (0.5)	6.8 (0.3)	6.5 (0.4)	6.0 (0.2)
5 (vac)		9.9 (1.2)	12.0 (1.2)	10.1 (0.5)	9.6 (0.2)	8.0 (0.3)	8.0 (0.2)	8.2 (0.8)
10 (vac)		10.5 (0.8)	13.5 (1.4)	11.5 (0.6)	10.0 (0.3)	9.2 (0.6)	8.6 (0.3)	8.6 (0.2)

Table 3.9 continued:

10% Resin + 10% Wax treatment time (min)	No. of Cycles	Specimen nos. and mid-distance from treated end (mm) and T½ standard deviation, minutes (3 replicates)						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
½ (dip)	0	131.0	75.0	0.7	0.7	0.7	0.6	0.6
		(14.0)	(12.0)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)
½ (vac)		144.0	115.0	102.0	90.0	70.0	63.0	58.0
		(15.0)	(11.0)	(9.0)	(6.0)	(5.0)	(6.0)	(5.0)
1 (vac)		150.0	130.0	110.0	97.0	84.0	72.0	60.0
		(19.0)	(12.0)	(7.0)	(5.0)	(4.0)	(5.0)	(6.0)
3 (vac)		155.0	140.0	125.0	110.0	95.0	88.0	81.0
		(20.0)	(19.0)	(12.0)	(6.0)	(7.0)	(4.0)	(5.0)
5 (vac)		183.0	173.0	157.0	135.0	112.0	103.0	92.0
		(17.0)	(19.0)	(13.0)	(11.0)	(11.0)	(7.0)	(7.0)
10 (vac)		195.0	180.0	163.0	144.0	131.0	117.0	108.0
		(19.0)	(18.0)	(12.0)	(10.0)	(7.0)	(7.0)	(8.0)
½ (dip)	5	111.0	68.0	1.2	1.0	0.7	0.7	0.7
		(16.0)	(10.0)	(0.2)	(0.1)	(0.1)	(0.1)	(0.1)
½ (vac)		122.0	105.0	93.0	84.0	67.0	52.0	48.0
		(19.0)	(18.0)	(12.0)	(7.0)	(9.0)	(7.0)	(5.0)
1 (vac)		126.0	113.0	95.0	97.0	92.0	81.0	79.0
		(18.0)	(19.0)	(8.0)	(12.0)	(10.0)	(6.0)	(12.0)
3 (vac)		137.0	132.0	105.0	94.0	91.0	92.0	90.0
		(12.0)	(12.0)	(10.0)	(9.0)	(7.0)	(11.0)	(7.0)
5 (vac)		150.0	162.0	148.0	127.0	111.0	99.0	104.0
		(21.0)	(21.0)	(15.0)	(17.0)	(9.0)	(7.0)	(14.0)
10 (vac)		172.0	173.0	155.0	141.0	124.0	115.0	98.0
		(19.0)	(17.0)	(14.0)	(13.0)	(12.0)	(14.0)	(8.0)
½ (dip)	10	102.0	65.0	0.8	0.8	0.8	0.7	0.7
		(8.0)	(9.0)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)
½ (vac)		117.0	109.0	93.0	79.0	62.0	58.0	51.0
		(12.0)	(9.0)	(8.0)	(6.0)	(7.0)	(6.0)	(5.0)
1 (vac)		123.0	127.0	120.0	112.0	90.0	81.0	69.0
		(17.0)	(21.0)	(18.0)	(22.0)	(8.0)	(9.0)	(7.0)
3 (vac)		145.0	138.0	129.0	121.0	102.0	88.0	87.0
		(22.0)	(17.0)	(13.0)	(20.0)	(9.0)	(7.0)	(8.0)

Table 3.9 continued:

10% Resin + 10% Wax treatment time (min)	No. of Cycles	Specimen nos. and mid-distance from treated end (mm) and T½ standard deviation, minutes (3 replicates)						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
5 (vac)	10	157.0 (11.0)	168.0 (26.0)	159.0 (21.0)	132.0 (13.0)	114.0 (9.0)	101.0 (10.0)	103.0 (12.0)
10 (vac)		165.0 (19.0)	183.0 (22.0)	168.0 (20.0)	143.0 (14.0)	130.0 (16.0)	117.0 (11.0)	106.0 (9.0)
½ (dip)	20	103.0 (12.0)	81.0 (15.0)	1.2 (0.1)	1.1 (0.1)	1.0 (0.1)	1.1 (0.1)	1.3 (0.2)
½ (vac)		107.0 (9.0)	112.0 (11.0)	102.0 (13.0)	80.0 (7.0)	84.0 (6.0)	62.0 (7.0)	69.0 (7.0)
1 (vac)		126.0 (21.0)	138.0 (13.0)	122.0 (17.0)	105.0 (7.0)	97.0 (11.0)	83.0 (8.0)	84.0 (9.0)
3 (vac)		139.0 (14.0)	152.0 (24.0)	136.0 (17.0)	110.0 (13.0)	98.0 (9.0)	87.0 (6.0)	84.0 (11.0)
5 (vac)		148.0 (18.0)	173.0 (22.0)	144.0 (18.0)	133.0 (12.0)	118.0 (11.0)	101.0 (10.0)	94.0 (7.0)
10 (vac)		175.0 (16.0)	191.0 (23.0)	182.0 (25.0)	166.0 (21.0)	139.0 (18.0)	135.0 (19.0)	121.0 (12.0)

Table 3.10 Difference Between Means of Water Absorption of 1st Specimen at Various Cycles ('t'-test)

Specimen	Treatment	Comparison Between Cycles	't' Value and Significance
Pine	10% Resin	0-5	1.08 n.s.
		0-10	2.68*
		0-20	3.23**
		Others	n.s.
Pine	10% Resin + 10% Wax	0-5	n.s.
		0-10	
		0-20	
		Others	

*p = 0.05, ++p = 0.01 and n.s.= nonsignificant.

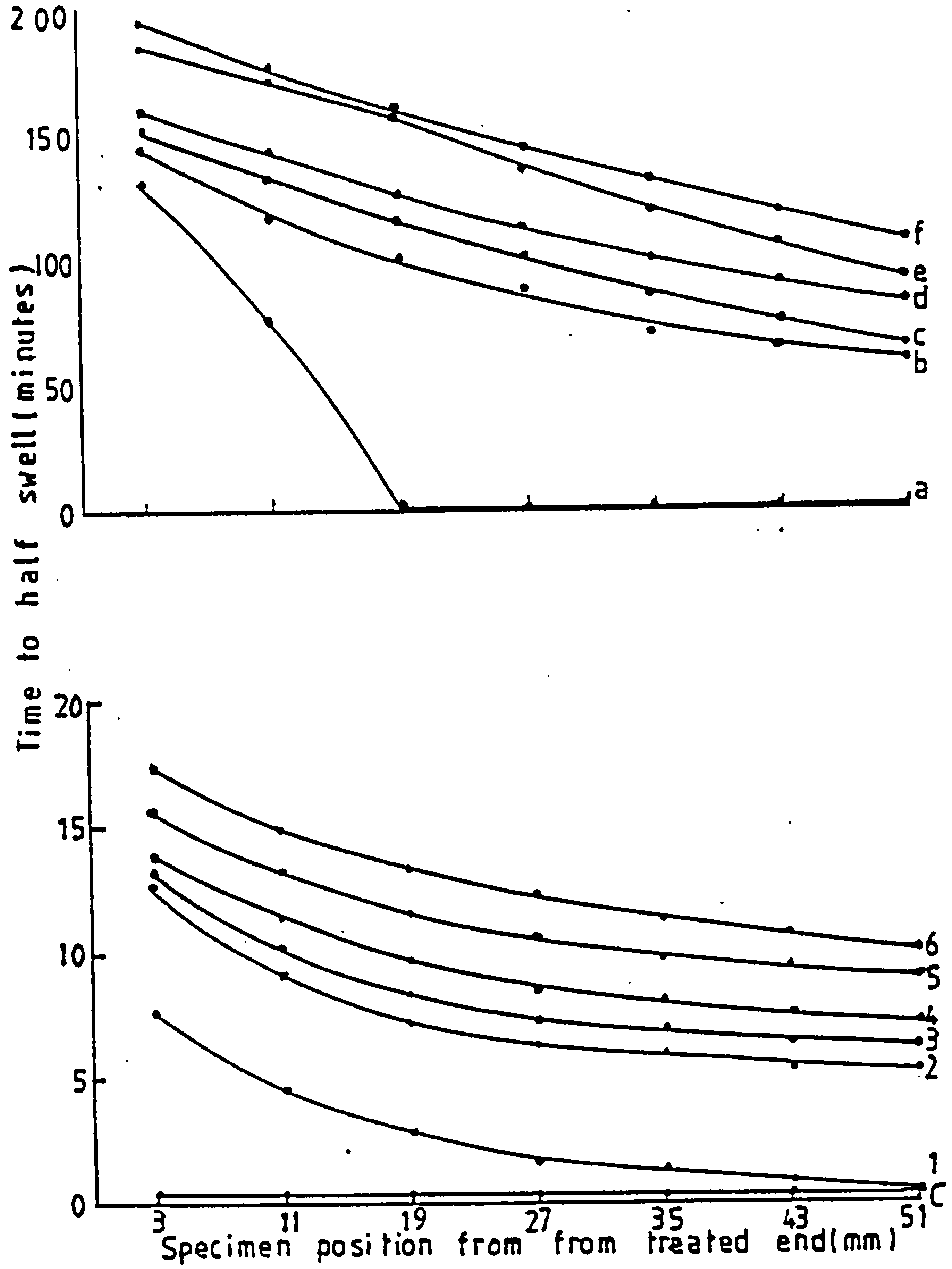


Figure 3.14 Time to half swell before cycling of transverse wafers cut along depth of treatment from pine long sticks (3 replicates). Curve code: 1-6 = resin and a-f = resin-wax treatment. C = control. 1, a = ½ min (dip); 2, b = ½ min (vac); 3, c = 1 min (vac); 4, d = 3 min (vac); 5, e = 5 min (vac); 6, f = 10 min (vac).

3.4.1 Swelling Data for Pine Transverse Wafers Before Cycling

Water repellency as indicated by time to half swell data (Table 3.9) in pine wafer specimens suggests that resin only treatment does not provide much protection. Brief (30 sec.) immersion treatment, without the application of any vacuum gives some water repellency to only the first centimetre or so from the treated end. It seems that with short immersion periods no significant penetration occurs beyond this distance. Treatment by vacuum leads to better performance in the wafer specimens (Table 3.9). Progressively improving water repellency is obtained with the increase in treatment severity.

The concentration gradient is steepest towards the outer (treated) surface. The general shape of the concentration gradient is similar for all the vacuum treatments, only the absolute values of time to half swell increasing with increasing severity of treatment. This is shown in Figure 3.14. The data presented demonstrate that, irrespective of the immersion period under vacuum, similar depth of deposit penetration is achieved in pine. Consequently, since variation in this time led to significant variation in solution absorption, the concentration of deposit throughout the treated zone must vary.

In planning the study it was assumed that process variation would lead to variation in depth of penetration. The data show this not to be the case. Probably the tendency for similar depth to be penetrated irrespective of immersion time is associated with the secondary penetration phenomenon described by Morgan and Purslow (1973).

With the resin-wax solution the water repellency in pine at positions within the treated zone is seen to increase 10 to 20 fold over the values for resin only treatment (Table 3.9). As with resin only treatments, water repellency afforded in treated specimens was dependent on the severity of treatment. The distribution of resin-wax solution, introduced by a simple immersion treatment.is characterized by a steep performance gradient at the treated end, indicating some penetration in the first centimetre of the treating end and nothing beyond this. Treatment under vacuum yielded gradients similar to those obtained with resin treated specimens, but with higher absolute time to half swell values. With all treatments a steep gradient of water repellent effectiveness towards the treated end was observed. This is probably due in part to a decrease in available flow paths with increasing distance penetrated (Banks, 1970b) and in part due to surface enrichment resulting from surface forces experienced during solvent evaporation (Smith and Cockroft, 1961).

3.4.2 Swelling Data For Pine Wafers After Cycling

Specimens subjected to simulated weathering for 5 cycles showed reduction in water repellency throughout the treated zone irrespective of level of treatment (Table 3.9). However, over this period, the greatest decrease in water repellency was observed in wafer specimens cut from the exposed surfaces. With continued exposure for 10 or 20 cycles further decrease of water repellency in the surface specimen was quite small (Table 3.9). There was very little significant decrease, if any, in the water repellency of the interior specimens. It seems, therefore, that loss of water repellency in resin-treated pine specimens is most pronounced during the initial weathering period (Table 3.10). Further cycling reduces the water repellency at a much slower rate.

On cyclic wetting and drying of long specimens, only the surface zone loses water repellency to a marked extent. A combination of breakdown of structure and loss of adhesion of resin is thought to be responsible for the loss of water repellency (Banks and Voulgaridis, 1980).

As in the case of resin treated specimens significant loss of water repellency with resin-wax treated specimens is confined to the exposed end, and to the first few (5) simulated weathering cycles. As a result of this loss in water repellency at exposed ends, the initial steep gradient of effectiveness is modified. However, resin-wax treatment restricts water entry so effectively that a very high degree of effectiveness remains even in the exposed end and the between cycles difference in T½ remains statistically insignificant with the small sample size employed (Table 3.10). After a period of such weathering in all but the immersion treated pine specimens, the outermost zone became less water repellent than some parts of the interior. Presumably the fact that the effect is not shown by the immersion treated specimens is due to the very shallow zone of treatment coupled with the very steep initial gradient within the zone. In this situation, although the outermost wood is that showing most degrade after exposure, the steepness of the performance gradient is such that wood even a little removed from

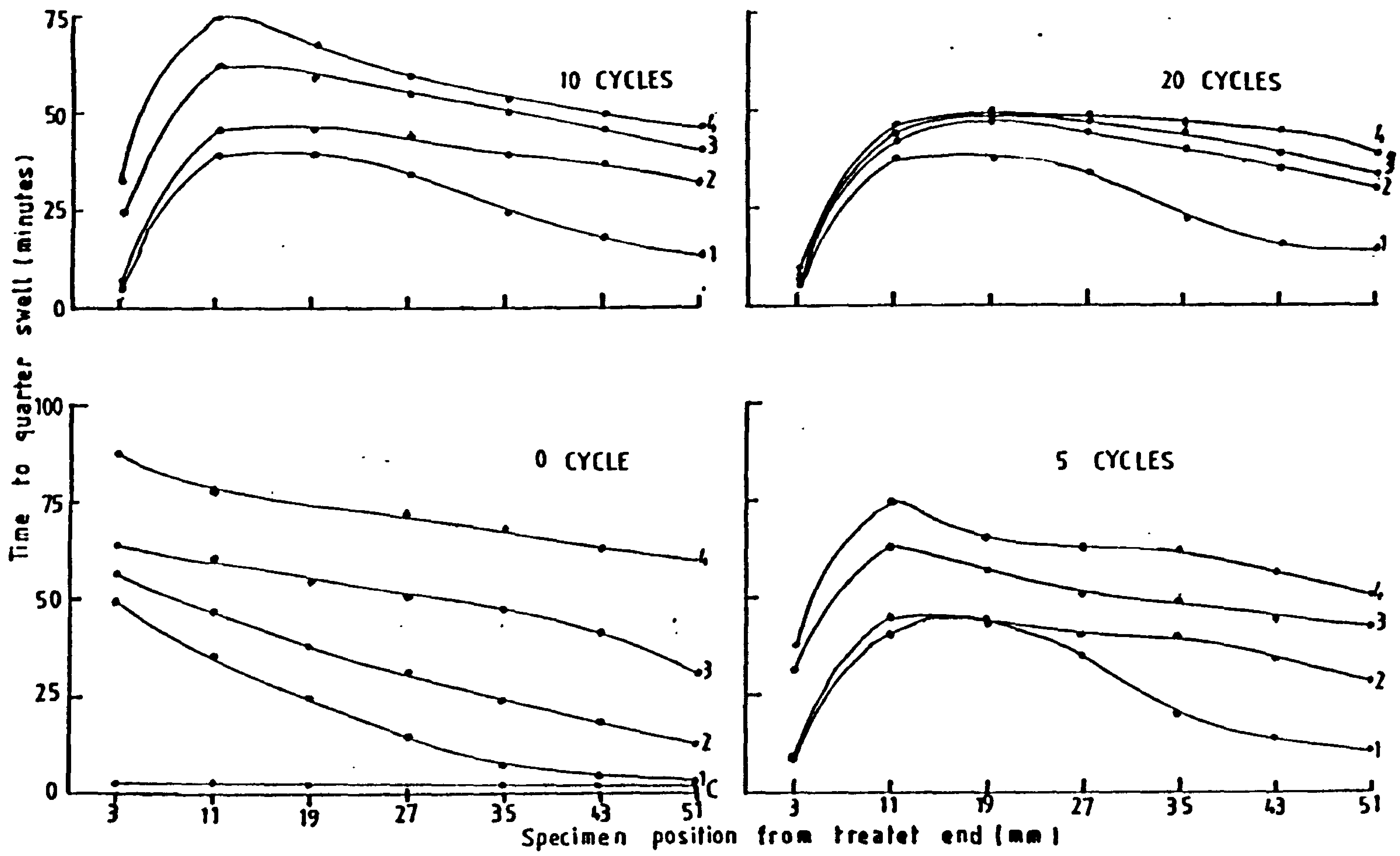


Figure 3.15 Time to quarter swell of transverse wafers cut along depth of treatment from resin-treated beech sticks after various cycles (4 replicates). Curve code: C = control; 1 = 1 ml; 2 = 2 ml; 3 = 3 ml; 4 = 5 ml.

the exposed surface is treated less well than is needed to match the performance of the degraded surface zone.

3.4.3 Swelling Data for Resin-Treated Beech Wafer Specimens After Various Weathering Cycles

As with pine, the water repellent effectiveness of treated beech shows a marked gradient of performance along the treated zone. With all the levels of treatment monitored by the gravity method (see Section 3.2.2) effectiveness expressed as time to quarter swell (T¼) is seen to decrease approximately linearly with increasing distance from the treated end (Table 3.11 and Figure 3.15). In all but the mildest (1 ml) resin only treatment this linear relationship was seen to hold over the whole sample distance ($\sim$50 mm). With the mild treatment mentioned T¼ reached an approximately constant (low) value close to that of untreated control wafers at about 35 mm from the treated end, suggesting that in this instance the deposit was restricted to this outer zone.

For all the treatments the shape of the performance gradient is broadly similar and the absolute values of T¼ can be seen to increase systematically with increase in volume of water repellent solution applied. Thus with the exception of the 1 ml resin only treatment noted above, it seems that, as with the vacuum treated pine specimens, the introduction of increasing quantities of solutions has led to increased loading within the monitored zone rather than to any marked extension of the water repellent treated zone. Again, as with pine, this is probably due to secondary penetration effects leading to the extension of the initial distance penetrated (Morgan & Purslow, 1973).

Swelling data obtained for resin treated beech specimens after exposure to cyclic wetting and drying show that this simulated weathering procedure leads to a reduction in effectiveness (Figure 3.15). Two features of this reduction are noteworthy:

1) As with pine, the exposed end region seems to be much more heavily degraded than the rest of the specimen.

2) Over the longer period of exposure (20 cycles) there appears to be a tendency for performance throughout the treated zone to fall. This effect is most marked with the heavier treatments (3 and 5 ml).

Table 3.11 Time to Quarter Swell of Beech Wafers Cut From Long Sticks After Various Weathering Cycles

10% Resin solution (ml)	No. of Cycles	Mean $T\frac{1}{4}$ of 4 replicates (1standard deviation), minutes. Specimen nos. and position (mm) from treatment end						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
Control	0	3.5	3.5	3.5	3.5	3.5	3.5	3.5
1		49.5	36.0	25.0	14.0	6.5	5.0	4.5
		(6.6)	(7.1)	(5.5)	(2.4)	(1.0)	(0.8)	(0.6)
2		57.0	46.0	38.0	31.0	22.0	18.0	13.0
		(6.0)	(5.2)	(6.2)	(5.3)	(4.3)	(6.7)	(3.6)
3		69.0	60.5	54.0	50.0	47.0	42.0	31.5
		(8.5)	(12.6)	(9.8)	(8.7)	(8.2)	(4.7)	(6.7)
5		87.0	78.0	73.5	70.0	67.0	63.0	60.5
		(12.9)	(7.4)	(5.5)	(8.0)	(8.4)	(10.2)	(6.0)
7		96.0	92.0	85.5	84.0	78.0	74.5	64.0
		(13.5)	(13.0)	(8.3)	(3.8)	(11.8)	(5.1)	(6.3)
Control	5	1.9	3.3	3.0	3.4	3.3	3.3	3.4
		(0.2)	(0.5)	(0.5)	(0.03)	(0.04)	(0.1)	(0.1)
1		7.5	45.0	42.0	34.0	17.0	14.5	11.0
		(2.1)	(4.0)	(5.0)	(3.0)	(6.0)	(3.0)	(3.0)
2		8.8	45.5	44.0	41.0	40.0	32.0	29.0
		(2.0)	(6.0)	(5.0)	(6.0)	(4.0)	(5.0)	(6.0)
3		31.0	64.0	56.3	51.0	51.0	44.0	46.0
		(8.0)	(3.5)	(6.0)	(8.0)	(5.0)	(6.0)	(7.0)
5		37.0	75.0	66.0	63.0	63.5	56.0	51.0
		(11.0)	(8.0)	(9.0)	(8.0)	(8.0)	(7.0)	(5.0)
Control	10	1.6	2.8	2.6	2.7	2.8	2.5	2.2
		(0.02)	(0.1)	(0.6)	(0.6)	(0.8)	(0.4)	(0.7)
1		3.5	40.0	35.0	34.0	23.0	18.0	13.5
		(1.3)	(4.0)	(6.0)	(3.0)	(2.0)	(1.2)	(2.0)
2		5.3	46.0	44.0	45.0	39.0	37.0	33.0
		(2.0)	(3.0)	(7.0)	(4.0)	(5.0)	(8.0)	(3.0)
3		24.0	63.0	59.0	56.0	50.0	49.0	41.0
		(0.7)	(4.0)	(8.5)	(5.0)	(6.0)	(5.0)	(4.0)
5		31.0	75.0	67.0	60.0	53.0	50.0	47.0
		(4.0)	(11.0)	(9.0)	(10.0)	(7.0)	(6.0)	(8.0)

Table 3.11 continued:

10% Resin solution (ml)	No. of Cycles	Mean T½ of 4 replicates (1 standard deviation), minutes Specimen nos. and position (mm) from treatment end						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
Control	20	1.6 (0.4)	2.3 (0.5)	2.8 (0.2)	2.8 (0.3)	2.4 (0.2)	2.5 (0.5)	2.0 (0.4)
1		3.0 (1.8)	38.0 (4.0)	37.0 (2.0)	34.0 (6.0)	18.0 (3.0)	17.0 (2.0)	16.0 (2.0)
2		3.3 (1.1)	47.0 (8.0)	44.5 (5.0)	44.0 (5.5)	38.0 (7.0)	36.0 (3.0)	31.0 (5.0)
3		3.2 (1.9)	48.0 (6.0)	48.0 (7.0)	47.5 (4.0)	45.5 (3.0)	40.0 (7.0)	33.0 (4.0)
5		10.0 (4.0)	47.5 (8.0)	51.0 (4.0)	48.0 (7.0)	47.5 (6.0)	46.0 (8.0)	39.0 (7.0)
10% Resin + 10% Wax solution (ml)		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
1	0	112.0 (9.5)	98.0 (7.4)	84.0 (10.0)	74.5 (17.2)	68.0 (13.0)	60.5 (18.3)	50.0 (12.6)
2		139.0 (27.3)	117.0 (16.5)	109.0 (12.5)	100.0 (10.1)	91.5 (9.7)	85.0 (15.1)	78.0 (12.4)
3		154.0 (14.5)	136.0 (15.9)	124.0 (6.9)	118.5 (8.4)	108.0 (5.5)	94.5 (14.0)	86.0 (16.7)
5		192.0 (9.9)	146.0 (11.6)	135.0 (23.8)	130.0 (11.0)	123.0 (12.0)	110.5 (12.8)	105.0 (12.8)
7		207.5 (16.3)	162.0 (4.8)	148.0 (9.3)	140.0 (14.5)	128.0 (22.1)	119.0 (14.9)	113.0 (17.0)
1	5	45.0 (7.0)	109.0 (11.0)	111.0 (13.0)	78.0 (6.0)	67.0 (5.0)	57.0 (7.0)	58.0 (4.0)
2		91.0 (12.0)	141.0 (10.5)	128.0 (17.0)	117.0 (7.0)	104.0 (8.0)	99.0 (11.0)	107.0 (9.0)
3		107.0 (21.0)	186.0 (17.0)	169.0 (14.0)	152.0 (13.0)	138.0 (8.0)	124.0 (9.0)	122.0 (5.0)
5		109.0 (16.0)	223.0 (31.0)	205.0 (15.0)	187.0 (21.0)	162.0 (12.0)	146.0 (11.0)	133.0 (12.0)

Table 3.11 continued:

10% Resin + 10% Wax solution (ml)	No. of Cycles	Mean T½ of 4 replicates (1 standard deviation), minutes Specimen nos. and position (mm) from treatment end						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
1	10	48.0 (9.0)	109.0 (11.0)	103.0 (8.0)	78.0 (10.0)	62.0 (7.0)	58.0 (5.0)	61.0 (6.0)
2		77.0 (10.0)	138.0 (12.0)	141.0 (16.0)	125.0 (24.0)	110.0 (19.0)	90.0 (8.0)	66.0 (5.0)
3		83.0 (7.0)	177.0 (22.0)	173.0 (8.0)	170.0 (9.0)	141.0 (16.0)	128.0 (10.0)	121.0 (8.0)
5		97.0 (12.0)	220.0 (31.0)	198.0 (26.0)	174.0 (18.0)	159.0 (13.0)	144.0 (11.0)	129.0 (9.0)
1	20	44.0 (5.0)	108.0 (11.0)	96.0 (12.0)	83.0 (9.0)	70.0 (11.0)	52.0 (6.0)	45.0 (5.0)
2		77.0 (11.0)	140.0 (14.0)	139.0 (14.0)	128.0 (12.0)	120.0 (22.0)	105.0 (11.0)	92.0 (8.0)
3		91.0 (8.0)	183.0 (14.0)	168.0 (21.0)	157.0 (16.0)	132.0 (20.0)	129.0 (12.0)	122.0 (10.0)
5		109.0 (12.0)	198.0 (23.0)	187.0 (14.0)	168.0 (24.0)	157.0 (13.0)	132.0 (11.0)	124.0 (8.0)

The first feature, that relating to end performance is probably associated strongly with the wood structural degrade occuring in this region (Banks and Voulgaridis, 1980). The second feature, loss of performance throughout the treated zone,may be due to the ability for liquid water to penetrate the whole of the resin only treated zone (since the hydrophobic effect is small) and thence to degrade either the lumen structure or the lumen/deposit interface. This effect is discussed fully in the section dealing with resin treated pine (Section 3.4.2).

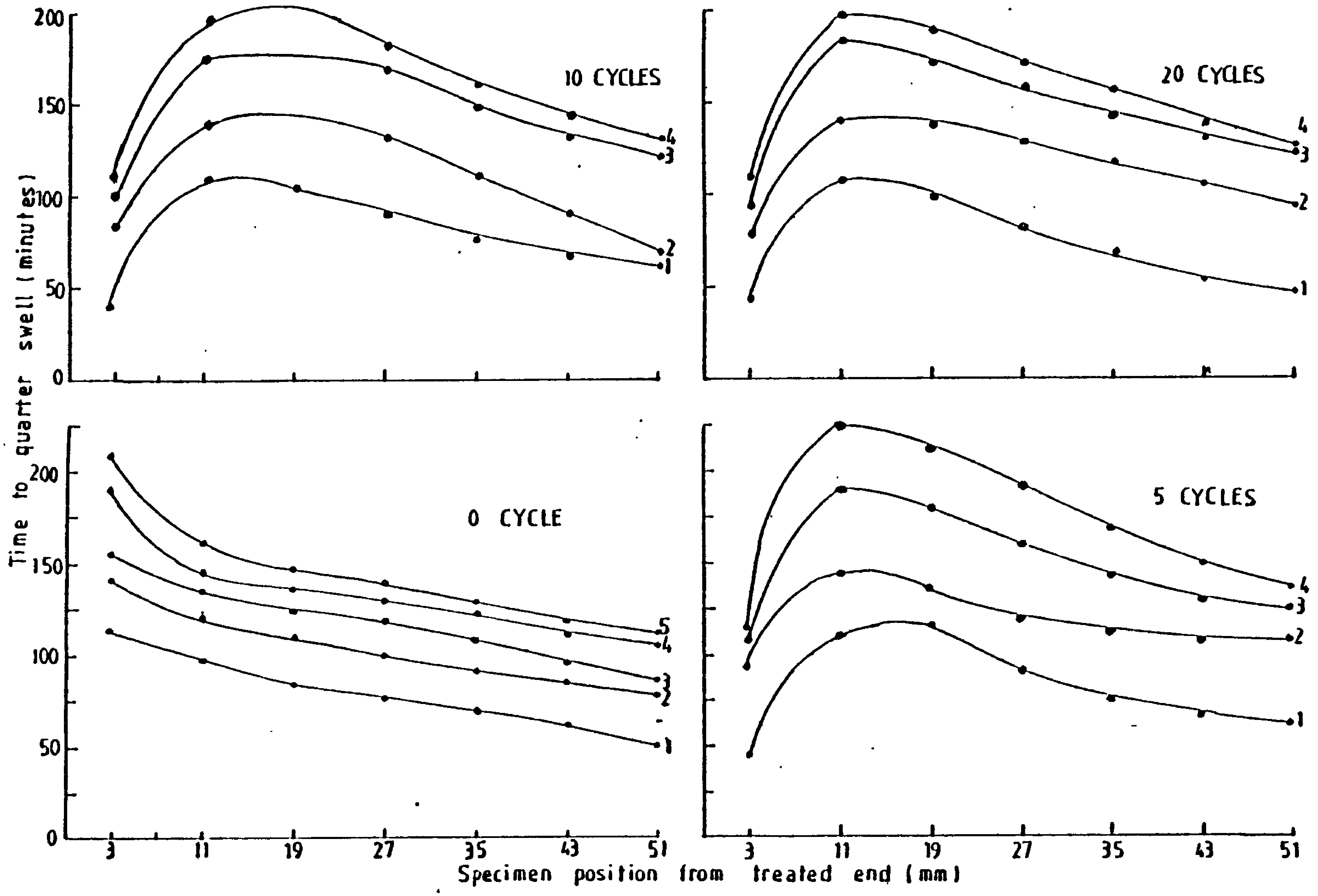


Figure 3.16 Time to quarter swell of transverse wafers cut along depth of treatment from resin-wax treated beech sticks after various cycles (4 replicates). Curve code: C = control; 1 = 1 ml; 2 = 2 ml; 3 = 3 ml; 4 = 5 ml.

Although all levels of treatment show marked loss of performance as a result of simulated weathering, especially in the exposed end region, the heavier treatments continue to offer better resistance to water uptake throughout the exposure period. This is probably because the initially more effective deposit continues to act as a reservoir allowing significant water resistance to remain in spite of the degrade caused by weathering.

3.4.4 Performance of Resin-Wax Treated Wafers at Various Cycles

As with the resin only treatments, a gradient of performance can be observed in resin-wax treated specimens throughout the impregnated zone, with the treated end region showing greatest resistance to water uptake before exposure to simulated weathering (Figure 3.16; Table 3.11). With exposure to the weathering process, marked loss of performance was seen to occur. From the graphs of Figure 3.16 it can be seen that almost all the loss of performance occurred within the first 5 wet/dry cycles and was largely restricted to the outermost centimetre of the long specimens. Similar to the treated pine specimens discussed above (Section 3.2.2), it is believed that this difference in the nature of performance loss compared with resin only treatments, is associated with the strongly hydrophobic character of the resin/wax deposit. With such a deposit, liquid water is unable to penetrate beyond the degraded zone. Hence, breakdown of the deposit/cell wall system can occur only slowly from the exposed surface inwards.

Throughout the weathering period corresponding points within the specimens can be seen to maintain their performance relative to one another. This suggests that the deposit thickness or the extent of its distribution within the cell structure in the treated zone has a significant effect on performance.

3.5 Assessment of the Distribution of Water Repellent Substances Within the Treated Zone

As suggested in the previous section, the effectiveness of a water repellent treatment is likely to depend on the amount of deposit and its precise location within treated wood. However, it seems likely that factors such as the coherence of the deposit and the quality of its bond to the wood may also markedly influence water repellent efficiency. To assess the relative importance of these factors the amount of deposit present in the transverse wafers, cut from the treated long specimens, was quantitatively estimated after completion of the swelling tests, described in Section 3.4.

3.5.1 Method of Extraction

Wafer specimens after swelling tests were dried at 35°C to constant weight. The protective styrene resin coating on the lateral surfaces of the wafers was carefully peeled off. The specimens were then split into several smaller sections and extracted for 2 hours with 25 ml of 60-80°C boiling range petroleum spirit in a refluxing system. The extracted solution was removed and the wood sections were washed twice with 10 ml portions of the solvent. All the washings were preserved. A second reflux extraction of the specimen sections was carried out with a further 20 c.c. of solvent for 1 hour. The wood sections, after decanting off the solvent, were washed again twice with 10 ml aliquot parts of solvent. A third extraction conducted with the first few specimens showed an absence of any further soluble substances after the second extraction. All extractives and washings from the extraction process for each treatment were slowly evaporated at 55-60°C over a constant level water bath in chemically clean, previously dried, desiccated and weighed porcelain basins. After drying, the deposits in the basins were desiccated and weighed to calculate the amount of water repellent substance removed from each section. Untreated control sections were used in order to correct for the natural extractive substances present.

3.5.2 Water Repellent Extraction Data and Discussion

The T½ and T¼ values obtained with the resin and resin-wax treated Corsican pine and European beech specimens at 0, 5, 10 and 20 cycles (Section 3.4) suggest that,

(a) natural water resistance in beech is more pronounced than in pine;

(b) ultrastructural differences in pine and beech allow a better coating action with resin solution in beech than in pine;

(c) the hydrophobic action of wax in treated specimens is, on the other hand, much more prominent in pine than in beech, probably again due to the same ultrastructural difference;

(d) higher treatment level affords better water repellency than lower ones both in pine and beech;

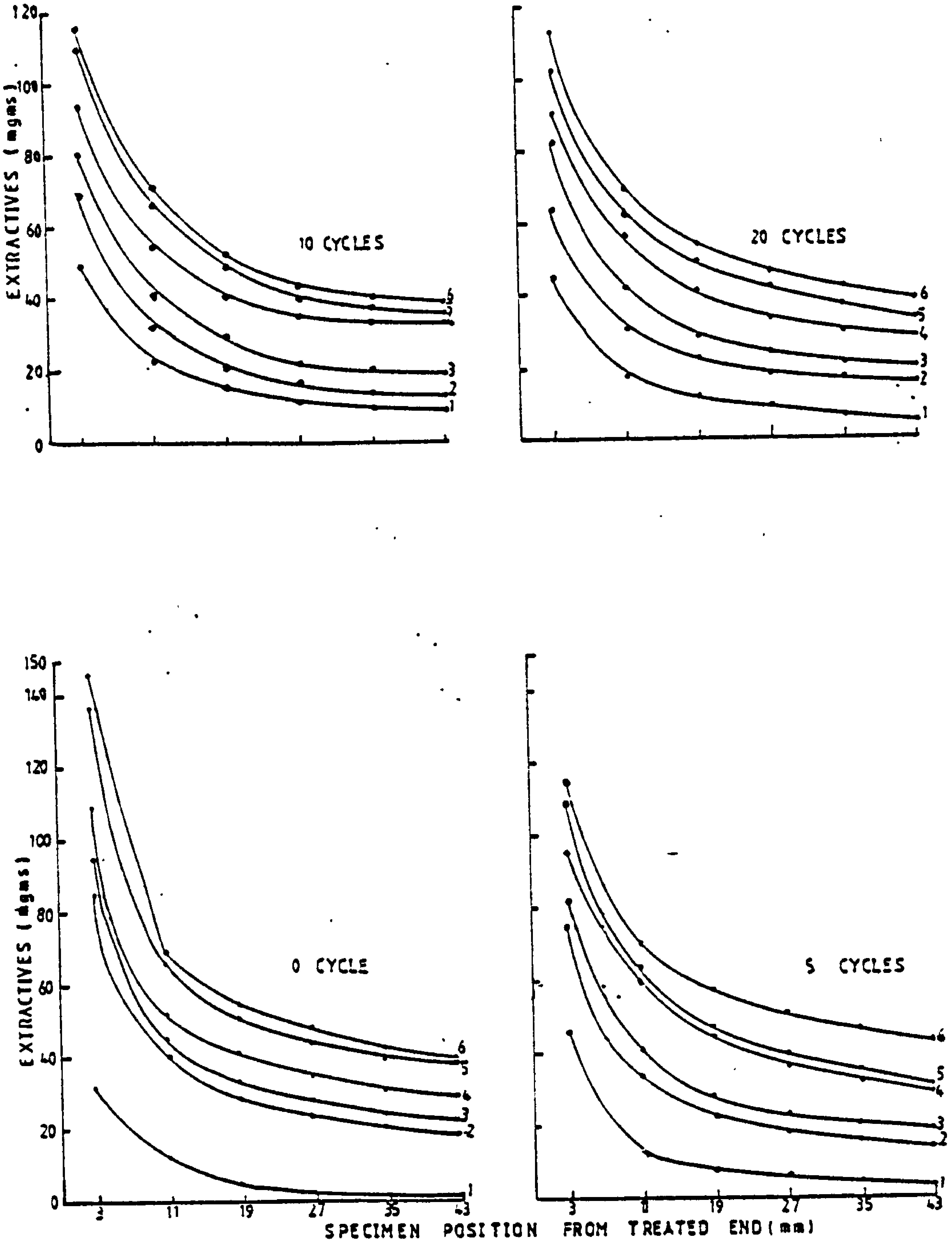


Figure 3.17 Distribution of resin along depth of treatment of pine long sticks gravimetrically determined by extraction after 0, 5, 10 and 20 weathering cycles (mean of 3 replicates). Curve code: 1 = ½ min (dip); 2 = ½ min (vac); 3 = 1 min (vac); 4 = 3 min (vac); 5 = 5 min (vac); 6 = 10 min (vac).

(e) a distribution gradient forms along the treated zone with both treating solutions and with both the species;

(f) exposure to cyclic wetting and drying degrades the end specimens more than the interior ones;

(g) wood degrade is more prominent in beech than in pine;

(h) resin treatments are affected by weathering more markedly than resin-wax treatments.

Part of the loss of performance due to the simulated weathering exposure is believed to be due partly to wood structural degrade and in part possibly due to alteration of the wood deposit system (Voulgaridis, 1980). The presence of resin-wax deposit, for example, in a treated specimen after cycling may be in a bonded state over important pit areas or in a dislodged state due to preferential wetting.

At the outset it should be emphasized that separate batches of specimens had to be used for various cycles of exposure, because the assay work involved specimen destruction. Therefore, some variation in solution absorption and distribution was inevitable.

The amount of water repellent extracted from resin treated pine specimens before cycling showed progressively larger amounts of resin present with increase in the severity of treatment (Appendix II, Table 3; Figure 3.17). When penetration was conducted by simple immersion treatment for very short time (30 seconds), most of the resin was located in the first wafer specimen. The second had a little measurable deposit, but the later ones had only nominal quantities. These amounts are close to normal wood extractives, as will be clear from the mean extractives (0.0017g) of six untreated control wafers. In vacuum impregnated pine specimens resin was found to be distributed in decreasing amounts from the end specimen inwards. However, the steep fall in the first 2 or 3 centimetres gave way to a flatter distribution pattern beyond this depth. The water repellency afforded for various treatment periods and at various depths of penetration in treated wood (Section 3.4) are in keeping with the amounts of resin extracted.

After 5 soak/dry simulated weathering cycles, the end specimen exposed to the rigours of weathering showed some loss of resin deposit (Figure 3.17). Breakdown in wood structure in the end specimen, weakening of wood/resin bond due to preferential wetting and subsequent

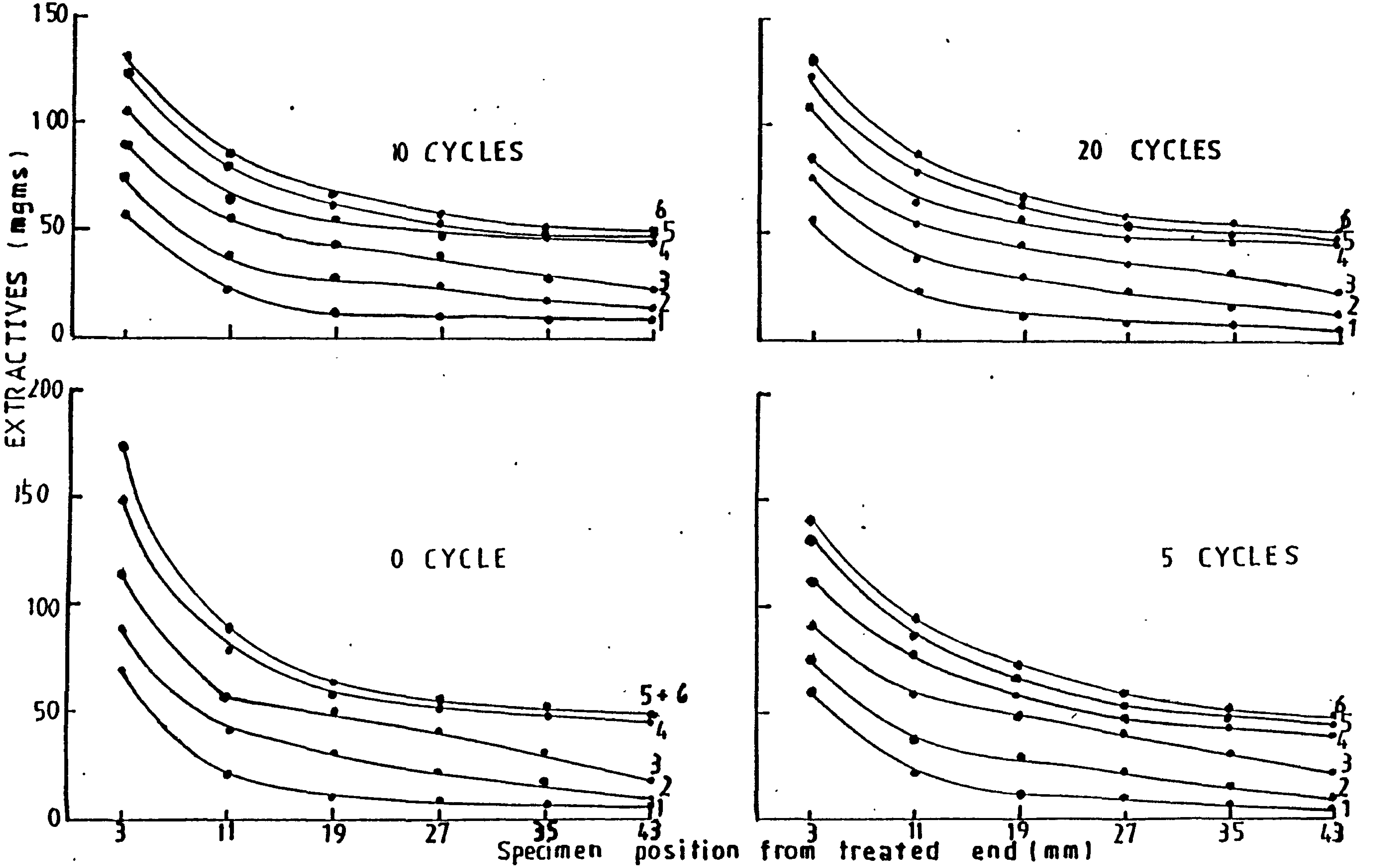


Figure 3.19 Distribution of resin-wax along depth of treatment of pine long sticks gravimetrically determined by extraction after 0, 5, 10 and 20 weathering cycles (mean of 3 replicates). Curve code: 1 = ½ min (dip); 2 = ½ min (vac); 3 = 1 min (vac); 4 = 3 min (vac); 5 = 5 min (vac); 6 = 10 min (vac).

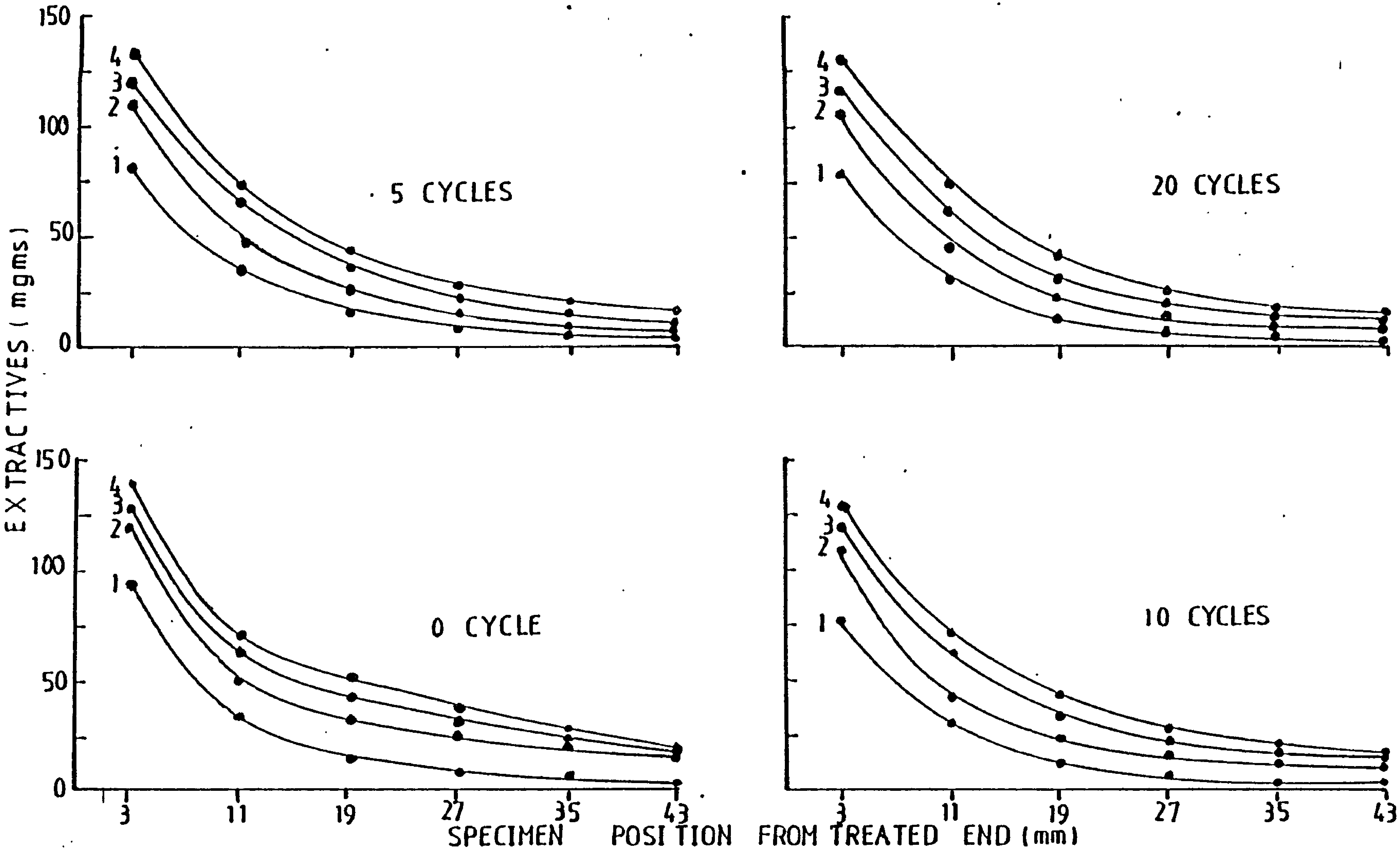


Figure 3.20 Distribution of resin along depth of treatment of beech long sticks gravimetrically determined by extraction after 0, 5, 10 and 20 weathering cycles (mean of 3 replicates). Curve code: 1 = 1 ml; 2 = 2 ml; 3 = 3 ml; 4 = 5 ml.

dislodgement or removal of some resin therefrom is suggested as the cause of this loss. The interior specimens beyond the outermost centimetre do not seem to lose much resin on cycling. The distribution curve, as a result, tends to be less steep after 5 cycles. Further weathering for 10 or 20 cycles appears to have little effect on the resin content, even of the outermost specimen. It is probable that maximum loss of water repellents takes place in the first centimetre or so of the weathered long sticks after 5 or so cycles. It seems likely that this rapid loss of deposit from the outermost specimen may be due to weakening of the bond between the outer wood surface and superficial deposit attached to it (Figure 3.18).

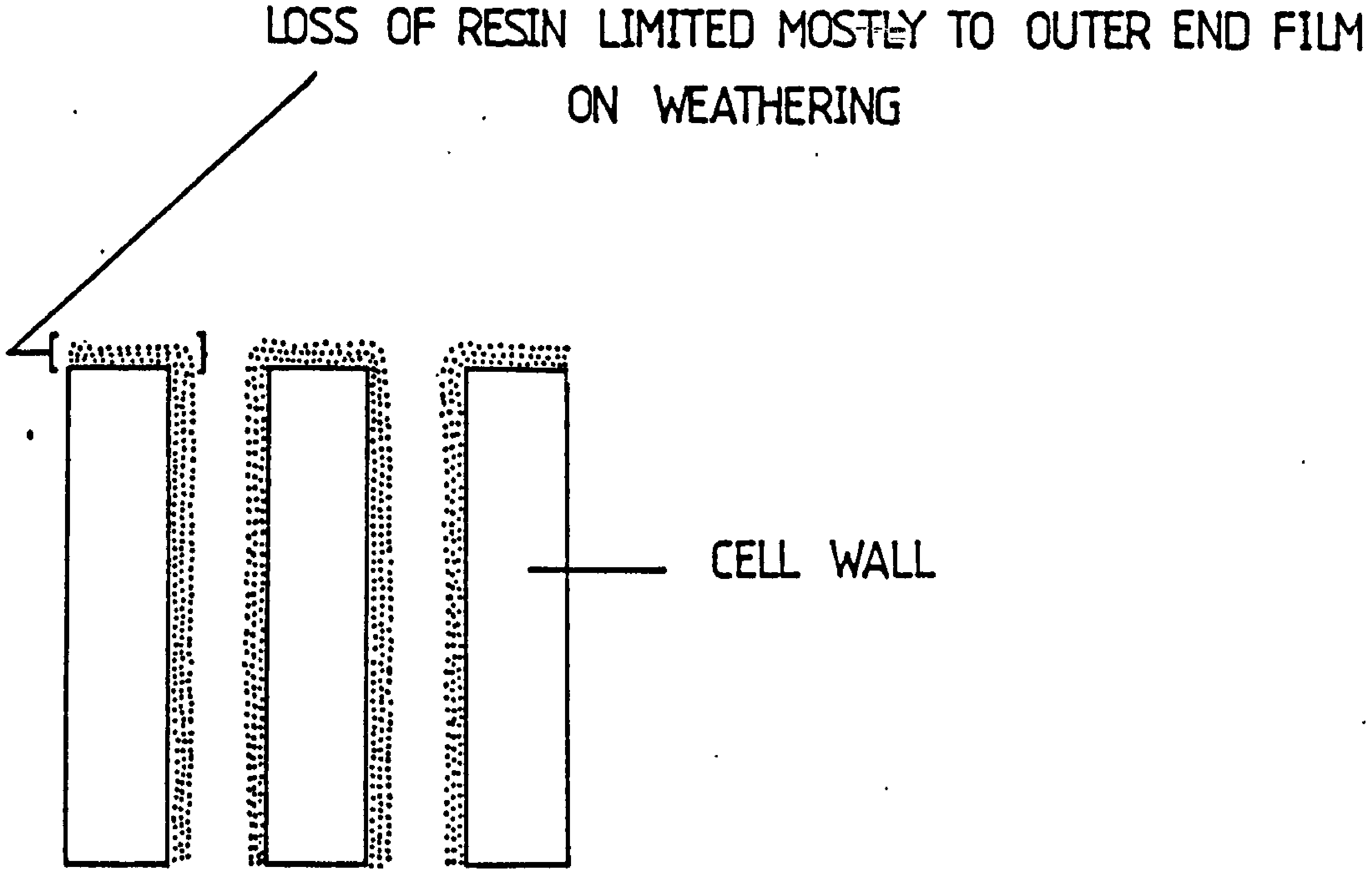


Figure 3.18 Loss of water repellent deposit limited to outer end film after 5 cycles of weathering.

After the initial period of cycling the wood/resin bond in the end (and second) specimen(s) may be weakened further on continued weathering. This may pave the way for some further loss of water repellency manifested as decreased time to half swell. Where such bond weakening occurs deeply within the treated zone the resin may not be removed from the wood cells, hence the amount extracted from interior specimens may be expected to remain relatively constant. The swelling of the wood specimens, on the other hand, may increase as a result of degradation of wood-resin bond.

Resin-wax treatment in pine follows almost the same pattern as in the case of resin treatment, both before and after cycling (Appendix II, Table 3, Figure 3.19). Quantitative loss of resin-wax from the first specimen is, however, more than in the case of resin treated specimens. This may be due in part to the presence of higher solids content. On a percentage basis, however, loss of resin-wax is also greater than with resin only. It seems, therefore, the weaker wood-wax bond is responsible for greater loss of resin-wax on cycling.

It is observed that the surface specimens of both the resin and resin-wax treated pine continue to lose water repellent effectiveness upon exposure to 10 or 20 weathering cycles to the extent that they exhibit lower water repellency than the specimens immediately beyond the surface zone (specimen no. 2; Section 3.4.1 and 3.4.2). However, in spite of the considerable loss of resin or resin-wax deposit from the outermost specimens (Figures 3.17 and 3.19), these still retain more deposit than subsequent specimens, even after such exposure.

This evidence lends support to the view that it is not only the quantity of water repellent deposited at a particular location which determines the degree of water repellency afforded within that zone. Rather, water repellency seems to depend also on distribution at the cellular or sub-cellular level and/or on the quality of bond between deposit and cell wall. Moreover, well-bonded and distributed water repellents will be of little help in protecting wood if water entry is made possible by exposing uncoated areas as a result of wood degradation in the vicinity of the treated zone.

Monitored quantities of water repellents (1, 2, 3 or 5 ml) introduced into 15 cm long beech specimens show a similar gradient of resin loading to that seen in vacuum treated pine (compare Figures 3.17 and 3.20). In the gravity treated beech specimens the resin concentration is greatest near to the treated end. Concentration falls steeply over the outer 2 cm or so and thereafter more gradually. It is possible that in the absence of any vacuum to enhance the penetration of water repellents into the pit system, penetration occurs mostly into the vessel system. Some secondary penetration occurring during drying may lead to fluid movement through the pit system from the vessels into fibre tissue. Because penetration was effected from the bottom upwards and also as a

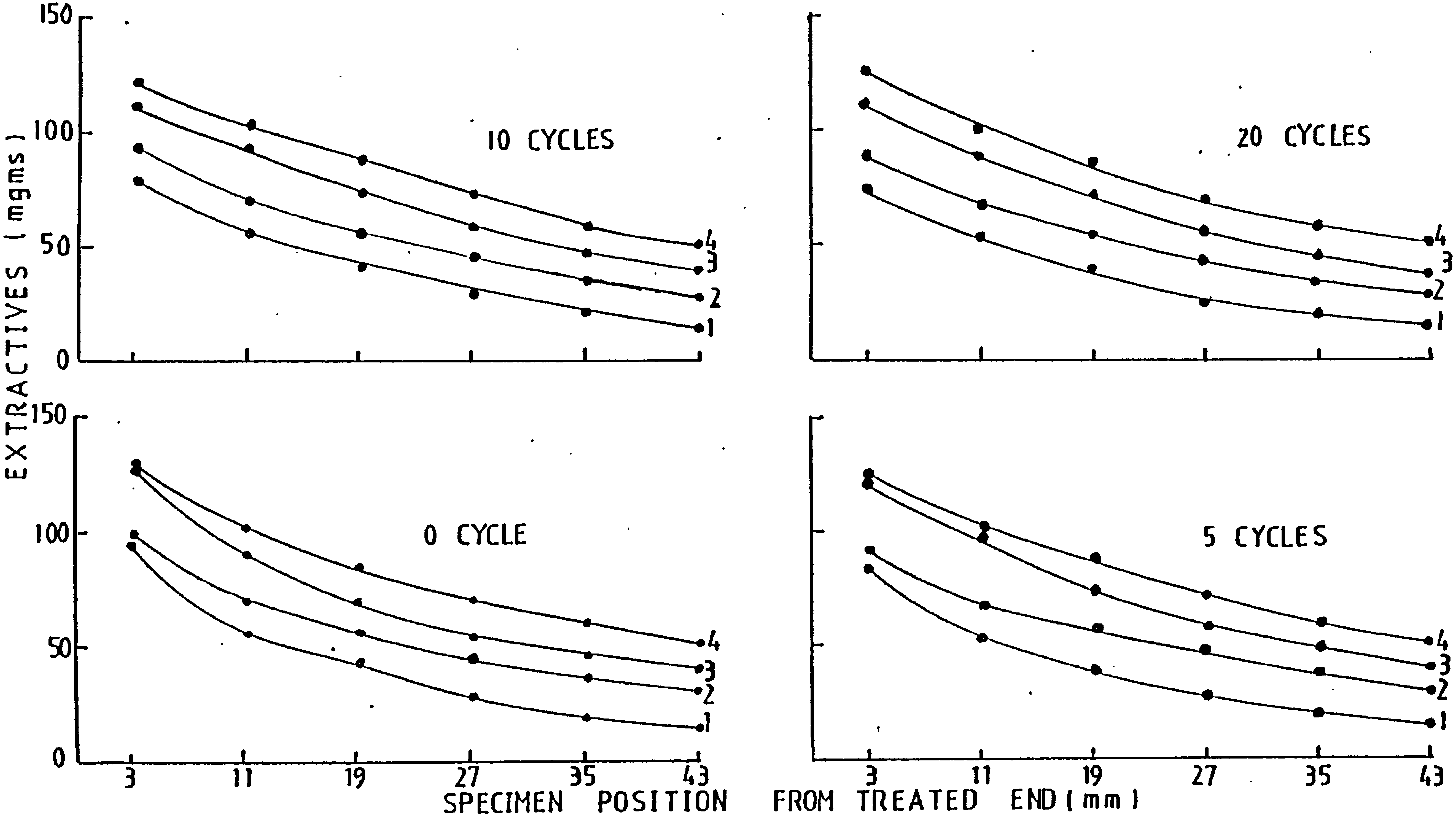


Figure 3.21 Distribution of resin-wax along depth of treatment of beech long sticks gravimetrically determined by extraction after 0, 5, 10 and 20 weathering cycles (mean of 3 replicates). Curve code:
1 = 1 ml; 2 = 2 ml; 3 = 3 ml; 4 = 5 ml.

result of evaporation from the exposed end grain, more water repellents are deposited towards treated end than in the interior.

After 5 wet-dry cycles most of the resin-loss from beech specimens seems to have occurred from the end specimen (outer 6 mm). In contrast to pine there is also some loss from the second specimen. Thereafter, along the depth of treatment the amount of water repellent present seems to be virtually unaffected by cycling. Probably due to the greater dimensional instability of beech compared to pine, more checks and splits developed in the end specimens of beech than in the pine specimens. Some of these splits appeared to extend far enough to affect water movement into the zone of the second wafer and this may contribute to the loss of some deposit from this region. On continuing exposure up to 10 cycles, a further loss of resin was recorded in the first and second specimens. Beyond this degree of exposure further cycling did not seem to cause significant further loss of resin. The distribution gradient, thus, become less steep with cycling up to 10 cycles.

A broadly similar pattern of distribution of resin-wax was observed both initially and after cycling except that unlike resin, the resin-wax is distributed along a smoothly falling gradient rather than one with inward steepness towards the treated end (Figure 3.21). It is noteworthy that the much higher solids content in resin-wax solution did not give rise to proportionately higher deposits compared to resin in the treated end. With resin-wax, the deposit is laid down more evenly throughout the treated zone. This is probably due to the resin-wax solution being closer to its solubility limit. Thus, as solvent evaporation occurs, solids begin to precipitate before a large volume of solvent is lost, reducing the tendency for the solids to concentrate towards the surface(s) from which evaporation occurs.

3.6 Measurement of Contact Angles of Extracted Water Repellents After Simulated Weathering

On rough and porous substrates it is difficult to obtain precise and reproducible estimates of contact angle. Hence the equilibrium contact angle made by water with the extracted water repellent deposit was measured by the sessile drop method after its deposition onto clean glass microscope slides (Figure 3.22; Gray and Wheeler, 1959; Nguyen and Johns, 1979; Rak, 1975).

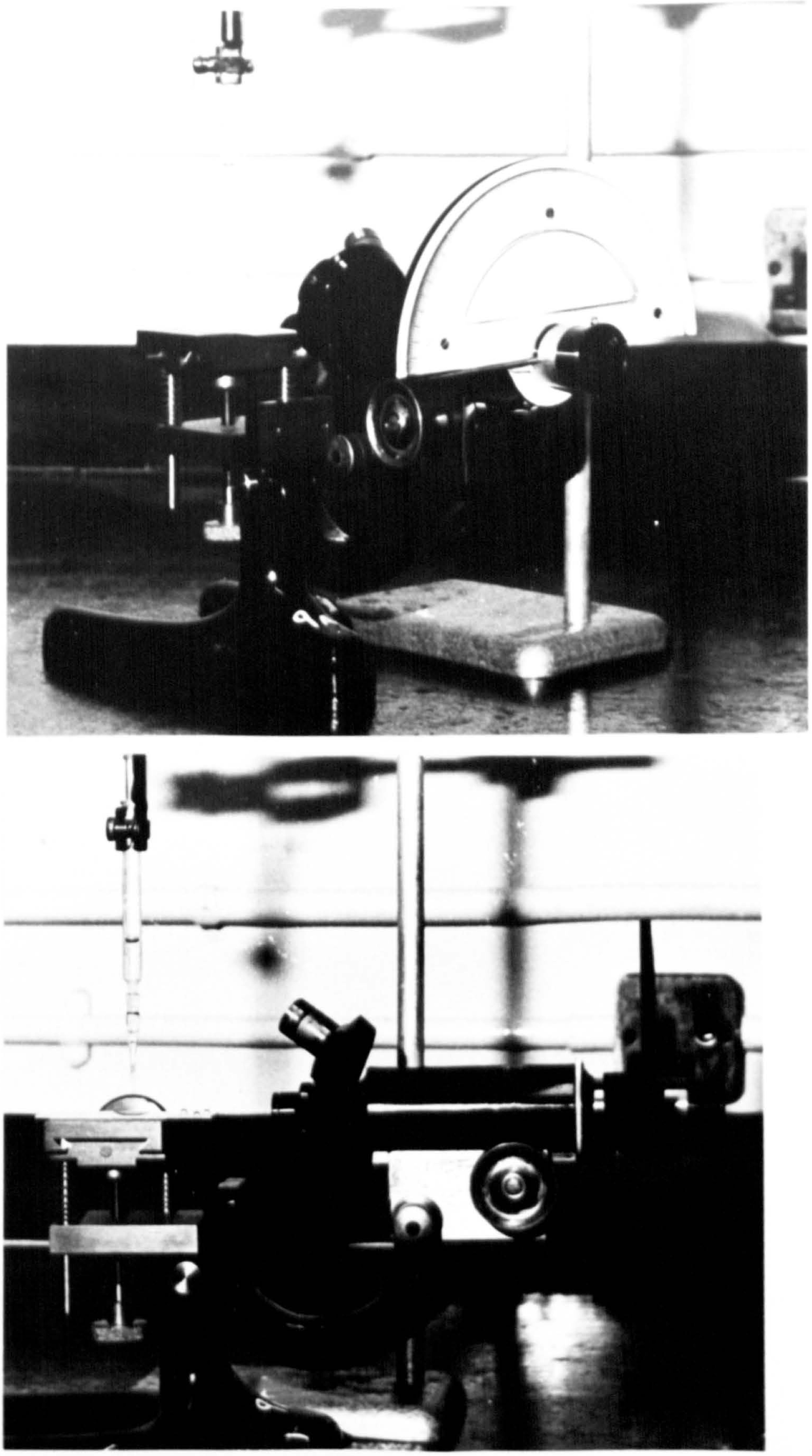


Figure 3.22. Measurement of equilibrium contact angle by sessile drop method. Water drop on glass slides coated with extracted water repellent can be seen in the lower picture.

The extractives from the extraction experiment (see Section 3.5.1) were dissolved in 5 ml of 40°-60°C boiling range petroleum spirit. The film on glass slide was made by placing a drop of this solution on a slide and rapidly drawing another slide over it. After drying, the slides were equilibrated in a desiccator containing silica gel for at least 48 hours before being subjected to test (Figure 3.22). Drops (0.01 ml) of distilled water were placed on the film from a microsyringe. Four drops were placed on each of 3 slides for each extract and their contact angles were measured at 65% RH and 20°C.

3.6.1 Contact Angle Data for Deposits Extracted from Cycled Specimens

Equilibrium contact angles of resin-wax extracted from pine and beech specimens and deposited on glass slides show no systematic change with time of exposure to simulated weathering cycles. Neither do the contact angles measured vary significantly with severity of treatment or location within the treated zone (Table 3.12; details are in Appendix II, Table 5). This suggests that no gross separation of the wax and resin occurs along the depth of treatment. The low contact angles obtained with interior specimens at 0 cycle of immersion treated (30 seconds) pine and 1 ml treated beech wood simply indicate the absence of any significant quantities of water repellents in these zones (compare data in Appendix II, Tables 3 and 4 with Table 5). Further contact angle measurements (after cycling) on extracts from untreated or minimally treated zones were not carried out.

The somewhat similar range of contact angles along the depth of treatment does not, however, mean equidistribution of water repellents. Quantitative estimation of deposits (Section 3.5.1) and swelling measurements (Section 3.4) demonstrate convincingly that a concentration gradient is established along the treated zone. Since a monomolecular hydrophobic layer is sufficient to give a high contact angle, varying quantities of water repellents present in excess of that required to form a monolayer cannot be expected to have a large effect on the contact angle. It is difficult to measure contact angle with precision better than ±2-3°. The variability observed at any sample position as a result of cycling generally falls within this bound. Hence, it can be seen that the simulated weathering process appears to have no significant effect on the hydrophobicity of the deposit.

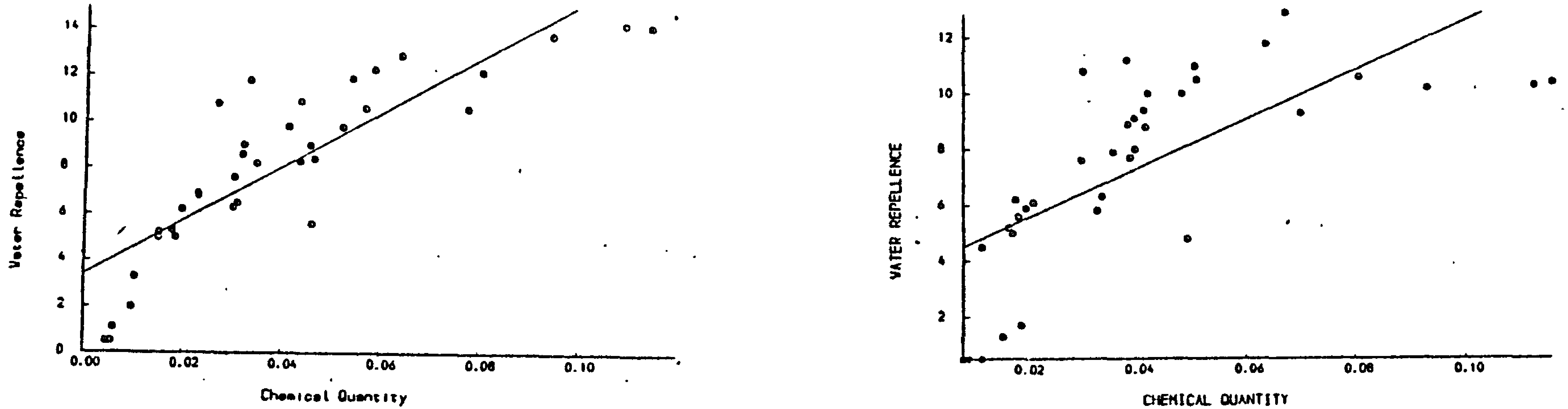
Table 3.12 Comparative Non-Variability of Contact Angle on Stable Substrate with Severity of Treatment or Weathering or Location Within Treated Zone with Resin-Wax Variability

PINE					No. of Cycles	BEECH				
Treatment	Specimen Position (mm)					Treatment	Specimen Position (mm)			
(min)	Contact angle (θ^o)		Deposit (gm)			(ml)	Contact angle (θ^o)		Deposit (gm)	
	3	27	3	27			3	27	3	27
3 (vac)	107	108	0.141	0.057	0	3	105	105	0.130	0.054
	110	111	0.118	0.053	5		109	110	0.122	0.058
	110	107	0.106	0.053	10		110	110	0.113	0.056
	107	108	0.108	0.053	20		110	110	0.112	0.054
5 (vac)	105	106	0.177	0.055	0	5	104	107	0.132	0.071
	104	108	0.134	0.053	5		112	107	0.125	0.072
	105	110	0.126	0.056	10		108	108	0.123	0.072
	103	108	0.122	0.052	20		112	107	0.126	0.071

3.7 The Relationship Between Distribution and Effectiveness of Water Repellents in Treated Wood

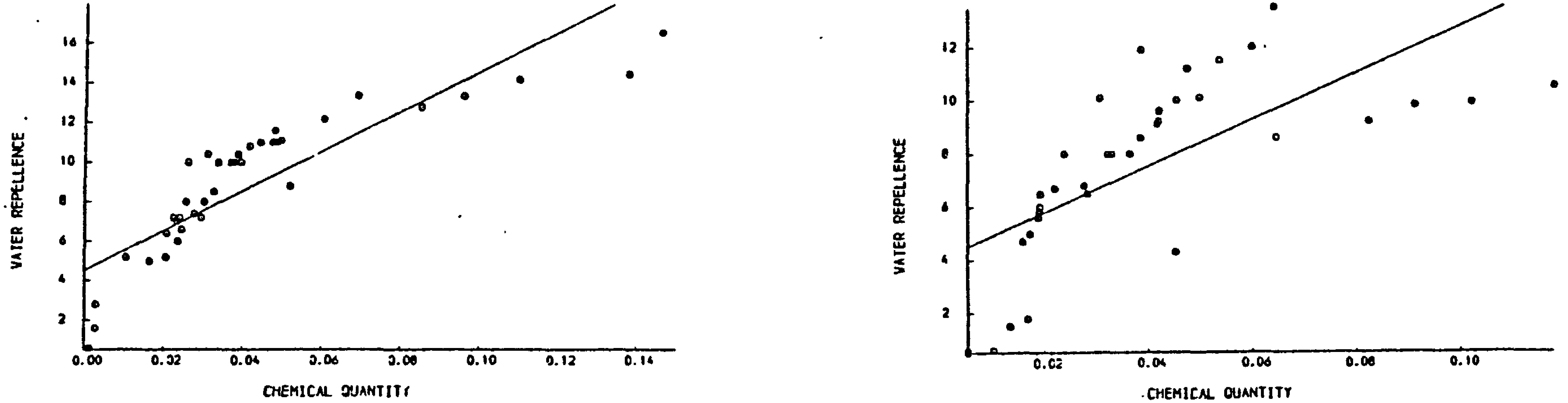
Scatter diagram of deposit amount against water repellent effectiveness (T½ and T¼) of variously treated pine and beech specimens are presented in Figures 3.23 to 3.26. Visual inspection of the data for all samples before exposure suggests that there is a positive correlation between amount and effectiveness of water repellent. This is confirmed by the regression analysis (see Table 3.13). Only in the case of the resin only beech treatment does the correlation coefficient fall below 0.8. Even in the case of the resin/beech treatment where the correlation coefficient is 0.67, analysis suggests that the correlation is significant at the 0.01 confidence level of probability.

In all treatment systems tested, exposure to cyclic wetting and drying leads to a decrease in the quality of correlation. In spite of this, the correlation remains significant at the 1% level with pine specimens throughout the exposure period. With beech, however, exposure for 5-10 wet/dry cycles brings about a loss of correlation to below the 5% level of



Regression line for Pine (Resin/5cycles)

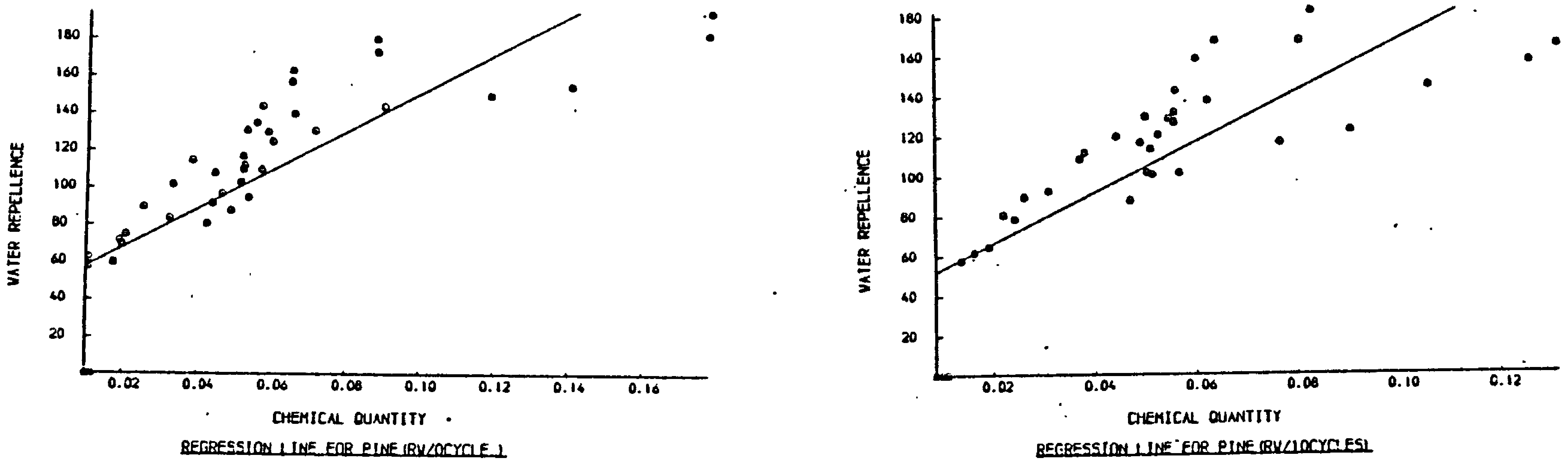
REGRESSION LINE FOR PINE (RESIN/10CYCLES)



REGRESSION LINE FOR PINE (RESIN/G CYCLE)

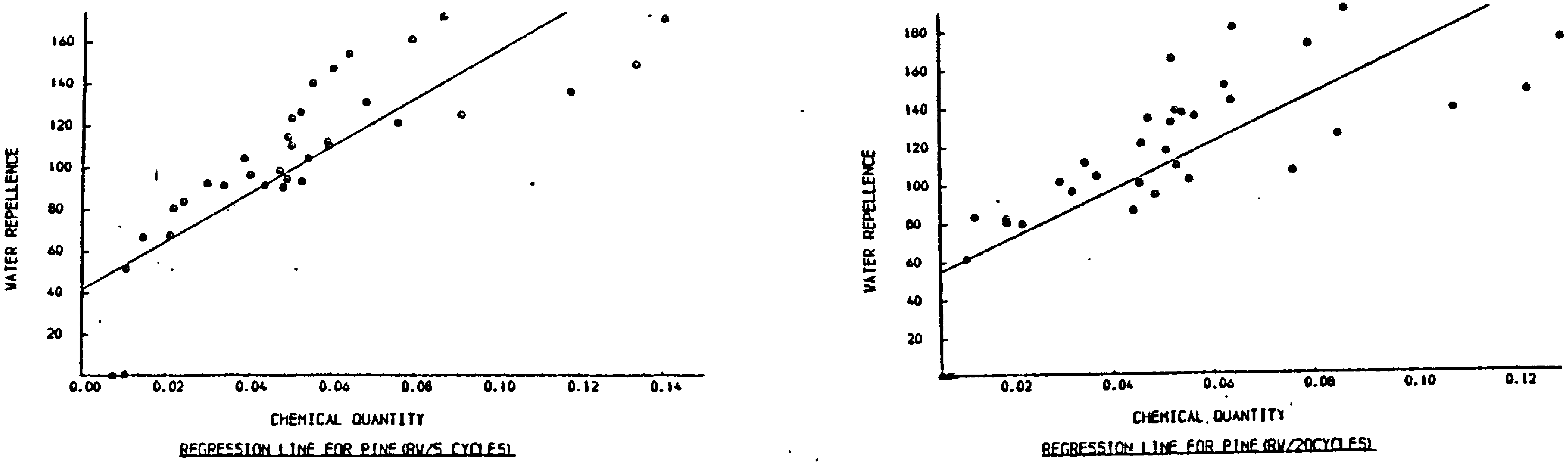
REGRESSION LINE FOR PINE (RESIN/20 CYCLES)

Figure 3.23 Scatter diagram of water repellency ($T_{\frac{1}{2}}$) and quantity of extracted water repellent(gm) in 10% resin treated Corsican pine specimens after various weathering cycles.



REGRESSION LINE FOR PINE (RV/0CYCLE)

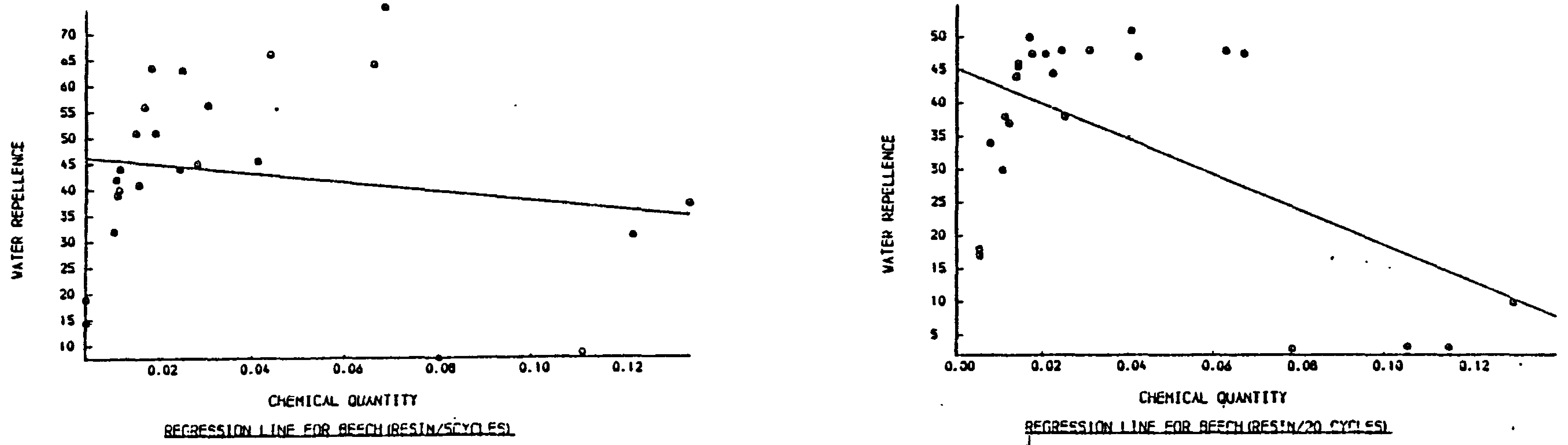
REGRESSION LINE FOR PINE (RV/10CYCLES)



REGRESSION LINE FOR PINE (RV/5 CYCLES)

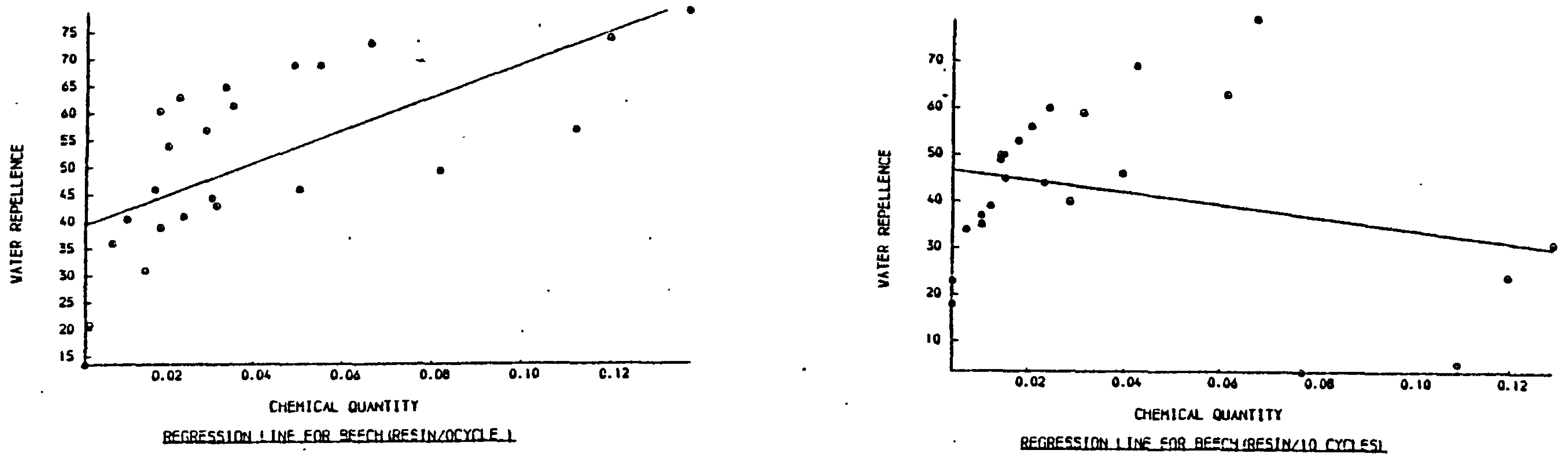
REGRESSION LINE FOR PINE (RV/20CYCLES)

Figure 3.24 Scatter diagram of water repellency ($T_{\frac{1}{2}}$) and quantity of extracted water repellents(gm) in 10% resin + 10% wax treated Corsican pine specimens after various weathering cycles.



REGRESSION LINE FOR BEECH (RESIN/5CYCLES)

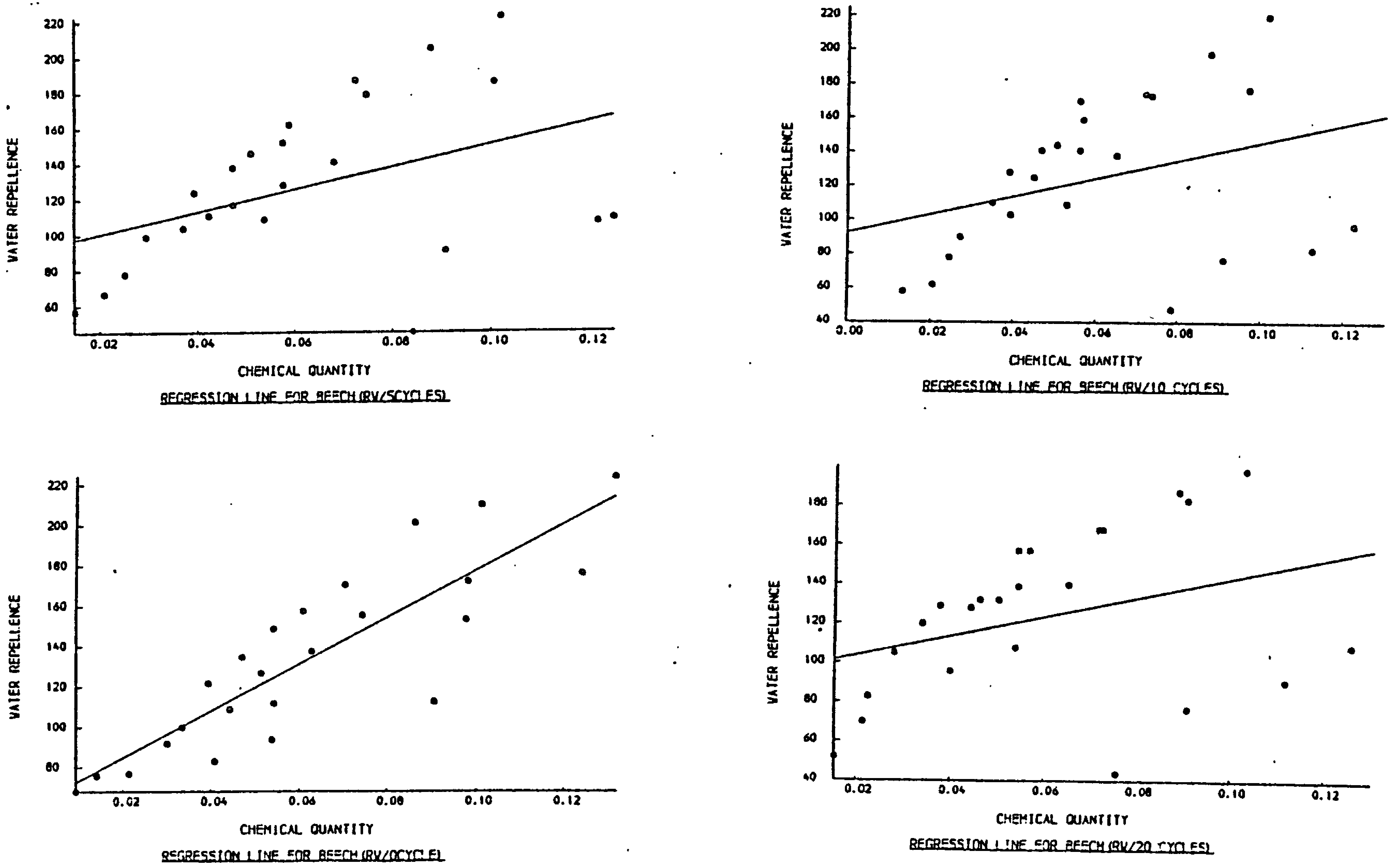
REGRESSION LINE FOR BEECH (RESIN/20 CYCLES)



REGRESSION LINE FOR BEECH (RESIN/0CYCLE)

REGRESSION LINE FOR BEECH (RESIN/10 CYCLES)

Figure 3.25 Scatter diagram of water repellency (T_1) and quantity of extracted water repellent(gm) in 10% resin treated European beech specimens after various weathering cycles.



REGRESSION LINE FOR BEECH (RV/5CYCLES)

REGRESSION LINE FOR BEECH (RV/10 CYCLES)

REGRESSION LINE FOR BEECH (RV/0CYCLE)

REGRESSION LINE FOR BEECH (RV/20 CYCLES)

Figure 3.26 Scatter diagram of water repellency (T_1) and quantity of extracted water repellents(gm) in 10% resin + 10% wax treated European beech specimens after various weathering cycles.

Table 3.13 Regression Data for Correlation Between the Quantity of Water Repellent Deposit and Water Repellent Efficiency ($T\frac{1}{2}$ or $T\frac{1}{4}$) in Variously Treated and Cycled Pine and Beech

Specimen	Water Repellent Solution	Weathering Cycles	Correlation Coefficient	Probability of Exceeding F	Regression Slope	Regression Constant
Pine	10% Resin	0	0.8588	0.0000*	100.16	4.545
		5	0.8553	0.0000*	117.11	3.402
		10	0.6979	0.0000*	88.89	3.758
		20	0.6781	0.0000*	87.66	4.029
	10% Resin + 10% Wax	0	0.8133	0.0000*	1036.30	47.595
		5	0.8155	0.0000*	1139.79	42.079
		10	0.8046	0.0000*	1268.00	41.423
		20	0.7764	0.0000*	1246.90	47.559
Beech	10% Resin	0	0.6710	0.0003*	303.98	38.697
		5	0.1876	0.3800^{n}	-88.10	46.550
		10	0.2667	0.2078^{n}	-134.35	47.228
		20	0.5883	0.0025*	-266.83	45.168
	10% Resin + 10% Wax	0	0.8635	0.0000*	1161.70	61.878
		5	0.4142	0.0442*	627.07	88.268
		10	0.3414	0.1026^{n}	533.56	92.627
		20	0.3459	0.0978^{n}	492.21	94.101

Table 3.13 continued:

Specimen	Water Repellent Solution	Weathering Cycles	Correlation Coefficient	Probability of Exceeding F	Regression Slope	Regression Constant
(Analysis with data pairs for first specimens omitted)						
Pine	10% Resin	0	0.9490	0.0000*	197.31	1.965
		5	0.8969	0.0000*	185.88	1.660
		10	0.8878	0.0000*	201.01	0.637
		20	0.9228	0.0000*	212.19	0.744
	10% Resin + 10% Wax	0	0.9100	0.0000*	2012.00	11.020
		5	0.9174	0.0000*	1969.90	12.300
		10	0.9305	0.0000*	2220.00	8.375
		20	0.9115	0.0000*	2168.00	17.357
Beech	10% Resin	0	0.7700	0.0001*	728.17	28.693
		5	0.7355	0.0002*	608.27	33.095
		10	0.8010	0.0000*	697.00	31.711
		20	0.5580	0.0106*	315.64	34.012
	10% Resin + 10% Wax	0	0.9208	0.0000*	1519.70	47.85
		5	0.9447	0.0000*	1741.40	40.94
		10	0.9344	0.0000*	1684.50	45.85
		20	0.9312	0.0000*	1533.50	52.22

Table 3.13 continued:

Specimen	Water Repellent Solution	Weathering Cycles	Correlation Coefficient	Probability of Exceeding F	Regression Slope	Regression Constant
		(Analysis for beech with first two specimens omitted)				
Beech	10% Resin	0	0.8302	0.0001*	1092.90	22.83
		5	0.7866	0.0003*	1145.10	25.68
		10	0.8778	0.0000*	1200.90	24.98
		20	0.7343	0.0012*	841.07	26.35
	10% Resin + 10% Wax	0	0.9381	0.0000*	1690.60	43.58
		5	0.9745	0.0000*	2054.00	30.42
		10	0.9664	0.0000*	1993.90	36.00
		20	0.9445	0.0000*	1769.70	44.99

$\bar{Y}$ = Reg. slope + Reg. coeff x X. * = p = 0.05, n = Nonsignificant.

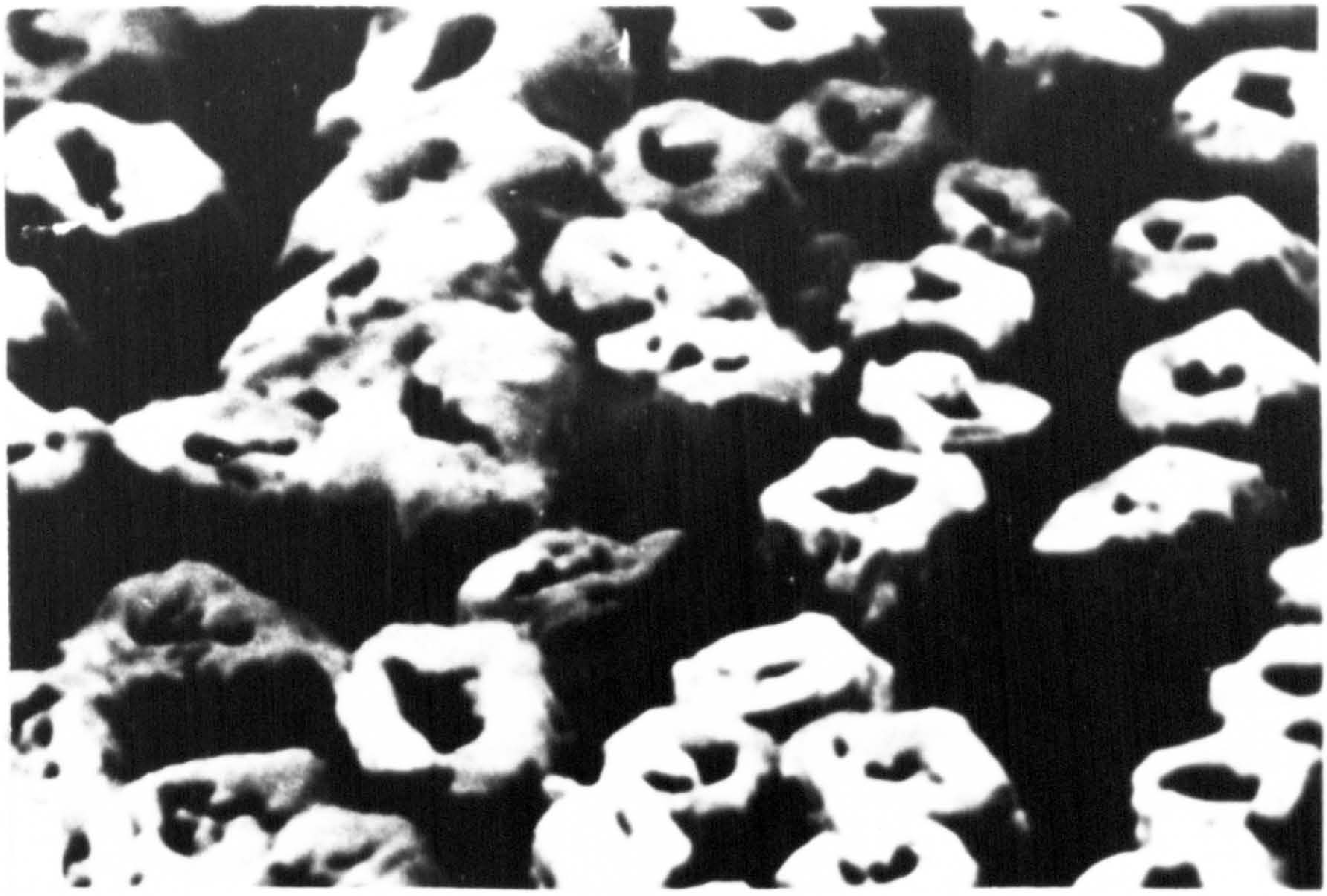


Figure 3.27 Exposed surface of a pine specimen treated with straight chain hydrocarbon resin and wax showing loss of intertracheid cell wall bond (560x; Voulgaridis, 1980).

significance. Excessive loss of effectiveness in the end specimen zone of variously treated beech compared to the loss of deposit yields absurd negative regression slope in cycled specimens.

Detailed study of the data (Tables 3.9 and 3.11, Section 3.4) show that the most significant change (decrease) in water repellency occurs in the outer centimetre or so of the long specimens (i.e. the zone represented by the outer 1 or 2 wafer specimens). It is also shown (Figures 3.17 and 3.19 to 3.21) that loss of water repellent deposit from this zone appears to be small, relative to the measured fall in water repellency. It seems likely, therefore, that the fall in goodness of fit of the data in the linear regression model is strongly associated with the marked loss of effectiveness in these outer zones. Consequently, regression analysis of the data were repeated, omitting the data pairs ("T¼ or T½" and "mass of deposit") relating to the outer zones. In the case of pine specimens just the outermost wafer data were omitted and for beech the data for the outermost one or two wafers. Details of this analysis are given in Table 3.13.

From the data of Table 3.13, it can be seen that by omitting the outer zone data, the regression parameters before and after exposure are quite similar. However, the slope of regression changes significantly as a result of the ommissions. Even in beech the correlation coefficients seem to change most with the omission of the first wafer specimen. Change from the omission of only the first wafer to two wafers is not as significant as the former. This means that the loss of water repellency is concentrated mostly in the first wafer zone. This supports the view that changes brought about by simulated weathering are restricted largely to this outer zone. This is probably due to either degradation of the surface cell walls leading to the provision of alternative water pathways as suggested by Voulgaridis, 1980 (Figure 3.27), or to loss of integrity between lumen surface and deposit in this zone, allowing capillary flow to occur in the gap so formed (Figure 3.6a).

PART 4

CHEMICALLY BONDED WATER REPELLENTS AFFECTING THE PERFORMANCE OF THE TREATED WOOD

The effectiveness of water repellent treatment is dependent on the nature of the wood pore system, the perfection of the water repellent deposit and the quality of the wood-deposit bond. The loss of water repellent effectiveness is thought to be mainly due to three factors:

1) Water repellent film displacement from the cell wall of treated wood due to preferential wetting.
2) Degradation of wood structure due to dimensional changes during wetting and drying periods.
3) Deterioration of the water repellent film due to movement in wood during wetting and drying.

Since the weak Van der Waal's forces bonding water repellent to wood are strongly affected by wetting and drying processes it is likely that exposure to wetting and drying may lead to detachment of the deposit from the cell wall. Covalent linkages between water repellent and cell wall, in addition to providing a superior bond may also block the water attracting OH group sites. It is believed that silanes and epoxides are able to react with hydroxyl groups in wood and that the products of the reactions give rise to hydrophobic properties (Gagliardi et al, 1966; McMillin, 1963; Schuerch, 1968; Varma and Bandyopadhyay, 1975).

4.1 Water repellent effectiveness in silanated wood

4.1.1 Mechanism of silanation

Silicon and carbon both belonging to the fourth group in the Periodic Table show similar chemical reactivity in many respects. Both are able to form a series of covalently bonded compounds, the bonds being directed towards the corners of a regular tetrahedron.

Silanes, corresponding to alkanes in organic chemistry, have an empirical formula $Si_n H_{2n+2}$. Each of the hydrogens in the silane molecule may be substituted by an electrophilic group, e.g. halogen or by methyl groups. The properties of the organochlorosilanes are dependent on the effects of silicon atoms, alkyl groups and halogen groups. Alkylchlorosilanes may be represented by the following general formula:

$$Si_n\,H_{(2n+2-y)}\,R_{(y-z)}\,Cl_3$$

where R = alkyl group i.e. $C_n\,H_{2n+1}$

'y' is an integer having values between 2 and 2n+2 , and

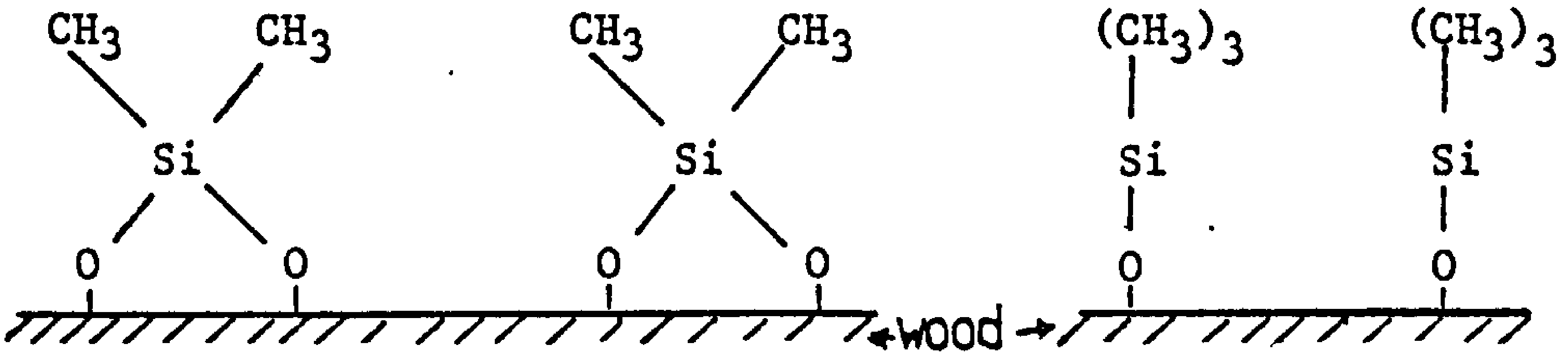
'z' is an integer having values between 1 and 2n+1

The reactivity of this series of compounds with wood varies with the length of the silicon chain, the nature of the alkyl group, the number of alkyl and chloro groups present and their position along the silicon chain. Generally, however, they react with hydroxyl groups in wood with the elimination of a proton:

$$ROH + R'_3\,SiCl \longrightarrow RO\text{-}SiR'_3 + HCl$$

where R is a polysaccharide residue and R' is an alkyl group

Preliminary experiments have shown that wood treated with the bifunctional substituted silane, dimethyl dichloro silane (DMDCS) has better water repellent properties than that treated with trimethylchlorosilane (TMCS). This maybe due to the cross-linking obtained with bifunctional groups:

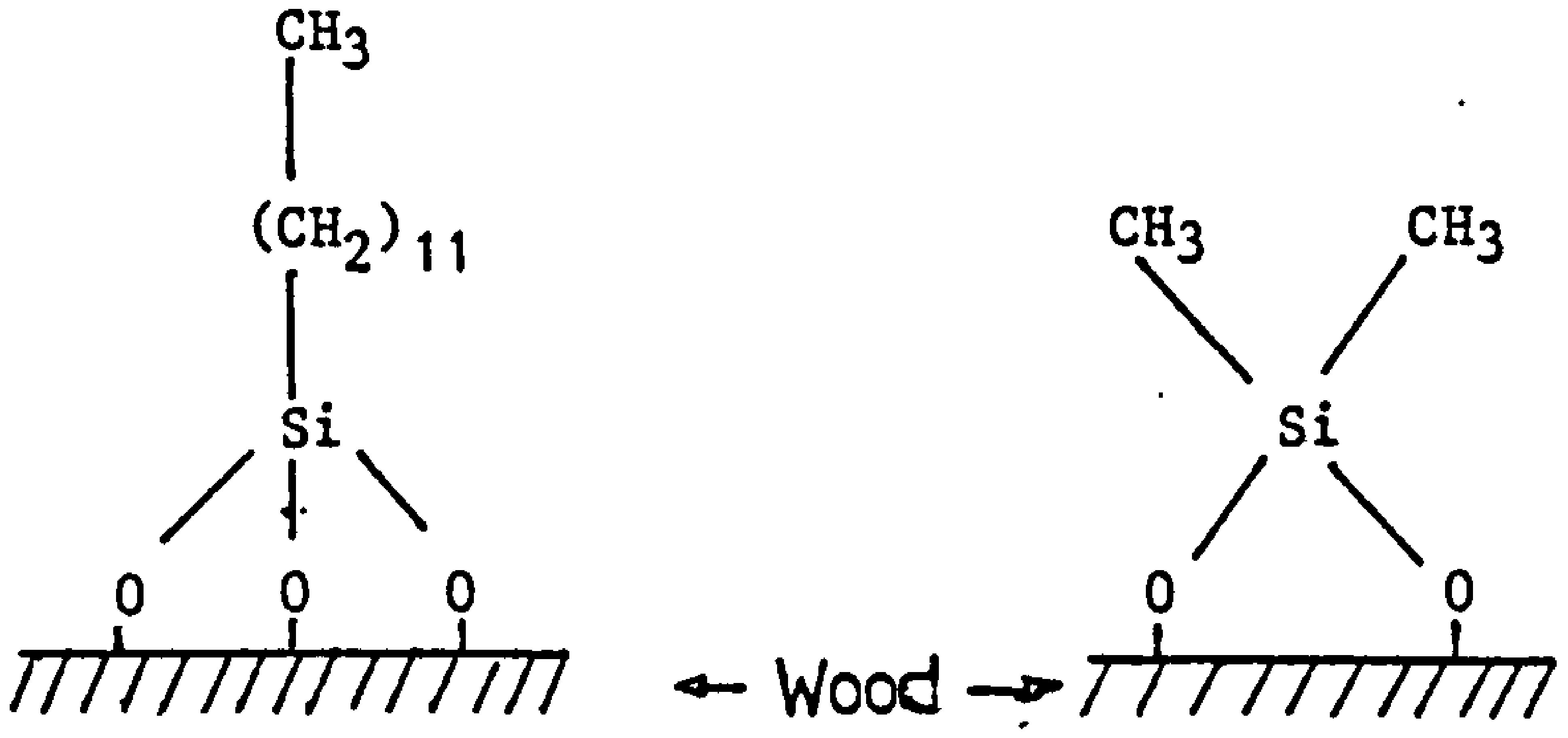


Cross-linked product

No cross-linking

Hypothetical wood silane reaction products

Reactions with n-dodecyl trichlorosilane (DDTCS) gave rise to a product slightly more water repellent than that formed with DMDCS. The effect may be due to the greater cross-linking as well as the presence of a more hydrophobic longer chain hydrocarbon, which surpass the benefit of the greater number of alkyl groups per substituted hydroxyl group in wood:



n-dodecyl product Dimethyl dichloro product

In this study vapour phase reactions have been carried out with DMDCS. Liquid phase reactions have involved the use of both DDTCS and DMDCS. Thus a reasonably broad range of silane characteristics has been investigated. In view of the many factors likely to influence reactivity and product performance, however, it is most likely that other reaction systems will give rise to somewhat different results.

Apart from the reactions between wood hydroxyl groups and chlorosilanes outlined (Schuyten et al, 1948) it is believed that resistance to water uptake by silane treatment may result from two alternative mechanisms.

i. Silanes may react with moisture in wood to form siloxanes which remain as a coating on cell surfaces. Such coatings are insoluble in water and common organic solvents (Rochow, 1951).

ii. In addition to attaching hydrophobic alkyl groups to wood polymer surfaces, the silyl groups replace hydroxyl groups and hence reduce the tendency for wood-water hydrogen bonds to be formed.

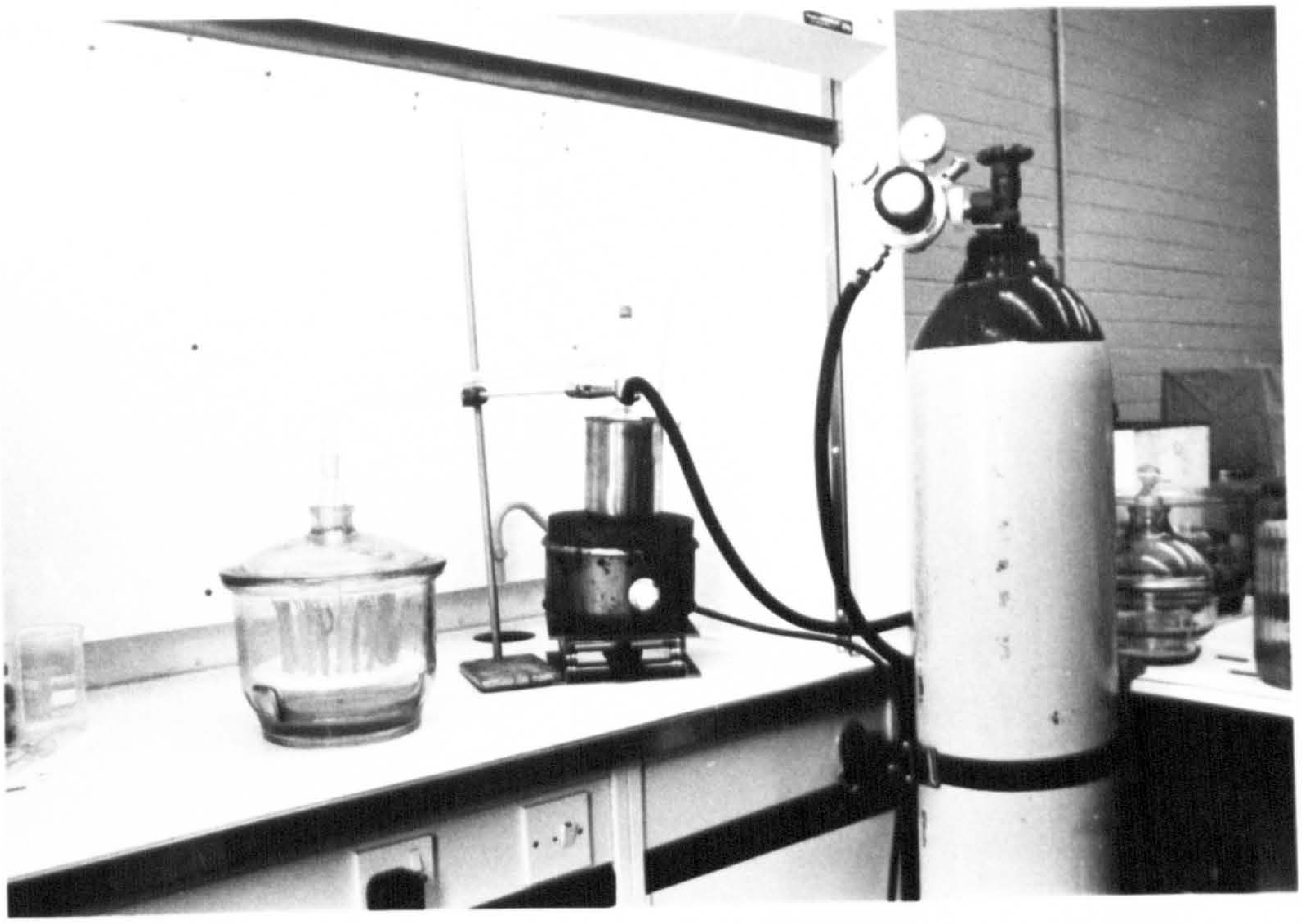


Figure 4.1. Experimental apparatus for silanation reaction with thin microtome specimens in the vapour phase in nitrogen atmosphere.

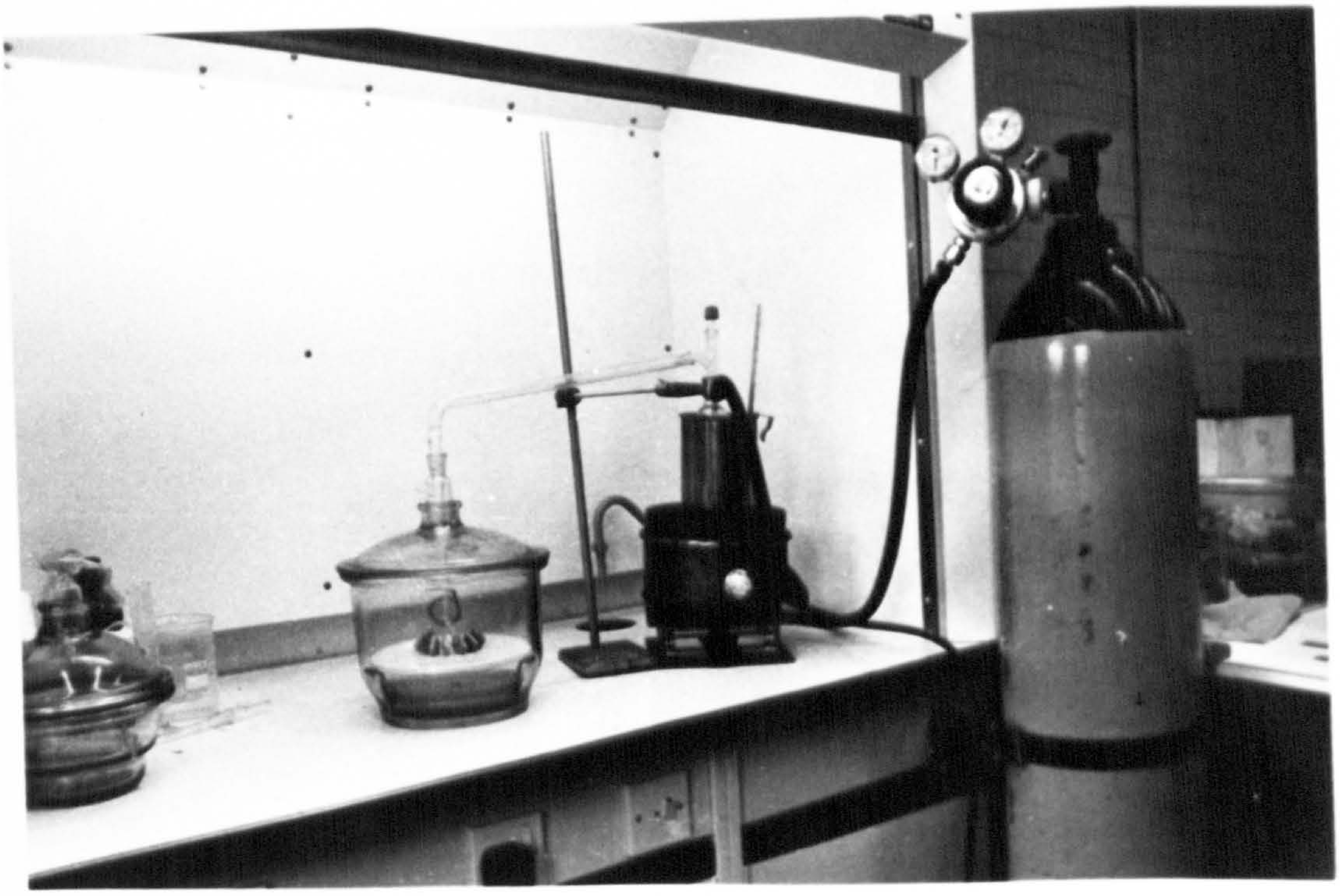


Figure 4.2. Silanation of wafer specimens by vapour phase.

4.1.2 Durability of chloro-silanation treatments in wood

4.1.2.1 Experimental procedure

Nominal 100 micron thick, 1cm wide and 10cm long radial/longitudinal microtome sections were cut from pre-soaked Corsican pine blocks. The specimens were conditioned at 20°C and 65% RH under light pressure for 7 days and were then dried over P_2O_5. The weighed specimens were treated with DMDCS (i) in the vapour phase and (ii) in the liquid phase. In the vapour phase reactions the microtome sections were kept in the vertical position in a desiccator reaction vessel with the help of a perforated porcelain platform. The silane was vapourized at 70°C in a round bottomed flask, fitted with nitrogen tube, thermometer and a side outlet tube, over an oil bath. The vapour was blown into the reaction vessel by nitrogen gas through a bent tube fitted to the ground glass connectors of the flask and the vessel (see Figure 4.1).

The liquid phase treatments were carried out using 5ml DMDCS dissolved in 50ml CCl_4 to treat 20 microtomed specimens. Nitrogen gas was bubbled through the liquid in the reaction vessel to carry away HCl gas. The reaction was allowed to proceed for 10 minutes.

Separate sets of weighed specimens were leached in running deionized water for 24 hours. These were then manipulated and treated in the same way as the unleached specimens. After silane treatment all the specimens were leached with flowing deionized water for 24 hours at ambient temperature.

4.1.2.2 Results and Discussion

The results of the above treatment and leaching experiments are given in Table 4.1.

Prior to any treatment the specimens were dried over P_2O_5, hence it is unlikely that significant quantities of siloxane polymer could be formed. Neither the silyl-cellulose formed by the reactions nor minor quantities of any siloxanes formed are likely to be leached by the cold water wash.

Table 4.1 Persistence of silanation in Corsican pine strips (20 specimens)

Pre-treatment leaching	Mode of silanation (DMDCS)	Weight loss/gain ± standard deviation, % Loss on initial leaching	Gain on silanation over initial wt.	Gain over 1st leached wt.	Loss on leaching based on silanated wt.	Retention after leaching. % of initial wt.	Retention based on 1st leached wt.
No	Vapour phase	-	31.7 (4.5)	-	4.7 (1.9)	25.5	-
No	Liquid phase	-	2.4 (0.5)	-	0.7 (0.3)	1.7	-
Yes	Vapour phase	3.8 (0.2)	27.9 (2.1)	34.1 (2.0)	4.0 (0.6)	22.8	27.6
Yes	Liquid phase	3.4 (0.2)	1.1 (0.3)	4.6 (0.4)	1.9 (0.2)	-0.9	2.6

Much greater weight gain was obtained by the vapour phase compared to liquid phase treatments and a high proportion of this weight increase achieved by both methods of treatment appears to be resistant to the action of water leaching. Of the weight loss which does occur, a proportion is probably wood breakdown products produced by the action of HCl released as a by-product of the silanation reaction. Hence, it seems likely that the primary products of silanation may be quite resistant to the effects of water.

4.1.3 Initial liquid and vapour phase reactions

Silanation reaction of wood specimens can be carried out either in the liquid or in the vapour phase (Varma et al, 1973; Marian and Stumbo, 1962). For comparing the relative merits of these two processes experiments were designed to treat 6mm thick transverse wafer specimens (2x2cm in the radial and tangential directions) of

Corsican pine with DMDCS.

In the liquid phase reaction 8 wafer specimens dried to constant weight over P_2O_5 were treated for 15 minutes in a solution of 5ml DMDCS in 15ml dimethyl formamide (DMF) as acid acceptor and 100ml CCl_4 solvent. The specimens were kept immersed and the solution was swirled at room temperature. After the reaction the specimens were kept in ammonia atmosphere for 5 minutes to ensure neutralization of any remaining HCl. They were then rinsed with water to remove any superficial NH_4Cl and then washed in acetone and dried at 70°C for 2 hours, before being equilibrated to constant weight at 20°C and 65% RH.

In the vapour phase reaction 8 wafer specimens, similar to those described above, were first pretreated with DMF and dried at 70°C for 4 hours. Some weight gain occured due to retention of DMF. The specimens were then put in a desiccator reaction vessel and connected to a source of DMDCS vapour in the apparatus shown in Figure 4.2. The chlorosilane was vaporized at 70°C over an oil bath. Dry N_2 gas was bubbled through the silane at a rate of approximately 5 bubbles per second. The vaporized silane was carried by the N_2 gas into the reaction vessel through the side tube. Another tube fitted to the ground glass stopper of the reaction vessel allowed the escape of excess gases. The reaction was allowed to continue for 10 minutes. After reaction the specimens were manipulated in the same way as in the case of those treated by liquid phase reaction.

The degree of silanation achieved and water repellent effectiveness data for these initial liquid and vapour phase reactions are given below in Tables 4.2 and 4.3 respectively.

From the data of Tables 4.2 and 4.3 it can be seen that the degree of substitution (weight gain) achieved by the two types of reaction are broadly similar. The initial water repellent effectiveness expressed as time to half swell ($T_{\frac{1}{2}}$) and the degree of stabilization achieved are also similar for specimens treated in the two ways.

Table 4.2 Liquid phase silanation

Specimens	Wt. gain on silanation (Std. deviation) % of dry unreacted wt.	$T_{\frac{1}{2}}$ (standard deviation) min.	Maximum Equilibrium swelling (mm)
Control	-	1.0	1.20
Treated	2.2(0.2)	71.4(3.4)	0.87 (72.5% of control)

Table 4.3 Vapour phase silanation

Specimens	Wt. increase on DMF treatment ± standard deviation (%)	Wt. increase on silanation over pre-treated wt. ± standard dev. (%)	$T_{\frac{1}{2}}$ (stand. dev.) (min.)	Maximum swelling (mm)
Control	-	-	1.1	1.31
Treated	2.3(0.03)	3.6(0.3)	75.7 (1.8)	0.98 75% of control

4.1.3.1 Reaction variables affecting silanation of wood

The silanes were found to react readily with wood specimens. In the liquid phase reaction it was observed that increase in temperature had no practical effect on the reaction. That is, in the time allowed (15 minutes) the reaction appeared to have proceeded to near completion even at room temperature. In vapour phase reaction the silane was vaporized at a temperature approximating the boiling point of the silane and carried over to the reaction vessel (maintained at room temperature) with the help of N_2 gas. No recognizable difference in the degree of reaction was observed when the reaction vessel was maintained at 70°C. It seems that fast room temperature reactions are possible and that they yield high water repellency. This is in agreement with the work reported by Gagliardi et al, 1966).

To study the effect of reaction time 2ml of silane and six wafer specimens of Corsican pine wood were used in both reaction phases. In the vapour phase reaction silane vapour was blown to the reaction vessel by N_2 gas for 5, 10, 15 and 30 minutes. The silane was entirely vapourized within the first 2-3 minutes. No significant increase in the gain in weight was observed over the reaction period of 5-30 minutes. In the liquid phase reaction the silane was dissolved in 100ml CCl_4 and N_2 gas was bubbled through the solution. The reaction was allowed to proceed for 5, 15, 30 and 60 minutes. Here a slight increase in weight gain was observed over the 5 to 15-30 minute period, but no further gain in weight was achieved by reaction beyond this time (Table 4.4).

Table 4.4 Effect of time on silanation reaction

Reaction phase	Reaction period (minutes)	Gain in wt. (mean of 6 specimens) ± standard deviation (%)
Liquid	5	0.88 (0.11)
	15	0.98 (0.17)
	30	1.07 (0.31)
	60	1.05 (0.23)
Vapour	5	1.35 (0.20)
	10	1.26 (0.16)
	15	1.40 (0.22)
	30	1.32 (0.24)

With the small amount of silane involved it seems that reactions are near completion after even 5 minutes or so of reaction time.

Unlike temperature or time, the wood to silane ratio affected the reaction to a marked extent. Liquid phase reaction was carried out with sets of 8 wafer specimens as described in Section 4.1.3 using DMDCS and DDTCS as the silanating agents. Reactions were carried out using 2 and 10ml quantities of the chlorosilanes dispersed in carbon tetrachloride. In the case of DMDCS treatment 15ml of DMF was used in one set of experiments in addition to the silane and solvent. The vapour phase reaction was carried out with DMDCS as described in Section 4.1.3 with the exception that in one set no DMF (acid acceptor) pretreatment was incorporated, using 2 and 10ml quantities of the chlorosilanes. In both liquid and vapour phase treatments, reactions were carried out for 5 minutes while N_2 was blownor bubbled through the reactants. Weight gains and water repellent effectiveness resulting from these reactions are given in Table 4.5.

Table 4.5 The effects of acid acceptor and silane concentration in the reaction mixture

Reaction phase	Silane used (ml)	DMF	Wt. gain ± stand dev. (%)	$T_{\frac{1}{2}}$ stand. dev. (min)
Vapour	DMDCS 2	-	1.7 (0.3)	51.4 (2.5)
Vapour	DMDCS 10	-	6.4 (1.2)	102.0 (3.6)
Vapour	DMDCS 2	Pre-treated	1.1 (0.2)*	46.0 (4.0)
Vapour	DMDCS 10	Pre-treated	5.4 (1.1)*	78.5 (3.0)
Liquid	DMDCS 2	-	1.4 (0.2)	45.5 (1.4)
Liquid	DMDCS 10	-	5.1 (0.3)	80.3 (2.8)
Liquid	DMDCS 2	15 ml	2.3 (0.6)	44.0 (5.6)
Liquid	DMDCS 10	15 ml	6.8 (0.6)	82.7 (7.9)
Liquid	DDTCS 2	-	1.5 (0.3)	65.0 (5.3)
Liquid	DDTCS 10	-	4.8 (0.3)	139.0(12.0)

* Over pretreated weight

N.B. In all subsequent work the acid acceptor DMF was omitted from the reactant mixture. This was for the following reasons:

1) No significant improvement in the degree of reaction was observed by its use.

2) Because of difficulty in removing DMF residues it was difficult to be certain to what extent observed weight increase and water repellent effects might be due to its presence, rather than to the presence of silanation products.

3) Provided the specimens were neutralized immediately after the reaction with a mild alkali (NH_4OH or Na_2CO_3), it was found that the use of DMF led to little reduction in wood degrade caused by silanation under the conditions used.

From the data of Table 4.5 it seems that increased weight gain and corresponding better water repellency is obtained with increase in the amount of reacting silane. It seems that the vapour phase reaction yields slightly better results. The longer alkyl chain substituted silane seems to be a little less reactive than the DMDCS. However, somewhat better water repellency is achieved with this longer chain compound.

Using the larger quantity (10 ml) of silane it was observed that significant further weight gain could be achieved by extended reaction periods. However, such an extension seemed to cause considerable degrade to the wood specimens. Hence, reactions for longer periods were not used.

4.1.4 Long term water repellent effectiveness of chlorosilanated wood

4.1.4.1 Experimental procedure

Cross-sectional wafer specimens, 6mm thick and 20x20mm cross section (with two edge faces radial and two tangential) were treated in both the liquid and vapour phases with dimethyl dichlorosilane (DMDCS). Similar specimens were treated in the liquid phase only, with n-dodecyl trichlorosilane (DDTCS). To give an idea of the variability of any effects produced, for the DMDCS treatments, 5 batches each containing 10 specimens were treated by both the vapour and liquid phase methods. Three batches of 10 specimens were treated with DDTCS. For each batch 5 ml of the appropriate chlorosilane was used in the reaction. In the case of the liquid phase treatments this was dissolved in 50ml carbon tetrachloride (CCl_4). Reactions were carried out exactly as described earlier (Section 4.1.3). After reaction, the specimens were immersed for a period in a mild alkali (Na_2CO_3 solution) to neutralize any HCl produced in the reactions. They were then thoroughly washed with water and dried first at (70°C) in an oven then in a desiccator over P_2O_5. Weight gain resulting from the silane treatment was recorded.

The contact angle made by water drops on transverse faces of the wafers treated with DMDCS was measured using the sessile drop technique described earlier (Sections 1.5.1.1 and 3.6).

Subsequently, these specimens were redried over P_2O_5. The water repellency of these and the specimens treated with DDTCS was then assessed by measuring their times to half swell ($T_{\frac{1}{2}}$), (see Sections 2.3.1 and 3.4). Maximum equilibrium swelling was estimated by keeping the specimens immersed for 12 hours.

After $T_{\frac{1}{2}}$ estimation, all specimens were again dried first at 70°C and then over P_2O_5 and rate of water sorption measurements were conducted with them, using the techniques described in Section 2.4. This series of tests was repeated on all the specimens after subjecting them to 5, 10 and 20 cycles of simulated weathering as described in Sections 2.2.4 and 3.2.3.

4.1.4.2 Results and discussion

From Table 4.5 below it can be seen that the silanation reactions are reasonably reproducible under the reaction conditions specified.

Contact angle measurements are given in Table 4.7. They showed no between batch variation, hence no attempt is made to show the results in batches.

Table 4.6 Weight percent gain (WPG) in different batches due to silanation

Silane Used	Reaction Phase	Batch No.	WPG ± Standard deviation
DMDCS	Liquid	1	4.13 (.28)
DMDCS	Liquid	2	3.51 (.45)
DMDCS	Liquid	3	5.47 (.42)
DMDCS	Liquid	4	4.82 (.52)
DMDCS	Liquid	5	4.37 (.38)
		Mean	4.46 (.66)
DMDCS	Vapour	1	4.26 (.09)
DMDCS	Vapour	2	6.16 (.17)
DMDCS	Vapour	3	4.88 (.28)
DMDCS	Vapour	4	5.76 (.37)
DMDCS	Vapour	5	5.63 (.22)
		Mean	5.34 (.68)
DDTCS	Liquid	1	3.77 (.34)
DDTCS	Liquid	2	4.48 (.36)
DDTCS	Liquid	3	4.22 (.25)
		Mean	4.16 (.29)

Table 4.7 Contact angles of DMDCS treated and weathered specimens (mean of 50 specimens)

Reaction Phase	Contact angle, degrees							
	Number of simulated weathering cycles							
	0		5		10		20	
	MEAN	RANGE	MEAN	RANGE	MEAN	RANGE	MEAN	RANGE
Liquid	123	120-127	120	115-124	118	116-121	120	116-122
Vapour	120	117-123	118	115-120	116	114-118	118	116-120

The specimens prepared by sawing were used in silanation treatments without further sanding or finishing. The very high contact angles monitored initially probably results in part as a consequence of this surface roughness (See Section 1.5.1.1). Interestingly, no marked decrease in contact angle is seen to result from simulated weathering for 5, 10 or 20 cycles. The reason is not fully established, but it seems possible that it may be associated with the fact that the hydrophobe is covalently bonded to the cell wall. Thus, in contrast to weakly bonded conventional water repellent deposits, mechanical stress arising from wetting and drying is unlikely to shear off the water repellents. Moreover, siloxane polymers formed due to any breaking of the wood-silane bond might compensate for any loss of contact angle due to superficial weathering effects.

Time to half swell ($T_{\frac{1}{2}}$) and maximum equilibrium swelling (MES) data monitored at 0,5,10 and 20 cycles are recorded in Table 4.8. The time to half swell of the treated specimens indicates that a high degree of water repellency is imparted before cycling, especially in DDTCS treated specimens. Simulated weathering for 5, 10 and 20 cycles led to a gradual decrease in the $T_{\frac{1}{2}}$ values in the case of DMDCS treated specimens. However, it is noteworthy that with a conventional water repellent, exposure of wafers to 20 similar simulated weathering cycles usually leads to a fall in $T_{\frac{1}{2}}$ to values around 10 minutes or so. It is suggested that the observed gradual decrease in $T_{\frac{1}{2}}$ occuring during simulated weathering may be the results of checks developing and allowing water to gain access by capillaries not treated with silane.

Table 4.8 Time to half swell and maximum equilibrium swelling of treated specimens

Each value is mean of 50 specimens for DMDCS and 30 specimens for DDTCS.

Treatment	Time to half swell ± standard deviation, minutes and mean MES (% of control)							
	0 cycle		5 cycle		10 cycle		20 cycle	
	$T_{\frac{1}{2}}$	MES	$T_{\frac{1}{2}}$	MES	$T_{\frac{1}{2}}$	MES	$T_{\frac{1}{2}}$	MES
Control	1.1 (0.1)	100						
DMDCS Liq. phase	80.3 (8.0)	80	73.3 (13.0)	84	62.1 (13.5)	85	47.2 (12.3)	87.3
DMDCS Vap. phase	89.8 (6.9)	80	78.4 (14.3)	83.3	63.3 (12.9)	85	37.7 (9.4)	85.3
DDTCS Liq. phase	122 (14)	60.6	97 (8)	66.3	84 (7)	66.3	84.5 (8.6)	66.9

Table 4.9 Rates of water absorption of silanated wafer specimens subjected to cyclic wetting and drying (50 replicates for DMDCS and 30 for DDTCS treated and 6 for control specimens)

Treating silane and phase	No. of cycles	Water absorption (1 standard deviation) % of wood wt.								
		Time of soaking (minutes)								
		1	3	5	10	20	30	40	50	60
Untreated	0	53.8 (1.3)	62.4 (1.4)	67.1 (1.3)	72.8 (1.5)	75.5 (1.8)	80.6 (1.6)	82.6 (1.4)	84.2 (1.1)	86.2 (1.2)
DMDCS (Liq)	0			2.54 (.20)	4.42 (.26)	6.03 (.35)	7.93 (.65)	9.15 (.61)	10.66 (.76)	11.87 (.64)
	5			3.58 (.20)	5.36 (.35)	7.49 (.27)	9.32 (.22)	10.62 (.23)	11.30 (.31)	12.32 (.30)
	10			4.43 (.38)	5.80 (.53)	8.57 (.65)	10.62 (.58)	11.91 (.61)	13.14 (.78)	13.36 (.74)
	20			4.47 (.76)	6.28 (.36)	9.27 (.77)	11.14 (.60)	12.62 (.74)	13.94 (.80)	15.06 (.57)
DMDCS (Vap)	0			2.63 (.26)	4.58 (.48)	7.16 (.48)	9.25 (.36)	10.31 (.49)	12.05 (.66)	13.03 (.53)
	5			3.30 (.32)	5.33 (.42)	7.34 (.38)	9.91 (.50)	11.22 (.58)	12.19 (.64)	13.66 (.68)
	10			3.43 (.34)	4.58 (.30)	6.68 (.24)	9.97 (.33)	11.82 (.79)	13.68 (1.74)	15.99 (2.38)
	20			3.41 (.28)	4.40 (.37)	7.76 (.34)	10.74 (.65)	13.00 (1.03)	14.92 (1.52)	16.32 (2.06
DDTCS (Liq)	0	0.36 (.30)	0.86 (.17)	1.42 (.50)	2.40 (.35)	4.61 (.30)	5.54 (.37)	6.78 (.36)	7.50 (.20)	8.32 (.31)
	5	0.67 (.13)	1.77 (.44)	3.11 (.30)	4.03 (.30)	5.70 (.27)	7.00 (.32)	7.98 (.28)	9.34 (.28)	9.82 (.34)
	10	1.43 (.45)	2.24 (.44)	3.79 (.46)	5.34 (.20)	7.46 (.45)	8.58 (.39)	9.64 (.29)	10.69 (.36)	11.44 (.32)
	20	1.04 (.34)	2.02 (.28)	3.19 (.36)	4.79 (.39)	6.81 (.29)	7.66 (.33)	8.53 (.33)	9.33 (.36)	10.55 (.37)

In DDTCS treated specimens the decrease is less marked and seems to occur only over the first 10 cycles.

DMDCS treatment leads to about 20% reduction in maximum equilibrium swelling compared to the control, whereas, about 40% reduction results from DDTCS treatment. It seems that the latter may restrict swelling more due to either a greater degree of cross-linking due to its tri-functionality or to its greater bulk or a combination of both effects. Better water repellency may result due to the presence of the larger hydrophobic group (see Section 4.1.2.1) in spite of the small gain in weight achieved compared to that with DMDCS. A small increase in M.E.S. was observed in DDTCS treated specimens on weathering for 5 cycles. Thereafter MES does not seem to be affected at all on further cycling. The initial small increase may be due to the removal of small quantities of non-bonded reaction products from the cell wall capillaries.

Water sorption results are given in Table 4.9. From the results it is evident that quite small variance is associated with the performance achieved with any treatment. It is further evident from the results that better water repellency is imparted by the longer alkyl chain silane (DDTCS) than the one with shorter chain (DMDCS). This is in line with the contact angle and $T_{\frac{1}{2}}$ results reported above. A gradual deterioration in water repellency can be seen to occur as weathering proceeds. Again, this is in line with the $T_{\frac{1}{2}}$ data. Incease in the rate of water sorption is, however, very modest and significant water repellent effectiveness is retained by all the treated specimens even after 20 cycles of simulated weathering.

The modest fall off in performance observed seems to occur during the first 10 cycles. Indeed, between 10 and 20 cycles, in some cases, some improvement in performance can be seen. It is difficult to account for this effect, but the low variance associated with the data suggests that it is a real one.

In comparison with untreated control specimens it is clear that silanation gives rise to significant water repellency in wood, judged by contact angle, rate of swelling and rate of water sorption. Furthermore, the effect produced seems to be quite persistent in comparison to that given by conventional resin/wax treatments (at about the 10% resin and 1% wax level), see for example, Voulgaridis and Banks, 1980. Hence it seems that covalent bonding of hydrophobes onto wood may offer advantages in the long term to control of water uptake.

4.1.5 Effect of chloro-silanation on the water repellency of long specimens

To investigate the depth of treatment attained with silanes and the performance achieved under conditions approximating service conditions, 2x2cm cross-sectional x 15cm long specimens of Corsican pine coated on all but one transverse face (see Section 2.2.2) were used.

4.1.5.1 Experimental procedure

The specimens were equilibrated to constant weight at 65% RH and 20°C. 24 specimens were treated by both liquid and vapour phase reactions. In the liquid phase 6 specimens were treated in each batch with 15ml DMDCS in 300ml CCl_4 for 15 minutes. In the vapour phase 5ml DMDCS was vapourized and blown with N_2 gas into the reaction vessel (see Section 4.1.2.1) holding 8 specimens, for 10 minutes. After reaction all the specimens were neutralized with dilute Na_2CO_3 solution, washed thoroughly with deionized water and then dried and equilibrated to constant weight at 65% RH and 20°C. Then batches of 4 sticks from each treatment were exposed to simulated weathering for 0, 5, 10 or 20 cycles and again dried and equilibrated as above. Rate of water absorption by these specimens was monitored as described in Section 2.2.4.2. They were then reconditioned (20°C, 65% RH) and cross-sectional wafer specimens (0.6cm thick) were cut serially from the treated ends. To evaluate the water repellency of these wafers, time to half swell ($T_{\frac{1}{2}}$) was measured using the technique described in Section 2.3.1.

Table 4.10 Rate of water absorption of control and DMDCS treated long specimens after various periods of simulated weathering (6 replicates)

No. of cycles	Soaking time (minutes) and water absorption (±stand. dev.) % of conditioned wt.											
	2	5	10	15	30	45	60	75	90	105	120	720
						UNTREATED CONTROL						
0	1.9 (0.1)	3.2 (0.2)	4.6 (0.3)	5.8 (0.4)	8.1 (0.5)	10.0 (0.6)	11.5 (0.7)	12.9 (0.8)	14.1 (0.9)	15.2 (0.9)	16.1 (0.9)	28.0 (2.0)
						LIQUID PHASE TREATMENT						
0	0.10 (0.04)	0.18 (0.02)	0.24 (0.02)	0.28 (0.03)	0.42 (0.04)	0.51 (0.05)	0.60 (0.04)	0.78 (0.08)	0.88 (0.12)	0.99 (0.15)	1.11 (0.16)	4.65 (1.18)
5	0.23 (0.08)	0.48 (0.18)	0.74 (0.23)	0.98 (0.24)	1.38 (0.33)	1.81 (0.39)	2.24 (0.41)	2.61 (0.47)	3.02 (0.50)	3.42 (0.56)	3.77 (0.60)	8.07 (0.85)
10	0.69 (0.13)	1.04 (0.20)	1.46 (0.28)	1.74 (0.30)	2.22 (0.30)	2.68 (0.29)	3.07 (0.38)	3.55 (0.39)	4.00 (0.57)	4.33 (0.63)	4.65 (0.51)	8.89 (1.12)
20	0.80 (0.30)	1.26 (0.28)	1.84 (0.39)	2.66 (0.41)	3.43 (0.48)	4.00 (0.32)	4.51 (0.53)	5.02 (0.38)	5.58 (0.66)	6.39 (0.71)	7.77 (0.89)	9.76 (1.14)
						VAPOUR PHASE TREATMENT						
0	0.02 (0.01)	0.04 (0.02)	0.08 (0.03)	0.15 (0.04)	0.18 (0.06)	0.28 (0.08)	0.32 (0.11)	0.38 (0.13)	0.43 (0.10)	0.50 (0.12)	0.55 (0.11)	3.07 (0.66)
5	0.31 (0.12)	0.50 (0.15)	0.73 (0.20)	1.14 (0.18)	1.59 (0.15)	1.92 (0.32)	2.66 (0.43)	3.36 (0.48)	3.86 (0.52)	4.46 (0.61)	5.05 (0.44)	10.77 (1.02)
10	0.39 (0.08)	0.74 (0.13)	1.36 (0.12)	1.81 (0.11)	2.79 (0.18)	3.67 (0.26)	4.43 (0.32)	5.13 (0.44)	5.89 (0.47)	6.49 (0.61)	7.06 (0.82)	13.05 (1.10)
20	0.43 (0.09)	0.71 (0.14)	1.43 (0.32)	2.66 (0.38)	4.08 (0.62)	6.30 (0.80)	7.52 (0.68)	8.68 (1.06)	9.59 (1.20)	10.35 (1.46)	11.01 (1.53)	17.45 (2.08)

4.1.5.2 Results and discussion

Water absorption data for the long sticks are given in Table 4.10. It can be seen that in pine, silanation leads to a marked reduction in the rate of water uptake. Over the first 5-10 cycles of simulated weathering, a marked increase in water sorption rate is observed. Visual inspection of the specimens showed that checks developed in the treated end surfaces over this period. It is believed that this creates non-hydrophobic pores allowing the observed increase in the rate of sorption to occur. Further cycling gave rise to little observable increase in the degree of checking and it can be seen from Table 4.10 that little further general increase in sorption rate occurs, particularly in the specimens trated in the vapour phase.

From Table 4.10 it can also be seen that the initial rate of water uptake (over about the first 30-60 minutes of the soak period) is broadly similar for both vapour and liquid phase treatments. This is so for all periods of exposure. Thereafter, up to 12 hours, the liquid phase treatment appears to perform rather better than the vapour phase treatment. It may be that this is associated with a rather deeper hydrophobic layer being produced by liquid phase treatment. Hence, in liquid phase treated blocks the water front must advance further before it encounters non-hydrophobic surfaces allowing rapid liquid penetration.

Water-repellency data ($T_{\frac{1}{2}}$ values) for wafer specimens cut from the treated ends of the long sticks are cited in Table 4.11. The data show that before exposure to the weathering cycles the liquid phase treatment gives rise to a greater degree of water repellency than corresponding vapour phase treatments. Even after 20 simulated weathering cycles detectable water repellent effect is present to a depth >5cm. With the vapour phase treatments, however, after simulated weathering the $T_{\frac{1}{2}}$ values measured fall towards control values at depths beyond 1-2cm. This supports the idea, suggested above, that the better performance of liquid phase treated specimens is associated with increased treatment at greater depth.

Table 4.11 **Swelling measurement of wafers cut from DMDCS treated long specimens (coated on all but one transverse face**

Liquid phase reaction

No. of cycles	Time to half swell of treated specimens (min)*						
	Specimen nos. and depth of treatment (mm) from treated end						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
0	104.3 (11.8)	27.0 (3.7)	5.9 (1.4)	3.8 (1.4)	3.6 (0.8)	3.3 (1.3)	3.2 (1.0)
5	23.8 (6.04)	8.6 (1.2)	4.7 (1.7)	3.3 (0.90)	3.0 (0.80)	2.2 (0.30)	2.5 (0.25)
10	16.75 (4.4)	6.25 (0.88)	3.8 (0.70)	4.0 (0.92)	4.0 (0.50)	3.5 (0.62)	2.3 (0.38)
20	14.3 (3.0)	5.5 (1.7)	3.25 (0.25)	3.5 (0.86)	3.3 (0.35)	3.0 (0.40)	3.15 (0.56)
	Vapour phase reaction						
0	36.8 (8.10)	4.8 (0.60)	2.8 (0.48)	1.9 (0.36)	1.9 (0.53)	1.95 (0.46)	1.6 (0.26)
5	10.83 (1.23)	2.9 (0.08)	1.8 (0.20)	1.3 (0.15)	1.2 (0.14)	1.3 (0.08)	1.0 (0.10)
10	5.8 (1.2)	2.8 (0.22)	2.1 (0.18)	2.0 (0.15)	1.8 (0.16)	2.0 (0.08)	2.0 (0.25)
20	5.0 (0.85)	2.1 (0.25)	2.0 (0.28)	1.3 (0.20)	1.2 (0.18)	1.0 (0.16)	1.0 (0.09)

* $T_{\frac{1}{2}}$ value of control wafers = 0.6 minute

From a comparison of the long stick (Table 4.10) and cross-sectional wafer (Table 4.11) data, it is apparent that with the covalently bonded silane treatment, a very shallow treated zone may give rise to a significant and persistent reduction in water uptake by long specimens.

4.1.6 Physical strength properties of wood affected by silanation

Physical strength properties of wood are likely to be affected adversely by silanation due to the formation of HCl in the reaction. Acid acceptors commonly used in such reactions may be unable totally to eliminate the degrading effect. Moreover, such chemically modified wood due to the substitution of silyl compounds for wood hydroxyl groups with consequent reduction in hydrogen bonding capacities is likely to be more brittle than unmodified wood. It was decided, therefore, to monitor the tensile strength properties of silanated radial-longitudinal microtome specimens. It is also thought that wood subjected to mild silanation reactions are treated only superficially. Nominal 100 micron thick microtome specimens are, however, likely to be treated through and through. Specimens of 1cm cross-sectional width were thus tested for static bending strength.

4.1.6.1 Experimental procedure

Microtome specimens, 100 micron thick, 1 cm wide and 10 cm long were cut from the radial face of Corsican pine blocks (see Section 4.1.2). These were dried under mild restraint at 65% RH and 20°C and then dried to constant weight over P_2O_5. They were then subjected to silanation with 1ml and 5ml silane vapour for 5 minutes in nitrogen atmosphere (see Section 4.1.2). Similarly, in the liquid phase, 1ml and 5ml silane in 50ml CCl_4 were allowed to react with microtome specimens. The same experiment in liquid phase was repeated adding 10ml DMF, as acid acceptor, with both 1ml and 5ml silane. The treated specimens after neutralizing, drying and equilibrating (at 20°C and 65% RH) were subjected to tensile strength tests over 2cm span using a Universal testing machine. The load was applied using a cross-head speed of 0.5 mm/min. The experiments were replicated using 20 specimens for each treatment condition.

For the static bending tests 16cm long and 1cm cross-sectional specimens of Corsican pine wood were used. The specimens were prepared with 2 radial/longitudinal faces parallel to each other.

Silanation reactions were conducted both in the vapour phase and the liquid phase with dimethyldichlorosilane (DMDCS). Vapour phase reactions were done in a tall reaction vessel using a mild (2ml silane), a medium (5ml silane) and a high (10ml silane) treatment level. Another set of specimens pre-treated with dimethyl formamide (DMF) was treated in the vapour phase using 5ml silane. The reaction time allowed in each case was 5 minutes. Similar mild, medium and high level treatments were carried out in the liquid phase using 5, 10 and 15ml DMDCS for 5 minutes respectively. In all cases 500ml toluene was used as a diluent. The high level treatment was repeated with addition of 25ml DMF in one reaction. In addition, a control reaction was carried out using solvent (toluene) and acid acceptor (DMF) only.

Liquid phase treated specimens were neutralized and equilibrated to constant weight at 65% RH and 20°C before mechanical testing. Modulus of rupture (MOR), Modulus of Elasticity (MOE) and Total Work Done (TWD) were calculated using the following formulae:

$$\mathrm{MOR} = \frac{3\,P_{max}\,L}{2\,BH^2}$$

$$\mathrm{MOE} = \frac{P_{PL}\,L^3}{4\Delta\,BH^3}$$

$$\mathrm{TWD} = \frac{\mathrm{I/C\ FSL\text{-}Velocity}}{10{,}000\ LBH}$$

where, I/C = Integer count

L = Span (mm)

B = Specimen width

Δ = deflection (mm) at midpoint of beam

$= \frac{\text{chart deflection} \times \text{velocity}}{\text{chart speed/min}}$

P_{max} = Maximum load in Newtons

P_{PL} = Load at proportional limit

H = Specimen depth (mm)

4.1.6.2 Results and discussion

Results of tensile strength tests and static bending tests are given in Tables 4.12 and 4.13 respectively. It is evident that in microtome specimens a high degree of strength loss occurs even on mild treatment. Liquid phase reactions, however, seem to retain the tensile strength better than vapour phase reactions. It is clear from the results that the chemical modification taking place drastically decreases tensile strength, suggesting that silanation occurs through the entire specimen thickness (100 microns).

Both vapour phase and liquid phase treatment bring about marked loss of strength. From the limited test programme carried out, it is not possible to decide which method of treatment is most deleterious. Even the process involving the acid acceptor does not lead to any significant reduction in the strength loss caused.

From the static bending tests of larger wood specimens it appears that the level of silanation achieved in these treatments leads to only a slight reduction in bending strength properties. However, it can be seen that as the severity of treatment is increased, a corresponding increase in strength loss is incurred. Comparison of these data with those for the thin strips suggests that the silanated zone is superficial, probably not extending to a depth greater than 1mm or so. As a result, most of the strength properties of the large specimens remain unimpaired. The modulus of elasticity values do not change much and seem to be inconclusive. Total work done was calculated only on the control, and one batch of vapour phase and one batch of liquid phase specimens.

At first sight, these loss of strength data appear to be quite encouraging. That is, in relatively large cross-sections the loss of strength caused is insignificant in comparison with naturally occuring strength reducing factors (relative to the strength of clear specimens) such as knots and sloping grain. However, as shown by the strength reduction caused to these sections, such strength reduction as does occur seems to be concentrated in a thin exposed surface zone. It is likely, therefore, that this zone may be rapidly eroded when exposed directly to weather, leaving unprotected wood at the surface. Even under a paint film, the situation may be little better. In this case the stresses encountered due to any differential movement of wood and paint may well lead to shearing of the weak surface layer of modified wood from the underlying sound material, and effectively detaching the paint from the wood surface. Hence, the observed strength reduction occurring as a consequence of silane treatment must impart a serious reservation on the possible utility of such wood modifying processes.

Table 4.12 Tensile strength of silanated microtome specimens (Mean of 20 specimens ± standard deviation)

Specimen treatment	Tensile strength Kg/mm^2	Loss of strength (basis:control) (%)
Control	8.29(0.67)	-
Vapour phase (mild)	5.55(1.15)	67
Vapour phase (high)	1.08(0.14)	87
Liquid phase (mild)	3.14(0.31)	62
Liquid phase (high)	2.18(0.19)	74
Liq. phase with DMF (mild)	3.09(0.10)	63
Liq. phase with DMF (high)	2.60(0.43)	69

Table 4.13 Static bending tests of silanated large specimens (Mean of 12 specimens ± standard deviation)

Specimen treatment	MOR(N/mm^2)	MOE(N/mm^2)	TWD(Nmm/mm^3)
Control	117.86(7.72)	10,769(837)	0.2168(0.04)
Vapour phase (mild)	112.69(7.27)	11,006(496)	-
Vapour phase (medium)	104.56(5.38)	10,453(588)	0.1876(0.02)
Vapour phase (high)	99.17(5.67)	10,752(691)	-
Vapour phase with DMF (high)	115.94(6.64)	10,780(880)	-
DMF alone	103.34(9.88)	12,798(1372)	-
Liquid phase (with DMF)	107.05(4.30)	11,328(715)	-
Liquid phase (mild)	110.12(8.48)	12,100(790)	
Liquid phase (medium)	107.11(6.38)	9,166(2869)	0.1715(0.03)
Liquid phase (high)	103.50(3.99)	12,631(1759)	-

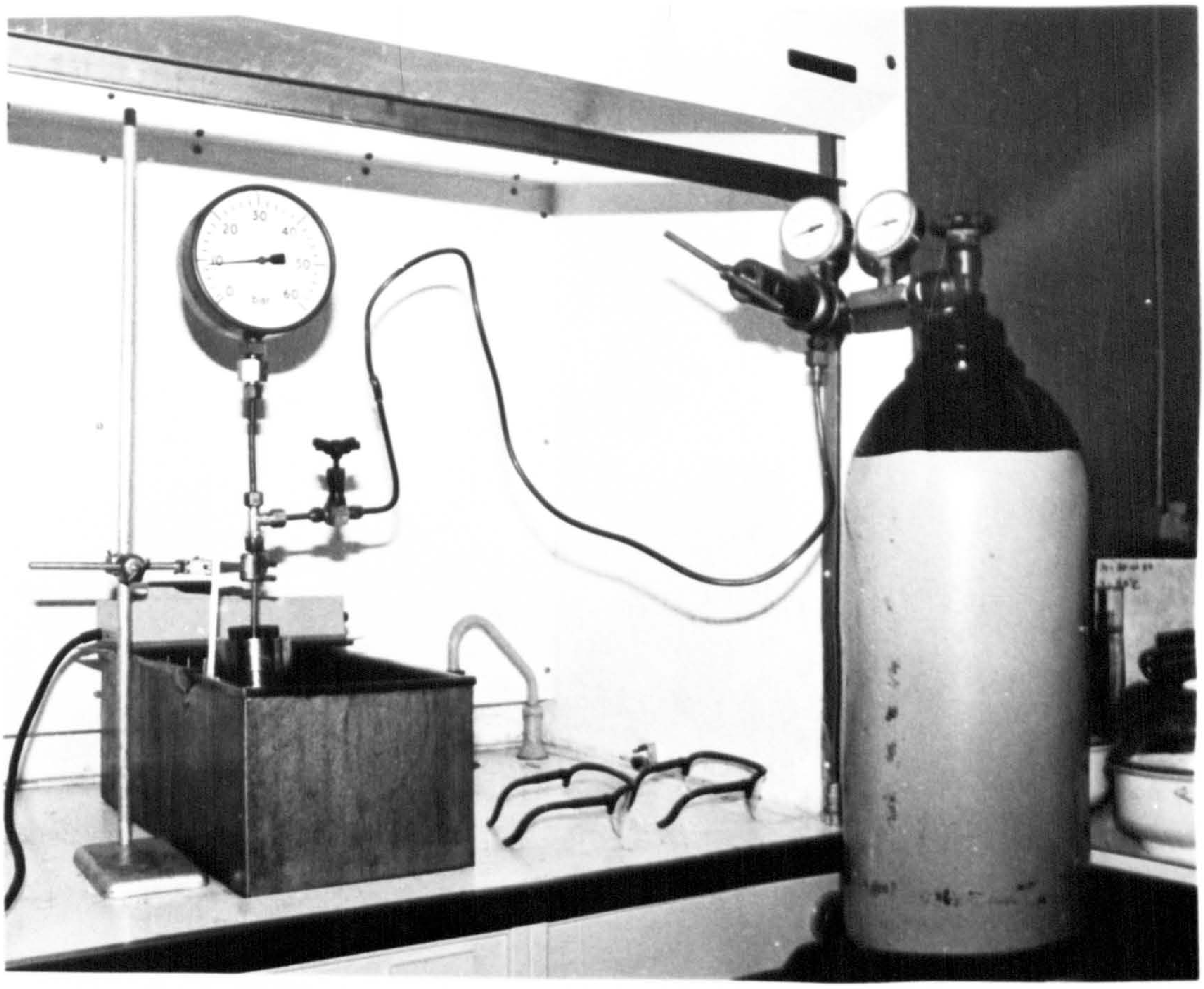


Figure 4.4. Epoxy treatment in pressure reaction bomb in nitrogen atmosphere.

Figure 4.3. The reaction bomb used for epoxy treatment.

4.2 Water repellent effectiveness in epoxy-treated wood

4.2.1 Reactions with propylene oxide (PO)

4.2.1.1 Objectives

The hygroscopic nature of wood is mainly due to the presence of reactive hydroxyl groups in both the polysaccharide and lignin components of the cell wall. Shrinkage and swelling in wood resulting from this hygroscopic property can be drastically reduced by blocking these groups. Excellent dimensional stabilization has been obtained in wood specimens by reacting them with the first three members of the alkylene oxide series (McMillin, 1963; Liu and McMillin, 1965; Rowell and Gutzmer, 1975). Reduction in moisture absorption by cellulosic materials due to such treatment has also been predicted by Liu and McMillin (1965). The objective of the work reported here is to investigate to what extent chemically bonded epoxides, such as propylene oxide (PO), butylene oxide (BO) and butadiene diepoxide (BD) impart water repellency to wood in addition to dimensional stabilization.

4.2.1.2 Experimental procedure

Chemical treatment of the specimens

Transverse wafer specimens (2x2x0.6cm) from Corsican pine sapwood were first dried at 105°C and then to constant weight over P_2O_5. Two different levels of treatment were achieved by varying the reaction conditions. In both experiments a mixture of 95% propylene oxide (PO) and 5% triethylamine (TEA) was used, the TEA acting as base-catalyst (McMillin, 1963; Rowell, 1975). In each experiment 20 wafer specimens were treated. The dry specimens were weighed, measured (with a micrometer) and placed in a steel high pressure reaction vessel (Figure 4.3) along with the reaction mixture. The vessel was sealed, connected to a nitrogen gas cylinder and the pressure was raised to 9 bar. The gas in the vessel was then allowed to escape in order to sweep out the air originally present. This process was repeated twice more.

In the first experiment, pressure in the bomb was increased to 10 bar and then the bomb was placed in an oil bath at 125°C (Figure 4.4). The reaction was allowed to continue for 90 minutes. In the second experiment, a lower level epoxy treatment was effected by keeping the pressure at 8 bar and heating the bomb at 125°C for 30 minutes. The specimens were then dried in a vacuum oven at 40°C and then over P_2O_5 in a desiccator. They were then re-weighed and measured to assess the effects achieved by the treatments.

As a further check of the degree of substitution achieved, the increase in dimension of dried treated specimens after 24 hours soak in water was determined. The results of these experiments were expressed as "Anti-Shrink Efficiency" (ASE) values (Stamm, 1964; Rowell and Gutzmer, 1975). The method of calculation is given below:

$$\text{Swelling coefficient,} \quad S = \frac{V_2 - V_1}{V_1} \times 100$$

where V_2 = Wet dimension

V_1 = Dry dimension

$$\text{A.S.E.} = \frac{S_u - S_t}{S_u} \times 100$$

where S_u = Swelling coefficient of untreated control

S_t = Swelling coefficient of treated specimen.

Assessment of water repellency

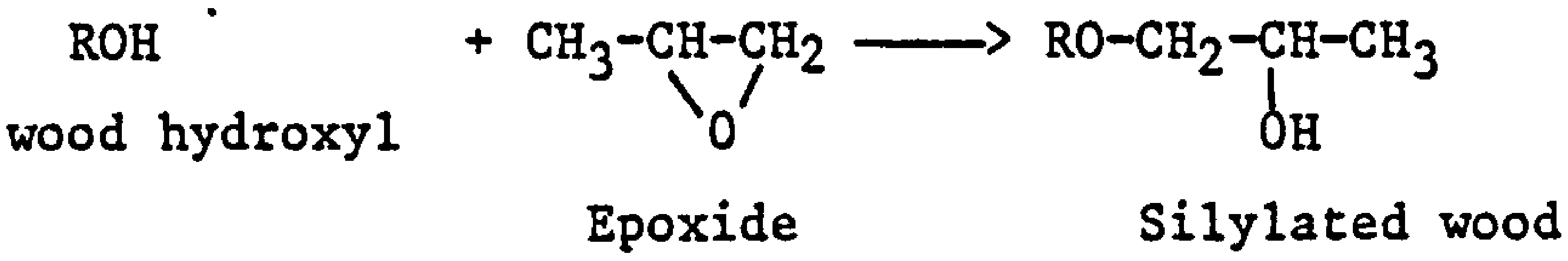
Because of the alteration to shrinking/swelling characteristics brought about by the treatments it is confusing to use swelling rate as an indication of water repellency. Hence, with wafer specimens treated with epoxides, rate of water uptake was used as the test parameter. Water sorption determinations were conducted by immersing the specimens and weighing periodically over 60 minutes period, as described fully in Sections 2.2.4 and 3.2.3. A further set of similarly treated specimens was subjected to simulated weathering using a variant of the cyclic wetting/drying procedure described in Section 2.2.3. In this series of tests each cycle consisted of 24 hours soaking (25°C) and 24 hours drying (35°C) and specimens were exposed for periods of 5 and 15 cycles. After these periods of simulated weathering, ASE values were again estimated to give a guide to the persistence of the epoxide treatments. A final batch of 8 wafer specimens was reacted in the pressure vessel with a mixture of 95% propylene oxide and 5% triethylamine to a weight gain of 33%. This set together with a set of 6 matched untreated control wafers was used to assess the change in sorption isotherm caused by such treatment. This was to provide an insight of how the wood/water relationship is altered by propylene oxide treatment. The sorption isotherm was developed by exposing the wafer specimens to successively increased levels of relative humidity using a range of saturated salt solutions (excepting P_2O_5 , which was used in dry condition) in evacuated desiccators. Details of the conditioning substances used are given below:

Salts used in desiccators		Approx. equilibrium RH(%)
P_2O_5 (dry)		0
KOH (sat. soln)		9
$MgCl_2$	"	33
$Na_2Cr_2O_7$	"	55
$(NH_4)_2SO_4$	"	81
KNO_3	"	93
Water		100

To ensure that the specimens approached closely to equilibrium moisture contents they were kept for 72 hours at each condition. After completion of the adsorption work, the process was reversed to give desorption data. The whole cycle was repeated to give a second adsorption/desorption loop.

4.2.13 Results and discussion

Reactions of epoxides with wood components form very stable ether bonds (Rowell and Gutzmer, 1975).



$$\underset{\text{wood hydroxyl}}{ROH} + \underset{\text{Epoxide}}{CH_3\text{-}CH\text{-}CH_2 \atop \;\; \backslash O/} \longrightarrow \underset{\text{Silylated wood}}{RO\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_3}$$

The additional hydroxyl group formed in the reaction product, originating from the epoxide, is believed to participate in a polymerization reaction (Schuerch, 1968). The presence of this polymer in the cell wall imparts dimensional stability. It is not known however, to what extent the β -hydroxy substituted alkane chain may impart water repellency.

Antishrink efficiency (ASE) data

The ASE values achieved as a result of the propylene oxide treatments are given in Table 4.14

Table 4.14 Antishrink efficiency of epoxy-treated specimens

PO:TEA	Treatment level	Wt. gain	Tangential	Radial	Volumetric
95:5	Low (8 bar, 30 mins)	9.4	24.8 (1.2)	36.3 (1.4)	32.0 (1.3)
95:5	High (10 bar, 90 mins)	43.4	55.9 (2.3)	86.4 (3.1)	76.6 (2.8)

From the Table 4.14 it can be seen that the treatments carried out led to a very significant improvement in dimensional stability. It can further be seen that the level of improvement brought about appears to be strongly and positively correlated with the degree of chemical substitution/polymerization achieved.

An indication of the permanence of the modification is provided by the data relating to ASE values of the specimens exposed after treatment to the simulated weathering procedure described above. These data are given in Table 4.15 below:

Table 4.15 ASE values of PO treated weathered specimens after 24 hours water soaking (mean of 20 replicates ± Stand. Dev.)

Treatment	Wt. gain on treatment (%)	No. of weathering cycles	Antishrink efficiency (%)	
			Tangential	Volumetric
PO:TEA 95:5 (10 bar, 90 mins)	43.4	0	64.0 (0.8)	81.7 (1.0)
		5	62.5 (0.9)	79.9 (0.9)
		15	60.9 (1.0)	83.3 (1.1)

From the data in Table 4.15 it can be seen that the treatment imparts effective resistance to exposure to quite severe simulated weathering.

The epoxy treatment causes significant increase in the dimension of the treated specimens (Table 4.16 below).

Table 4.16 Effect of treatment level on swelling of wood (mean of 20 wafers ± Stand. Dev.

Treatment (PO:TEA)	Wt. increase achieved	Increase in dimension caused by treatment			
		Tangential	Radial	Longitudinal	Volumetric
95:5 (10 bar, 90 mins)	43.4	11.7 (1.0)	4.3 (0.7)	2.1 (0.4)	18.0 (1.4)
95:5 (8 bar, 30 mins)	9.4	3.0 (0.1)	2.0 (0.1)	0.3 (0.1)	5.4 (0.3)

Here it is clear that the material introduced must be within the cell wall. The fact that it resists leaching due to simulated weathering (Table 4.16 above) suggests that this introducted material is strongly (probably covalently) bonded to the cell wall, as suggested by Rowell and Gutzmer, 1975 (see above).

Water repellency data

The results of the water sorption experiments carried out on propylene oxide treated (wt. gain on treatment 9%) and control specimens are given in Table 4.17 below:

Table 4.17 Water absorption rate for control and treated specimens (Mean of 8 specimens ± Stand. Dev.)

Specimens	Soaking time (minutes) and water absorption (%)									
	½	1	3	5	10	20	30	40	50	60
Treated	39.0 (1.5)	44.3 (1.5)	49.5 (1.1)	51.8 (1.2)	52.2 (1.1)	53.7 (1.1)	54.8 (1.0)	55.2 (1.0)	55.9 (0.9)	56.5 (0.9)
Control	43.8 (1.3)	52.4 (1.4)	58.1 (1.5)	64.0 (1.9)	66.8 (1.6)	75.2 (1.1)	76.6 (0.8)	77.9 (0.7)	78.4 (0.8)	79.1 (0.9)

It is apparent from the data of the Table 4.17 that the epoxide treatment leads to a relatively small reduction in rate of water uptake, in comparison to that produced by treatment with simple resin/wax water repellents (See Sections 2.2.4.2.1 and 3.2.3.1).

The relatively modest reduction in water sorption rate seems likely to be associated with change in the cell wall/water relationship rather than with the development of any significant hydrophobic effect. Hence, it seems that treatment with propylene oxide, whilst giving rise to a marked reduction in dimensional instability, does not impart significant water repellency. This is probably because of the presence of free hydroxyl groups remaining attached to the propyl chain after reaction (see above).

Sorption isotherms of propylene oxide treated wood

Absorption and desorption data for control and treated specimens are given in full in Table 4.18. The data are presented graphically in Figure 4.5. From the figure it appears that the isotherms for the control specimens are typical of those of normal pine wood (see for example, Browning, 1967; Koch, 1972). The general shape, the magnitude of moisture sorption and the hysterisis are all similar to published data (Stamm, 1964; Wangaard and Granados, 1967). Hence, it seems that the method used is reliable. With the modified specimens a noticeable change in the isotherm is evident. At low values of relative humidity such specimens absorb and retain less moisture than controls. Above about 55% RH, however, the modified wood starts to absorb increasing quantities of water and in the 95-100% RH region, the equilibrium moisture content of treated wood is slightly greater than that of controls.

Dimensional changes corresponding to the various levels of sorption were monitored for one absorption cycle. These data are given in Table 4.19 and presented graphically in Figure 4.6.

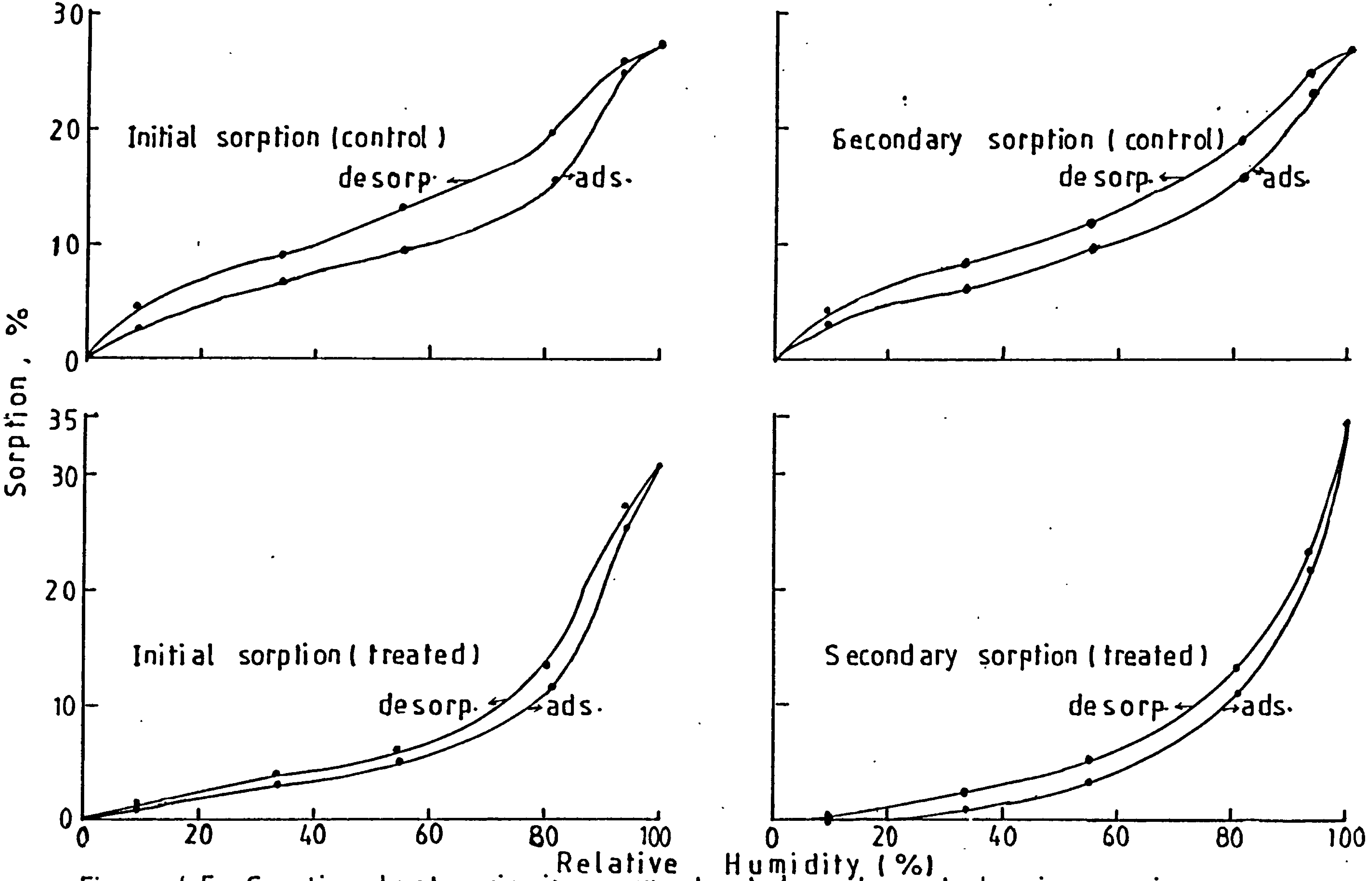


Figure 4.5 Sorption hysteresis in epoxy treated and control pine specimens.

Table 4.18 Changes in weight in control and epoxy treated specimens due to sorption under different RH conditions.
(Control: Mean of 6 specimens ± S.D.;
Treated: Mean of 8 specimens ± S.D.)

	INCREASE IN WEIGHT (%)			
RH%	1st absorption-desorption cycle		2nd sorption cycle	
	CONTROL	TREATED	CONTROL	TREATED
9	2.57(0.05)	0.87(0.05)	2.78(0.08)	0.03(0.00)
33	6.29(0.07)	2.79(0.09)	6.00(0.08)	1.71(0.23)
55	9.03(0.08)	4.69(0.11)	9.67(0.08)	4.32(0.32)
81	15.53(0.08)	11.52(0.08)	15.63(0.13)	10.26(0.53)
93	24.75(0.22)	27.61(0.19)	23.20(0.17)	23.28(0.29)
100	26.52(0.25)	30.74(0.62)	28.12(0.21)	35.06(0.73)
93	25.62(0.10)	25.01(0.10)	25.05(0.20)	26.67(0.38)
81	18.85(0.14)	11.75(0.40)	19.20(0.11)	12.24(0.40)
55	13.05(0.09)	6.31(0.21)	12.02(0.09)	5.17(0.33)
33	8.93(0.07)	3.59(0.15)	8.65(0.08)	2.99(0.26)
9	4.58(0.04)	1.05(0.09)	4.14(0.10)	0.48(0.20)
0	0.54(0.06)	(-)0.93(0.21)	0.32(0.10)	(-)0.88(0.18)

Table 4.19 Dimensional changes in control and epoxy treated specimens due to sorption under different RH conditions (Mean of 6 control and 8 treated specimens ± St. Dev.)

RH%	CONTROL SPECIMENS		EPOXY-TREATED SPECIMENS	
	Wt. increase %	Volumetric increase %	Wt. increase (%)	Volumetric increase %
9	2.6(0.05)	0.9(0.17)	0.9 (0.05)	0.2(0.18)
33	6.3(0.07)	2.8(0.31)	2.8 (0.09)	0.9(0.18)
55	9.0(0.08)	4.5(0.31)	4.7 (0.11)	1.5(0.19)
81	15.5(0.08)	8.4(0.27)	11.5 (0.08)	2.0(0.43)
93	24.8(0.22)	13.6(0.45)	27.6 (0.19)	2.5(0.44)
100	26.5(0.25)	15.8(0.65)	30.7 (0.62)	4.1(0.33)

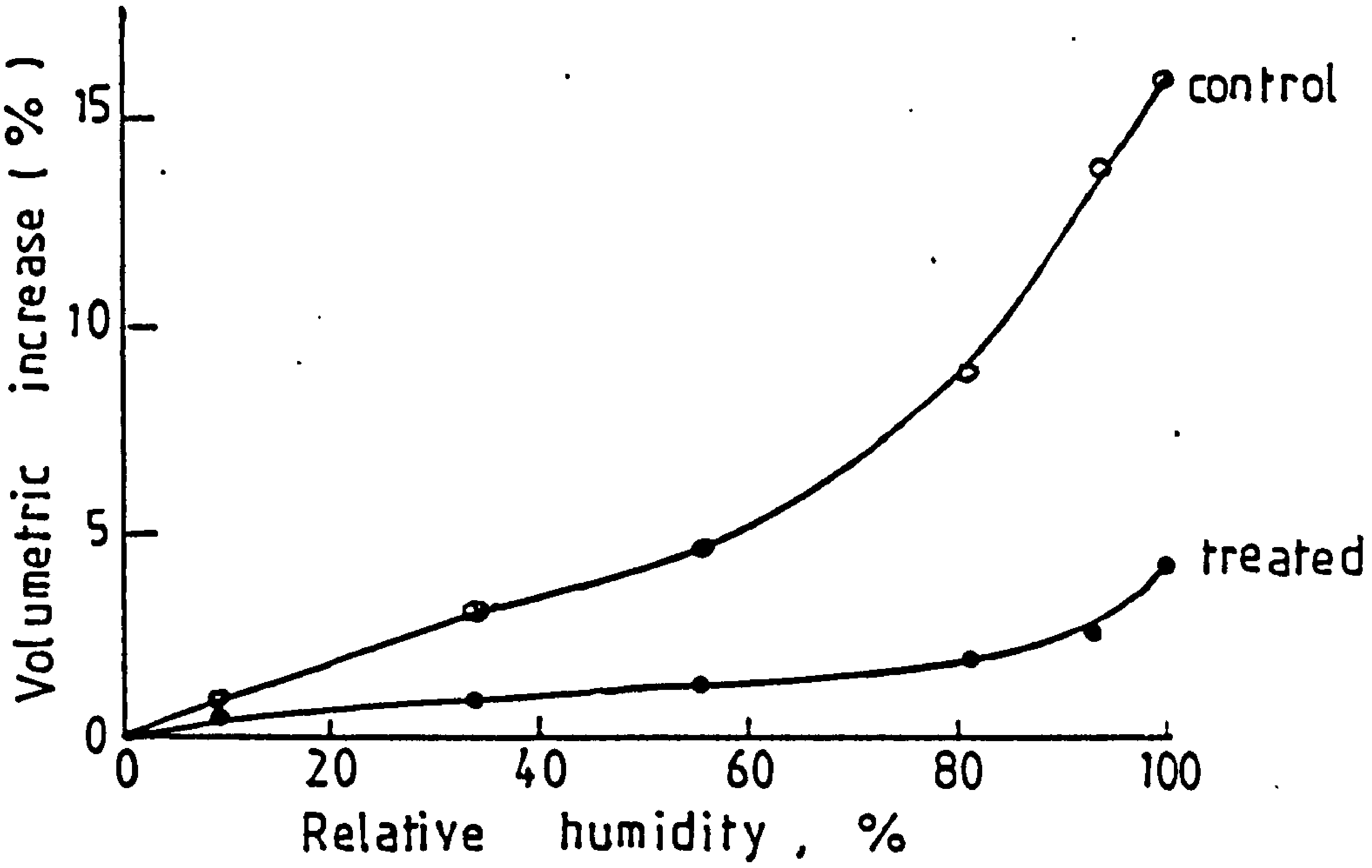


Figure 4.6 Dimensional change in control and epoxy treated specimens with variation in relative humidity

The data in Table 4.19 (and Figure 4.6) suggest that reduction in the degree of swelling of treated compared to control specimens is reasonably constant throughout the sorption range. Certainly, there is no evidence to support the idea that the high moisture sorption exhibited at high levels of relative humidity is accompanied by a corresponding large increase in dimensional change. This large water uptake is probably due to the rigid bulky propane chains retaining the cell wall in a swollen but relatively porous state. This then allows some water to enter without bringing about a corresponding volumetric increase in specimen size rather like water entering a sponge. At a practical level, the data suggest that treatment with propylene oxide leads to significant improvement in dimensional stability throughout the hygroscopic range.

4.2.2 Reactions with butadiene diepoxide and cetyl alcohol

4.2.2.1 Objectives

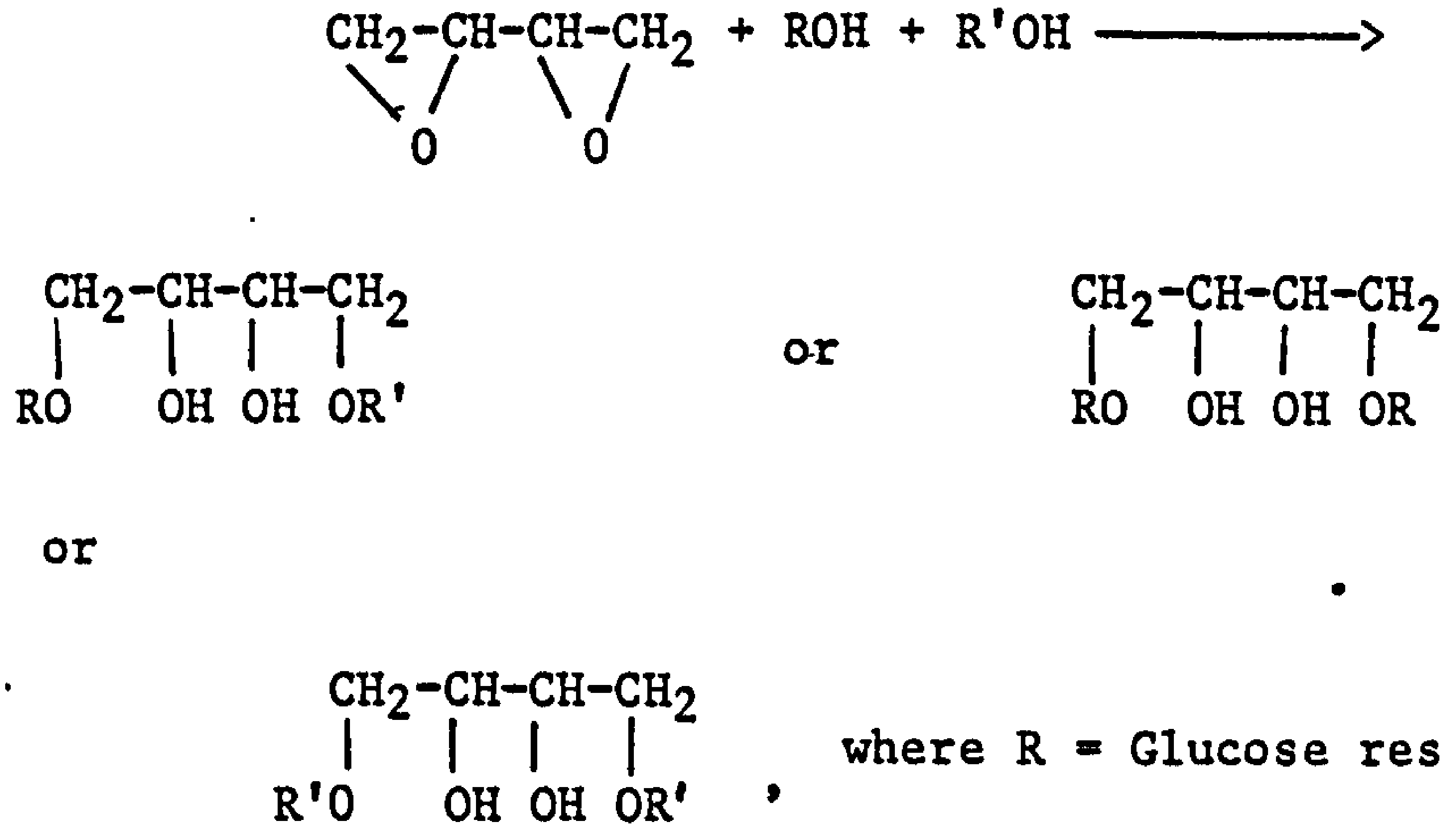
Short chain epoxides have been shown to impart excellent dimensional stability to the treated wood. No significant water repellency, however, accompanies the chemical modification involved in the reactions. From the high and stable antishrink efficiency (ASE) values of alkylene oxide treated wood, it is assumed that the polymers are covalently bonded to the cell wall. It was thought that large groups copolymerized in the cell wall might introduce some degree of hydrophobicity in the treated wood. It is well known that organic aliphatic alcohols react easily with epoxides under conditions of base catalysis (Chitwood and Freure, 1946; Long and Pritchard, 1956; Pritchard and Long, 1956; Reeve and Christoffel, 1950). In some cases, the reaction proceeds even without a catalyst (Schroeder and Condo, 1957; Shechter et al., 1956). In an attempt to copolymerize large groups in the cell wall, 1,3-butadiene diepoxide (BD) and cetyl alcohol (hexadecan-1-ol; CA) (i.e. 16 carbon chain alcohol) were chosen to copolymerize with the wood hydroxyl groups in the presence of triethylamine (TEA) as a catalyst.

4.2.2.2 Experimental procedure

Eight transverse wafer specimens (2x2x0.6cm) of Corsican pine sapwood were reacted in the reaction vessel described in Section 4.2.1, at 120°C and 9 bar nitrogen gas pressure for 90 minutes.
The reactants were in the ratio of BD:CA:TEA::90:5:5. Preliminary reactions showed that in presence of a catalyst BD and CA react vigorously to form products which solidify to a hard resinous mass, encapsulating the wood specimens. Reaction between BD and CA to yield a polymer substance proceeds unabated even in the presence of a diluent solvent (CCl_4). Reactions were then carried out with the exclusion of the catalyst, with BD and CA in the ratio of 95:5. Further experiments were carried out with only 5ml BD in the absence of CA.

4.2.2.3 Results and discussion

From the reactions, it seems that in the presence of a catalyst BD and CA react with each other more readily than with the wood hydroxyl groups. In CCl_4 medium the resinous mass formed in the reaction between BD and CA in presence of TEA darkens the specimens due to heavy deposition on the wood surface. Under microscopic examination the specimens seemed to be coated in patches of uneven thickness with the resin formed. From the results given in Table 4.20 it seems likely that BD reacts with both CA and wood even in the absence of any catalyst, whereas CA probably preferentially reacts with BD and takes no part in any direct reaction with wood, reaction in the presence of a catalyst being mostly limited to that between BD and CA. The main objective of attaining cross-linking the wood hydroxyl groups with larger reacting groups from the reactants is not achieved. Moreover, cetyl alcohol showing little affinity for the wood hydroxyl groups, it is only the epoxide which modified the wood. The reactions probably proceed in the same way as in the cases of mono-epoxides:



where R = Glucose residue and R' = $C_{16}H_{33}$

Much of the weight gain achieved in reactions involving a catalyst was lost on water soaking. This points to the fact that homo-polymers or copolymers formed by BD and CA are not chemically bonded to the cell wall. Some degree of reduction in water uptake obtained in the preliminary reactions (not shown) was probably due to the blocking of gross capillaries in wood by these polymers. These polymers, however, contributed little in imparting any water repellency to the treated wood. Comparatively clear wood specimens in uncatalyzed reactions indicate scant homo-polymerization of the reactants in the absence of any catalyst. Weight gain and dimensional stability achieved by such reactions must then arise from wood-epoxide reaction. It is interesting to note that mono-epoxides react significantly with wood only in presence of a catalyst (McKelvey et al, 1959). The bifunctional epoxide used in this experiment seems to react with wood without a catalyst.

Weight gain and swelling coefficients under the reaction conditions described and water soaking data (Section 4.2.2.2) are given below:

Table 4.20 Treatment data with BD and CA and performance of treated specimens on 24 hour water soaking (Mean of 8 specimens ± Stand. Dev.)

Reactants	WPG	Vol. swelling coeff. on reaction %	Water Abs. (%) 5 min	Water Abs. (%) 24hrs	Vol. increase on water soaking %
CA+TEA+ CCl_4	6.98	0.33 (0.19)	-	110.13	21.55 (1.76)
BD+CA	34.62	21.45 (0.87)	-	74.36	2.95 (0.46)
BD	20.05	20.54 (0.94)	77.0	78.23	4.54 (0.43)
Control	-	-	79.0	122.62	29.55 (0.41)

From the data in Table 4.20 it appears that CA itself probably does not react with the wood cell wall. Some gain in weight is most probably due to the bulking effect of the solid alcohol. This also explains some reduction in water absorption and swelling compared to the control specimens, on soaking. Similarly, increased weight gain and slight reduction in water absorption and swelling on soaking of specimens treated with BD and CA compared to those of BD only treated specimens is probably due to bulking of gross capillaries by CA or the polymer resulting from BD reacting with CA.

From the data in Table 4.20 it can be seen that much of the water absorbed over the 24 hour period is taken up within the first few minutes. These data indicate that the treatment imparts good dimensional stability but little, if any, water repellency. The dimensional stability has been found to remain unchanged even after 5 extended weathering cycles.

4.2.3 Envelope treatment of large specimens with epoxide monomers

4.2.3.1 Experimental procedure

In preliminary experiments, attempts were made to examine the effect of an envelope treatment of 10cm long and 2x2cm cross-sectional specimens on their water absorption and dimensional stability. After soaking the end sealed speciemns for 3 minutes in a mixture of propylene oxide and triethylamine (95:5) they were placed in the pressure reaction vessel (Figure 4.3) without any further addition of reactants to the vessel. After treatment for 60 minutes at 125°C and 8 bar nitrogen pressure the specimens were found to develop axial checks and to exhibit minimial increase in weight and dimension.

Experiments were then conducted using the same mixture and with similarly manipulated specimens (transverse faces sealed) in the following manner. The same technique of presoaking in reaction mixture was employed. Then the specimens were placed in an elevated platform in the reaction vessel and 15ml of the reaction mixture was poured into the vessel which remained below the level of the platform top. The reaction was then carried out for 90 minutes at 125°C and 8 bar nitrogen gas pressure (taking similar precautions to those described in Section 4.2.1.2, i.e. sweeping out air from the reaction vessel). The presence of the free reagents in the vessel should provide a saturated atmosphere during the reaction time, thus minimizing any tendency for the reagents to evaporate from the impregnated wood specimens. Under these conditions it is difficult to say if the reaction occurred in the liquid or the vapour phase.

After completion of the reaction the sealant was removed from transverse surfaces and the specimens were vacuum dried overnight at 40°C. They were then dried over P_2O_5 to constant weight and monitored for weight and dimensional gains (Table 4.21).

The specimens acquired a light brown colour and externally seemed to be uniformly treated. The specimens were then converted to 6mm transverse wafer specimens. The light brown colour was seen to extend a little way into the specimens, leaving a natural coloured core (Figure 4.7).

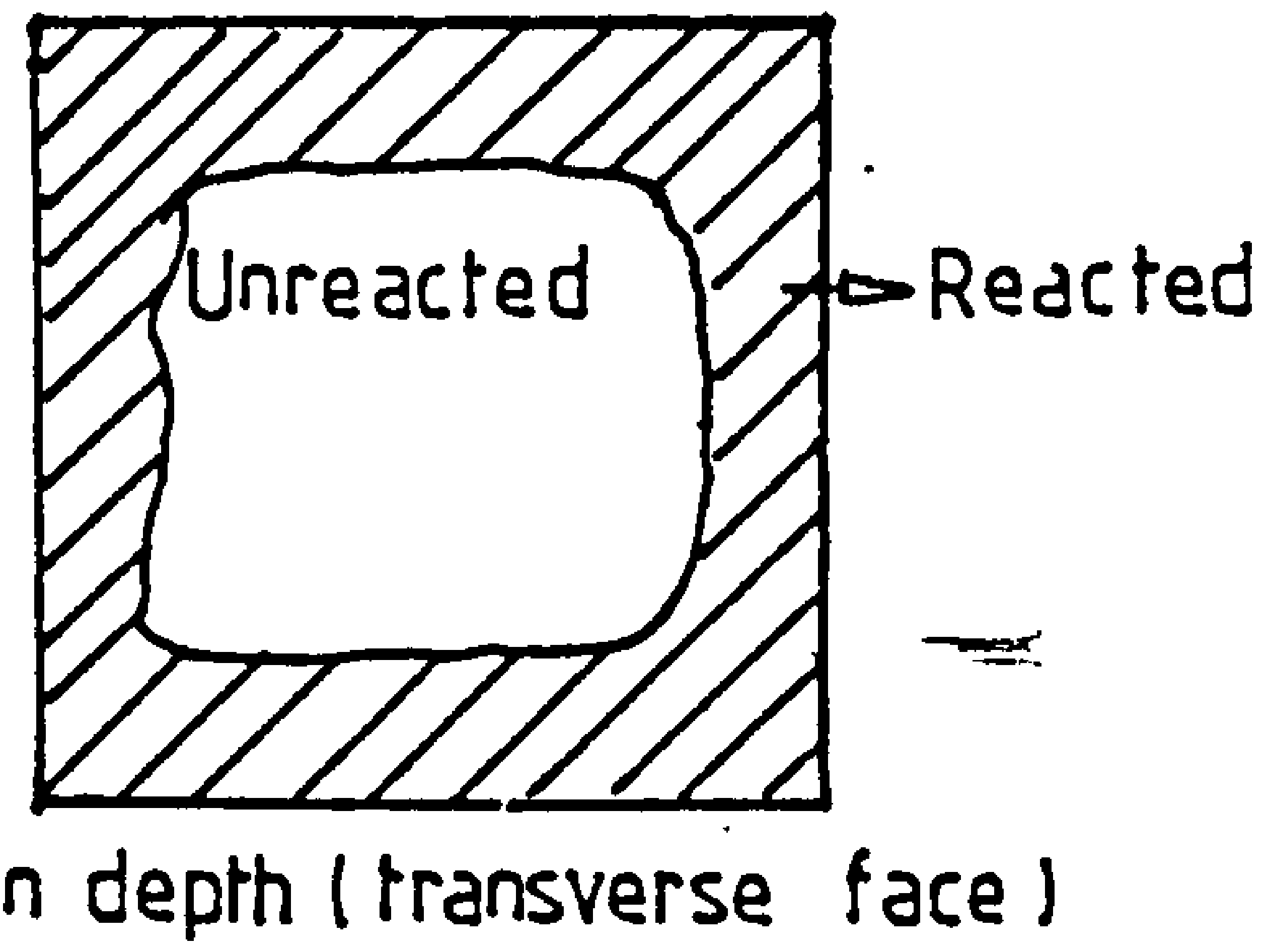


Figure 4.7 Envelope treatment of large specimens with epoxide leaves an untreated core surrounded by modified wood.

4.2.3.2 Results and Discussion

It is evident from treatment data that rather low weight gain and dimensional increase results from the treatment (Table 4.21).

Table 4.21 Increase in weight and dimensions of large specimens on envelope treatment with epoxide (PO). Mean of 5 replicates ± Stand. Dev. (%)

Treatment	Wt. increase on reaction	Dimensional increase caused by treatment		
		Tangential	Radial	Volumetric
PO:TEA 95:5	18.0 (1.7)	5.2 (1.0)	2.9 (0.8)	8.2 (1.9)

It is reasonable to infer from these various data that the cores of the specimens were not fully treated.

The wafer specimens cut from the long sticks were then subjected to 0, 5 and 15 extended simulated weathering cycles (see Section 4.2.1.2) and then dried to constant weight over P_2O_5. Initially and then at the end of 5 and 15 weathering cycles the specimens were soaked in slowly stirred deionized water at 25°C for 24 hours and the amount of water absorbed and dimensional change incurred was measured. Control wafers from the off-cuts of the sticks before treatment were also soaked and similarly monitored. The data are given in Table 4.22.

Table 4.22 Dimensional increase and ASE values of wafers cut from long sticks after 24 hours soaking at various weathering cycles. (20 replicates)

Treatment	No. of cycles	Dimensional increase (1 Stand. Dev.) %			Antishrink efficiency (%)		
		Tangential	Radial	Volumetric	Tangential	Radial	Volumetric
Control	0	8.8 (0.3)	4.9 (0.4)	15.3 (0.9)	-	-	-
PO:TEA	0	4.7 (0.3)	0.5 (0.3)	5.5 (0.6)	46.5	89.8	64.1
	5	5.2 (0.4)	0.4 (0.2)	5.7 (0.6)	41.2	92.9	62.4
	15	5.2 (0.3)	0.3 (0.1)	5.6 (0.8)	41.4	94.9	64.4

By comparison of the data of the Table above with those given in Tables 4.15 and 4.20 it becomes clear that the dimensional stability achieved by complete impregnation treatment of the wafers is considerably greater than that brought about by the envelope treatment. However, the substantial ASE values obtained with rather small amounts of reagents are worth noting.

4.2.3.3 Distribution of the stabilizing effect in envelope treated specimens

To assess the level of stabilization achieved throughout the section, the wafers were cut into small sub-samples and swelling characteristics of these sub-samples were assessed. The wafers were cut as shown in Figure 4.8 to separate the core from the treated periphery. The number 5 specimens (Figure 4.8) and 6 others selected at random from the peripheral ones (40 in total) were tested for water absorption and dimensional swelling after 24 hours soaking in water at 25°C.

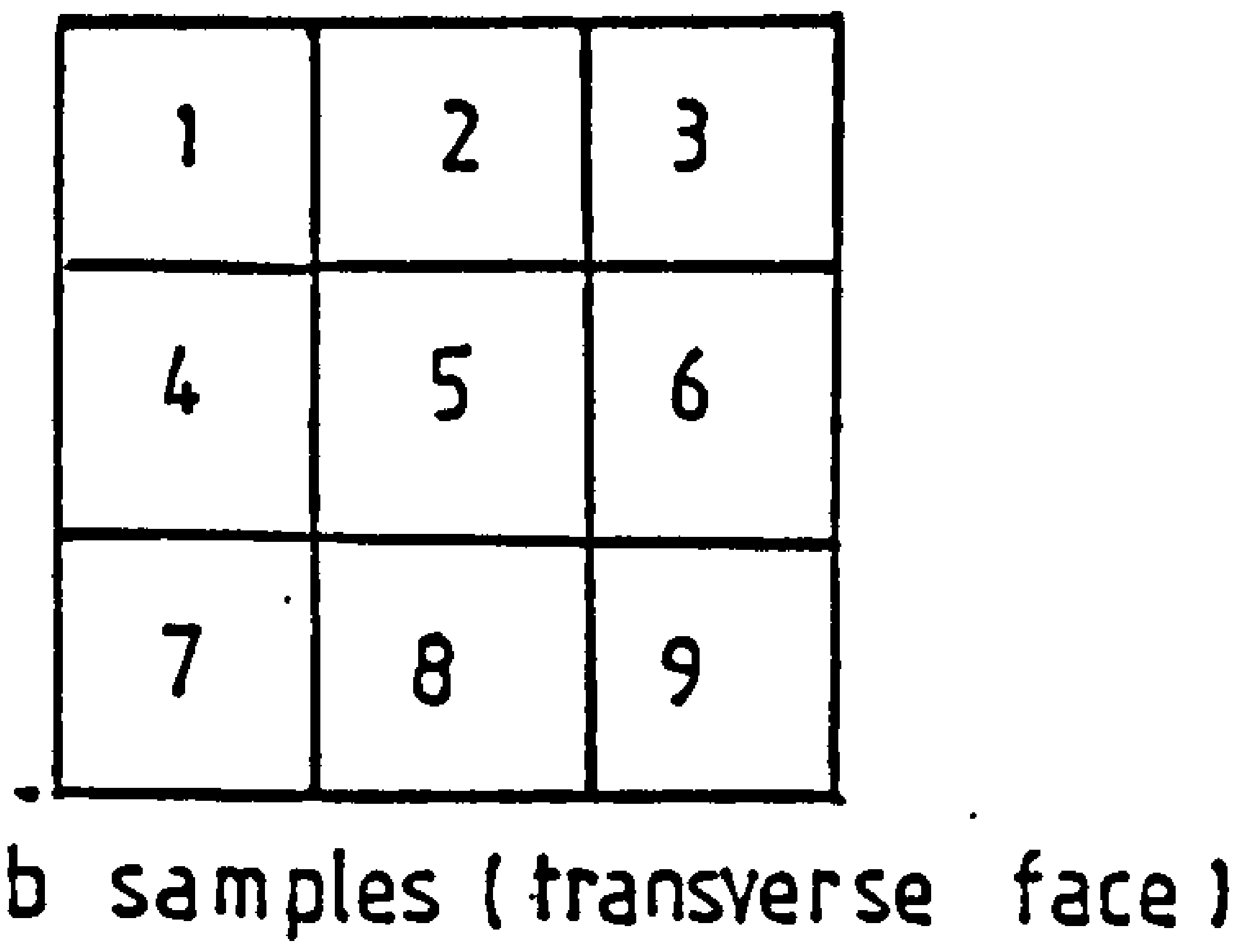


Figure 4.8 Sub-division of wafers cut from envelope treated sticks

The results of the tests are given in Table 4.23 below:

Table 4.23 Water soaking data of treated and apparently untreated sub-samples from envelope treatment (Mean of 6 specimens ± Stand. Dev.)

Treatment	Position of Specimen	Water absorption	Dimensional increase (%)		
			Tangential	Radial	Volumetric
PO:TEA	Periphery	58.4 (5.2)	3.5 (0.3)	2.1 (0.1)	5.7 (0.2)
	Core	78.0 (0.7)	5.9 (0.4)	2.8 (0.6)	8.6 (1.4)

The data show that the reduction in water uptake and dimensional instability is greatest in the outer envelope of wood. This confirms the observation made visually that the treatment schedule adopted produced a well-treated envelope with a much less reacted core.

4.2.4 Static bending strength properties of epoxy-treated specimens

Convenional resin/wax water repellents have no effect on wood strength properties. Where chemical reaction is involved there is a possibility that strength properties may be significantly altered. It has been shown that silanated wood loses some strength due to the degrading effect of HCL formed during the reaction (see Section 4.1). Wood specimens treated with ethylene oxide in the vapour phase are reported to retain their strength properties unimpaired (McMillin, 1963).

Static bending properties of Corsican pine specimens, 9cm long and 0.5cm cross-sectionally were prepared from defect-free wood: The specimens after oven-drying were treated with propylene oxide and triethylamine in the mass ratio of 95:5 in a sealed reaction vessel. They were then reacted at 130°C and 9 bar N_2 pressure for 45 minutes. A weight gain of about 21% was achieved by the reaction. The specimens after the reaction were dried and equilibrated to constant weight at 20°C and 65% RH. These were then subjected to static bending test using a Universal testing machine. The results obtained (Table 4.24) were calculated using the equations given in Section 4.1. The span used in this case was 7cm, and the rate of strain was 1.7mm/minute.

From Table 4.24 it is evident that there was no adverse effect caused by the epoxy treatment on the static bending strength properties. In fact a small improvement in all strength properties was indicated. This improvement may partly be ascribed to the increase in dimensions of the treated specimens. The calculations were based on the initial dimensions before treatment. The increase, for example, in the tangential and radial directions were about 8 and 4% respectively. Calculated on the basis of these increased dimensions the modulus of rupture value is about 208 N/mm^2. On this basis there seems to be approximately 14% loss in static bending properties. However, it is known that swollen wood loses a substantial part of its physical strength properties. For example, green Corsican pine wood has

Table 4.24 Static bending strength properties of propylene oxide treated wood

Specimen	Strength properties (Mean of 12 control and 20 treated specimens ± Standard deviation) %		
	Modulus of rupture N/mm^2	Modulus of elasticity N/mm^2	Total work done mmN/mm^2
Control	242.41 (29.43)	19113 (2029)	0.3505 (0.046)
PO treated	251.80 (24.14)	21594 (1066)	0.3929 (0.072)

only 50% of the modulus of rupture values of that of air dry wood (Lavers, 1969). From the slight loss of modulus of rupture value of epoxy-swollen wood, based on swollen dimensions, it seems that epoxy treatment causes little strength loss in treated wood.

4.3 Double treatment of wood with hydrophobes and bonded stabilizers

Epoxides react chemically and bond with wood blocking the hydrophilic hydroxyl groups and thereby reducing water absorption and dimensional instability in wood, without adversely affecting the physical strength properties of wood. These reactions slightly decrease the rate of moisture absorption by treated wood and decrease the equilibrium moisture content (Schuerch, 1968; Liu and McMillin, 1965). Reaction with epoxides, however, appears not to lead to any water repellency (see Section 4.2.1.3).

It has been shown that the performance of wood treated with conventional water repellent decreases quite markedly during relatively brief exposure to natural or simulated weathering. Evidence has been produced suggesting strongly that this loss of effectiveness is associated with wood structural degrade or with degradation of the wood-deposit bond, rather than with loss of the deposit per se (Section 3.5.2; Voulgaridis, 1980). It seems likely that such breakdown is due in part, at least, to the fatiguing effect of repeated wetting/drying cycles. Hence it is possible that the performance of conventional resin-wax water repellents applied to a partially stabilized substrate may show increased resistance to the effects of the weather. Consequently, a batch of specimens were reacted with propylene oxide as described in Section 4.2.1.2, and then treated with a resin-wax solution for water repellent evaluation.

4.3.1 Experimental procedure

Wafer specimens (2x2x0.6cm) of Corsican pine sapwood were prepared as depicted in Figure 2.1 and oven-dried before treatment. The dried specimens were treated with propylene oxide (PO) using triethylamine (TEA) as catalyst to a high degree of weight gain (Table 4.25). The specimens (12 replicates) were then vacuum dried and half of them were treated by soaking for 30 seconds in a solution of 0.5% wax and 10% resin in white spirit (R_{10} $W_{0.5}$). The resin and wax were the same as described in Section 2.2.1.

Table 4.25 Weight and dimension changes on double treatment

Wt. gain of controls on resin-wax treatment	Gain in wt. and dimensions on epoxy treatment (Mean of 12 specimens ± Stand. Dev) %			Gain in wt. over epoxy-treated wt. on resin-wax treatment
	Wt. gain	Tan. dimensional gain	Volumetric gain	
6.6 (0.4)	51.0	11.3 (0.7)	18.1 (1.2)	0.9 (0.1)

From Table 4.25 it can be seen that the epoxy treatment interferes with the capacity of the specimens to absorb hydrocarbon borne water repellent solutions. The reason for this interference is not known. It is unlikely to be due to pore blocking by deposits of polymer in the lumen or on pit membranes, since it has been shown by Rowell and Ellis (1979) that such deposits are generally absent after epoxy treatment. Furthermore, the presence of any such deposit would lead also to marked reduction in rate of water sorption. Such reduction is not generally observed (see Table 4.27). It may be associated with a 'lipophobic' action due to the hydroxyl groups attached to the bonded alkane chains.

All the specimens (resin-wax, epoxy and double treated) were soaked in slightly stirred water at 25°C for 24 hours and monitored for gain in weight on soaking. The specimens were again dried and equilibrated to zero moisture content and soaked in water for monitoring the rate of water absorption. These tests were repeated after simulated weathering for 5 and 15 extended cycles, each cycle consisting of 24 hours soaking and 24 hours drying.

4.3.2 Results and Discussion

The water soaking data after various weathering cycles are given in Table 4.26 and the rate of water absorption in Table 4.27.

Table 4.26 Gain in weight after 24 hours soaking (Mean of 6 specimens ± Stand. Dev.)

Specimens treatment	No. of cycles	Gain in wt. on soaking (%)
Control	0	116.0(5.0)
PO		57.0(3.6)
$R_{10}W_{0.5}$		52.5(3.0)
PO+$R_{10}W_{0.5}$		55.5(1.4)
PO	5	60.4(3.3)
$R_{10}W_{0.5}$		62.4(2.2)
PO+$R_{10}W_{0.5}$		56.5(3.1)
PO	15	63.2(5.5)
$R_{10}W_{0,5}$		66.9(1.1)
PO + $R_{10}W_{0.5}$		58.1(2.2)

From the data in Table 4.26 it can be seen that prior to simulated weathering on 24 hours soaking resin-wax treated specimens absorb slightly less water than epoxy treated specimens. It is doubtful if the differences observed have any practial or statistical significance. After cycling it is difficult to detect any systematic differences in the water sorption over the 24 hour period.

Table 4.27 Rate of water absorption of double-treated specimens at various cycles (Mean of 6 specimens ± Stand. Dev.)

Treatment	No. of cycles	Rate of water absorption (%) and time of soaking (minutes)									
		½	1	3	5	10	20	30	40	50	60
Control	0	43.8	52.4	58.1	64.0	66.8	75.2	76.6	77.9	78.4	79.1
		(1.3)	(1.4)	(1.5)	(1.9)	(1.6)	(1.1)	(0.8)	(0.7)	(0.8)	(0.9)
RW		1.8	4.1	4.9	5.6	8.2	10.5	12.5	14.8	16.1	17.6
		(0.4)	(0.6)	(0.4)	(0.4)	(0.7)	(0.7)	(1.0)	(1.0)	(0.6)	(0.6)
PO		24.8	28.8	31.1	32.3	32.9	34.6	35.5	36.6	37.6	37.6
		(3.7)	(3.9)	(3.2)	(2.8)	(3.1)	(2.7)	(2.8)	(2.6)	(2.6)	(2.8)
PO+RW		5.5	9.4	14.9	18.3	20.5	23.8	26.2	27.4	28.7	29.6
		(1.0)	(1.4)	(0.8)	(1.6)	(1.3)	(1.1)	(1.2)	(1.2)	(1.2)	(1.3)
RW	5	2.6	4.1	7.5	9.0	13.9	19.5	22.6	24.9	26.5	27.8
		(0.4)	(0.4)	(0.8)	(1.3)	(1.4)	(1.4)	(1.4)	(1.4)	(1.5)	(1.7)
PO		54.0	54.8	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0
		(4.3)	(3.2)	(2.3)	(2.3)	(2.3)	(2.4)	(2.3)	(2.3)	(2.3)	(2.4)
PO+RW		4.0	8.4	17.4	23.6	30.3	34.9	36.7	37.3	38.5	39.3
		(1.2)	(1.7)	(1.7)	(1.6)	(1.5)	(1.2)	(1.2)	(1.4)	(1.0)	(1.0)
RW	15	3.1	6.9	13.7	18.5	24.2	27.2	29.0	29.9	30.5	30.9
		(0.1)	(0.2)	(0.4)	(0.3)	(0.3)	(0.5)	(0.3)	(0.4)	(0.5)	(0.8)
PO		59.6	60.8	60.9	60.8	60.8	60.8	60.8	60.8	60.8	60.8
		(5.8)	(4.9)	(4.4)	(4.5)	(4.5)	(4.5)	(4.5)	(4.4)	(4.5)	(4.5)
PO+RW		10.5	24.0	35.1	38.9	41.5	43.2	43.7	44.3	44.7	45.0
		(2.0)	(2.6)	(3.7)	(2.0)	(2.0)	(1.9)	(1.9)	(1.6)	(1.4)	(1.6)

Study of the sorption rate data of Table 4.27 indicates positively that the initial water repellency effect is greatest for the resin-wax only treatment and least for the epoxy only treatment. The relatively poor (compared to the resin-wax treatment) performance of the double treated specimens prior to exposure is thought to be due to the puzzling low water repellent solution uptake (Table 4.25). It is difficult to visualize a situation where similar quantities of hydrophobe would perform less well on a stable than an unstable substrate. Similarly, after cycling, the double treatment remains markedly less effective than that obtained with resin-wax solution only.

It has to be recognized that stabilization of the wood substrate does not appear to lead to any improvement in water repellent persistence. Unfortunately, the data are confused by the fact that the stabilized specimens absorbed so little water repellent solution. Time did not allow the effect to be studied further, making efforts to introduce larger quantities of water repellent. However, to help resolve the part played by substrate instability to loss of effectiveness, a more complete study of the effect would be worthwhile.

PART 5

GENERAL DISCUSSION

The degree of protection afforded to treated wood has been shown to vary directly with the concentration of the treating solution. Despite reports that further wax loading after about 2% wax in a 10% resin solution leads to no significant improvement in the performance of treated wood (Palejowski, 1980), it appears that improved performance is afforded to treated wood by increasing the loading of both resin and wax. This effect has been found to hold good both initially and in the long run, after a period of weathering (section 2.2.4.2). Even so, in line with the findings of other workers (Voulgaridis and Banks, 1979) evidence suggests that resin and resin-wax seem to provide protection by two different mechanisms. It is believed that conventional water repellents form a coating film on the vessel and tracheid lumina including the pit pore areas. Resin has the attribute of a good film-forming material and the degree of perfection of the coating film determines its ability to protect wood from water sorption and consequent dimensional instability. It appears that higher resin content in a formulation leads to a better chance of forming a coherent film (section 2.3). Wax, on the other hand, seems to provide protection to treated wood by a completely different mechanism. Deposition of wax on the treated wood increases the angle of contact to more than 90°, making water entry difficult. This hydrophobic action (Banks, 1973; Voulgaridis, 1980), theoretically, is not dependent upon solution concentration beyond a low limit, since a monolayer of wax deposit is enough to provide the necessary hydrophobicity. However, it has been shown in practice that higher loading and deeper penetration afford better protection (Borgin, 1965). The reason for this is not clearly understood, but the finding that progressively higher wax concentration provides increasing resistance to water ingress (section 2.2.2.1) is in line with this.

The fundamental difference between the two components of the water repellent solutions is clearly shown by their performance at similar solids content. Both initial and long-term performance of resin-wax treated wood is many times better than that of the resin only treated wood (section 2.3.2). It seems that effectiveness of resin only treatment is dependent upon the wood/resin bond strength. Weathering not only weakens the wood/resin bond but also opens up alternative water entry routes by degrading the exposed end of the wood (sections 2.3.2, 3.4.3 and 3.4.4). Resin-treatment on weathering, thus, fails to afford effective protection against water entry. Under similar circumstances resin/wax treated wood, even after suffering extensive end grain degrade due to weathering goes on resisting water entry into the interior beyond the degraded zone, due to the presence of hydrophobic deposits (section 2.3.2). The difference in the mechanism of the provision of protection to treated wood by resin and wax varies to a great extent depending on the nature of the substrate. It has been found that resin provides much better initial effectiveness with increasing solution concentration in beech than in pine (sections 2.2.4.2 and 3.2.3.1). On the other hand,in beech, resin-wax provides only 2-3 times improvement in performance over that of resin compared with a 10-15 times improvement in pine (sections 2.3.2 and 3.4). This difference in behaviour of pine and beech is attributed to their different ultrastructures (Banks and Voulgaridis, 1980; Voulgaridis, 1980; Voulgaridis and Banks, 1979). The widely-set margo strands in the bordered pit pores of pine prove inferior to the closely-meshed microfibrillar structures in the pit membranes in beech in enabling the build up of a coherent resin film. On addition of wax in the solution, hydrophobic action improves the water repellency in pine phenomenally, whereas, an effective coating action in beech provides a limited scope for improvement with a hydrophobe.

The distribution of water repellents in long wood specimens depends on the mode of treatment. Simple immersion treatment for a short period deposits significant amounts of both resin and wax in the outer one centimetre or so of the treated wood (section 3.4). Treatment under a mild vacuum distributes the water repellents to a greater depth. Increasing treatment periods, however, have been found to lead to increased loading in about the outer 6cm of the treated wood rather than extending the treatment zone to a greater depth. Increased and probably more effective distribution of water repellents with increasing treatment periods provide enhanced water repellency with both resin and resin/wax treatments. However, the initial effectiveness in the superficially treated specimens is lost to a great extent on weathering (sections 3.4.2

and 3.4.3). Wood degrade in the outer zone, having a shallow treatment, exposes untreated areas. This factor, coupled with the loss of wood/deposit bond, leads to decreased performance in shallow treated specimens to levels approaching that of untreated wood. The interior wood, about two centimetres from the exposed end was hardly affected by the weathering process. With increasing severity of weathering the resin-treated specimens slowly go on losing some water repellency even in the interior. This points to the possibility of loss of wood/resin bond from water conduction pathways due to the stresses set up by cyclic soaking and drying. In resin/wax treated specimens loss of water repellent effectiveness is limited, by and large, to the exposed zone (sections 3.4.3 and 3.4.4). The hydrophobic property of the wax probably inhibits water entry beyond the degraded zone. With both increasing concentration and treatment period increased resistance is offered by the interior wood against water ingress. In either case, it seems, better distribution is responsible for this superior performance. Even with resin only treatment where loss of effectiveness can occur to some depth, the performance remains better when treatment is with a more concentrated solution or carried out for a longer immersion period (sections 2.3.2 and 3.4).

The increased initial effectiveness observed in long specimens with increasing solution absorption and consequently more effective distribution is also apparent in specimens treated with monitored doses of water repellents. However, surface enrichment occurs, probably due to surface forces set up during solvent evaporation and water repellent effectiveness in long specimens depends mostly on the efficiency with which the surface zone can repel the ingress of water, especially in resin-treated specimens. Quantitative estimation of water repellent distribution in treated long specimens has confirmed the distribution pattern of surface enrichment assessed by measuring the swelling rate of successive sections cut from the long sticks (section 3.5.2). The distribution and effectiveness of water repellents at various distances from the treated end have been shown to be significantly correlated initially (section 3.7).

However, the loss of water repellent effectiveness after weathering becomes most pronounced in about the first centimetre of the exposed end. The loss of water repellent substances in this zone after weathering is also comparatively more than in the interior sections. But the loss of water repellent substances in this critical zone does not seem to be of the order of the loss of water repellent effectiveness. Thus the pronounced decrease in water repellent effectiveness in the exposed end zone compared to the comparatively less loss of deposits seems to be due to the combination of extensive breakdown of wood structure and weakening of wood/deposit bond. Significant correlationship of data of the interior wood, beyond this zone, supports this idea.

The large specimens show the cumulative effect of weathering throughout the entire specimen, whereas the wafers cut from long specimens show water repellency in accordance with the physical state of wood and wood/deposit interface of the small zones represented by the wafers. As a result, the water repellent behaviour of long specimens initially represent approximately the state of treatment of the outer exposed zone only. After exposure to the weather, the pattern changes roughly to that of the state of the wood substrate and the wood-water repellent bond immediately beyond the degraded zone. The assessment of water repellency with successive wafer specimens presents the general picture of maximal loss of effectiveness in the outer 1 or 2 centimetres (exposed zone) and little loss in the interior. Thus the outer zone, initially most effective in resisting water uptake, after a period of weathering, becomes less effective than some interior sections. With resin/wax treatment, even after extensive loss of water repellency in the outer (exposed) zone, in most cases, that zone retains significant water repellent effectiveness.

Loss of water repellency in the treated wood has been shown to be mainly due to wood degrade and loss of wood/deposit bond near to the exposed end. The action of weathering, especially the detrimental effects of rapid water absorption and desorption due to changes in weather,builds up a stress in wood which gives rise to wood degrade in the form of checks, splits and end grain defibrillation. This, in its turn, acts with the detrimental effects of moisture in weakening the wood/deposit bond. Effective stabilization of wood substrate may largely prevent end-grain wood degrade with weathering. At the same time, the contribution of wood degrade to the breakdown of wood-water repellent bond may be significantly reduced. The contribution of moisture itself in weakening the wood-water repellent bond can best be prevented by covalent bonding of the water repellents to the wood cell walls. Unlike weakly bonded deposits, such a bond should resist the degrading actions of water and heat.

Alkylchlorosilanes and alkylene oxides covalently bonded to wood cell walls have been shown to act differently to one another. The former has been shown to provide a good degree of water repellency and the latter excellent dimensional stabilization. The hydrophobicity of silanes has been suggested to be due partly to the blocking of hydrophilic hydroxyl groups in wood and partly to the presence of hydrophobic alkyl groups pointed outwards from the treated wood surface. The possibility of formation of some hydrophobic siloxane polymers in the treatment has been suggested by Rochow (1951). But scanning electron microscopic studies conducted on silanated wood showed no deposits on the wood or bordered pit areas.

Epoxy-treated wood should provide some water repellency due to the bonding of the alkane chain to the wood hydroxyl groups. A certain degree of reduction of water uptake is evident, due probably to cell wall bulking and possibly to blocking of natural polymer hydroxyl groups, but little water repellency is shown by the treated specimens. It has been argued (sections 4.2.1.3 and 4.2.2.3) that the formation of a secondary hydroxyl group attached to the alkane chain probably counteracts any water repellent effect by the treatment.

Electron micrographs of epoxy treated wood show no polymer in the lumen (Rowell, 1975), dispelling the idea of short chain polymer formation (Schuerch, 1968) with the new hydroxyl group.

The value of silanation as a process of imparting water repellency to treated wood is reduced because of the level of wood degradation brought about by the reaction, probably due to the production of HCl as a by-product. While silanated wood shows little sign of bond degrade on weathering, wood degrade causes substantial loss of water repellency on long exposure. On the other hand, the remarkable bond strength and dimensional stability exhibited by epoxy treated wood do not achieve any noteworthy water repellency.

Resin treatment, by its coating action, reduces the rate of water uptake, but does not impart any water repellency. Silanation imparts a good degree of water repellency in wood. Both the treatments, however, depend heavily on the effectiveness of treatment in the exposed zone. In the case of resin, the deposit is concentrated heavily in the first one centimetre of the treated end, the concentration slowly decreasing inwards. In the case of silanation, the reaction has to be kept at a low level to avoid excessive wood degradation. Hence only a surface treatment is realistically feasible. Thus, in both the cases degradation of the most effectively treated zone leads to reduction in water repellency. Resin treated wood suffers from the dual degradation of wood substrate and wood/deposit bond with weathering. Silanated wood affords a persistent wood/silane bond but suffers due to the wood degradation effect. In both the cases, weathering degrade of the wood opens up untreated or uncoated areas connecting the outside environment to the interior of the specimens.

Addition of a wax component to the resin solution endows the latter with water repellent properties when applied to wood. The distribution of resin/wax, like resin only, is dependent upon solution concentration and treatment period and the pattern is also the same. The water repellency imparted to wood by resin-wax varies greatly with the level of treatment. Hydrophobicity in silanated wood is achieved with a mild treatment with very small quantity of chemicals.

Time to quarter swell in pine and beech wafers treated with 10% resin + 0.5% wax is approximately 20 and 50 minutes (Voulgaridis, 1980). Similar pine wafers treated by vapour and liquid phase silanation show the following results:

Silane (ml)		Reaction Phase	Time to Half Swell (min)
Dimethyl-dichloro-silane	(2)	Vapour	51
	(10)	"	102
	(2)	Liquid	45
	(10)	"	80
n-Dodecyl trichloro-silane	(10)	"	139

Voulgaridis (1980) reports that resin/wax treated pine specimens retain only a third of the initial effectiveness after 20 wet/dry cycles (initial $T_{\frac{1}{2}}$ 37 minutes, after 20 cycles 13 minutes). The data given below for silanated wood compare favourably with the data cited above.

Silane	Reaction Phase	$T_{\frac{1}{2}}$ (minutes) and no. of cycles			
		0	5	10	20
Dimethyldichlorosilane	Liquid	80	73	62	47
	Vapour	90	78	63	37
n-Dodecyl trichlorosilane	Liquid	122	97	84	84

Initial water absorption data for 15cm long pine specimens vacuum treated with 10% resin + 1% wax and 10% resin + 10% wax and for similar sticks treated with dimethyl dichlorosilane in liquid and vapour phases are given below:

Water Repellent	Treating conditions	Water Absorption (%) After 2 hrs. soak	Water Absorption (%) After 24 hrs. soak
$R_{10}W_1$	3m, 200mm Hg vac	1.0	3.1
$R_{10}W_{10}$	3m, 200mm Hg vac	0.4	1.5
DMDCS	Liquid phase	1.1	4.7
DMDCS	Vapour phase	0.6	3.0
Control	-	79.8	110.9

From the data it is clear that initial water repellency of silanated long specimens is similar to that of resin/wax treated wood. On prolonged soaking the resin-wax treatment proves to be superior. Nonetheless, the water repellent effectiveness of silanated wood even after 20 soak/dry cycles remains far superior to that of untreated controls.

It has been seen that in spite of the excellent dimensional stability imparted by epoxy treatment it does not lead to significant water repellent effectiveness (sections 4.2.1.3 and 4.2.2.3). Attempts to treat the epoxy treated specimens with resin/wax solution proved difficult due to poor solution absorption. These specimens (double treated) absorbed less than 1% resin-wax solution, based on their weight after epoxy treatment. They showed reasonable water repellency, but not to the level achieved by normal resin/wax water repellent treatment. No evidence of improved resistance to weathering due to this double treatment was produced. However, as pointed out in section 4.3.2, this may be due to the low level of solution absorption achieved. Further work is needed before the possibility of achieving improved water repellent performance as a result of substrate stabilization can be realized.

PART 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 Conclusions

(1) Water repellent formulations based on resin only provide protection to treated wood mainly by forming a coating film, the effectiveness of which depends on the degree of perfection of the film. Resin-wax formulations, on the other hand, imparts hydrophobicity to the treated wood. Long term effectiveness of both of them depends on the strength of their bonds with the wood substrate. Because of the ultrastructural differences in the pit pore openings, the coating effect is dominant in European beech, whereas the hydrophobic effect is of more importance in Corsican pine wood.

(2) On weathering, end treated long specimens lose their water repellent effectiveness mostly in the surface zone because of breakdown of wood structure and wood-water repellent bond. The interior zone has been shown to go on resisting water entry even after long exposure. The effectiveness of water repellent treatments was found to vary in accordance with the water repellent formulation concentration used. Progressively higher concentrations yielded progressively higher water repellent effects. Advancing simulated weathering progressively decreased water repellent effectiveness. The increased effectiveness of higher concentrations was evident even after simulated weathering.

(3) Distribution and water repellent effectiveness in long specimens was found to vary with the pressure differential used during treatment and the time they remained immersed in the water repellent solution. The hydrophobic effect of the resin-wax treatment was found to be much more effective than the coating effect of resin only treatment. Due to surface forces occurring during solvent evaporation a distribution gradient is formed in the end-treated long specimens, the treating end having the maximum concentration. The water repellent effectiveness along depth of treatment from the treated end was initially well correlated with the amount of water repellent deposit present.

With advancing simulated weathering the exposed surface zone was shown to lose a large part of its water repellency, whereas the interior zone was only slightly affected. Breakdown of the exposed zone was more noticeable in beech than in pine. Loss of water repellent substances followed the pattern of the loss of water repellent effectiveness during early stages of weathering. However, with advanced weathering, loss of water repellency became more pronounced than the loss of water repellent substance.

Contact angles formed by water on water repellent films of extracted water repellents on inert substrates manifest no obvious change along the depth of penetration or with simulated weathering.

(4) Chemically bonded water repellents provide protection to treated wood by blocking the water attracting sites and imparting hydrophobicity by presenting hydrophobic groups at the treated surface. Epoxy treatments carried out on pine wood gave rise to a significant reduction in water sorption and dimensional instabilities but did not impart any water repellency. Weathering was found to have little adverse effect on epoxy-treated wood, suggesting that the bonds formed are resistant to the simulated weathering process employed. Further treatment of epoxy-treated wood with resin-wax water repellent solution did not lead to a marked cumulative benefit deriving from the two treatments. In part, however, this may have been due to a failure to achieve high resin-wax loading in epoxy-treated wood.

(5) Excellent water repellent effectiveness was obtained with silanated wood. Wood degradation due to simulated weathering, however, led to loss of effectiveness, even though the wood-water repellent bond appeared to remain unaffected.

6.2 Suggestions for Further Work

This work has raised some topics which need further clarification to allow better understanding of the subject. Some of these topics are listed below:.

(1) Low melting point wax (49°C) was used in this study. Much higher temperature may develop in wood surface during warm and sunny periods. Wax softening may adversely affect the water repellent effectiveness and as such,experiments to investigate the performance of formulations based on higher melting point waxes are desirable.

(2) It seems that complete removal of carrier solvents from the treated wood takes an inordinately long time. Presence of traces of solvents may affect the water repellent effectiveness in wood. Experiments with highly volatile solvents, where complete solvent removal can be

guaranteed, are desirable. Solvent evaporation tends to give rise to distribution gradient with surface enrichment. Since loss of water repellent effectiveness depends to a great extent on the breakdown of the surface zone, investigation of systems allowing control of the degree of surface enrichment will be interesting.

(3) Loss of water repellent effectiveness seems to be associated with loss of wood-deposit bond strength coupled with dimensional instability of specimens. Silanes and epoxides partially overcome these effects. Search for a truly water repellent chemically bonding substance not having adverse side effects, may pay rich dividends.

(4) Chemically modified wood somewhat inhibits absorption of resin-wax solution. If such hindrance can be overcome, investigations of the performance of conventional water repellents applied to chemically stabilized wood, may help to illuminate the part played by dimensional instability in breaking down the wood-water repellent bond.

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APPENDIX I

Standard deviation values, where applicable, have been put in parentheses. For all treated specimens these values are based only on 3 individuals and as such have limited validity. They are cited simply to indicate the degree of variability. For control specimens the number of replicates have been separately mentioned.

Table 1. Rates of water absorption in Corsican pine and European beech control long-specimens (15x2x2cm coated on all but one transverse face) at various cycles (9 replicates)

Species and no. of cycles		Soaking time (minutes) and water absorption (1 standard deviation), %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
Pine	0	1.33 (0.09)	2.37 (0.19)	3.23 (0.23)	4.63 (0.31)	5.82 (0.38)	8.12 (0.49)	9.95 (0.62)	11.50 (0.71)	12.90 (0.78)	14.10 (0.86)	15.17 (0.89)	16.11 (0.94)	27.98 (2.04)
	5	1.76 (0.32)	2.54 (0.34)	3.71 (0.38)	4.98 (0.38)	6.11 (0.42)	8.67 (0.63)	10.29 (0.40)	11.99 (0.66)	13.62 (0.42)	14.90 (0.61)	16.05 (0.53)	17.90 (0.68)	31.22 (1.88)
	10	1.88 (0.28)	2.70 (0.24)	3.84 (0.52)	5.22 (0.83)	6.91 (0.53)	8.89 (1.14)	11.00 (0.88)	12.38 (1.24)	13.76 (1.04)	15.22 (0.35)	17.10 (0.70)	18.66 (0.51)	32.46 (1.36)
	20	2.02 (0.33)	2.82 (0.48)	3.88 (0.48)	5.35 (0.56)	7.00 (0.73)	8.96 (0.85)	11.15 (1.08)	12.48 (1.01)	14.00 (0.76)	15.38 (0.86)	17.18 (0.73)	18.95 (1.11)	33.22 (2.39)
Beech	0	0.57 (0.13)	1.13 (0.31)	1.60 (0.39)	2.11 (0.48)	2.43 (0.51)	2.95 (0.53)	3.39 (0.52)	3.85 (0.49)	4.24 (0.50)	4.77 (0.40)	5.21 (0.38)	5.60 (0.36)	12.85 (0.65)
	5	0.75 (0.20)	1.40 (0.24)	1.87 (0.26)	2.55 (0.25)	3.06 (0.34)	3.74 (0.58)	4.28 (0.56)	4.75 (0.67)	5.22 (0.76)	5.70 (0.78)	6.14 (0.73)	6.87 (0.82)	14.29 (1.29)
	10	0.88 (0.23)	1.65 (0.30)	2.20 (0.47)	2.68 (0.53)	3.12 (0.47)	4.01 (0.47)	4.89 (0.49)	5.67 (0.68)	6.15 (0.79)	6.59 (0.85)	6.98 (0.90)	7.34 (0.98)	14.89 (1.74)
	20	1.04 (0.16)	1.80 (0.29)	2.32 (0.43)	3.02 (0.55)	3.68 (0.76)	4.40 (0.87)	5.05 (0.68)	5.98 (0.62)	6.57 (0.72)	6.92 (0.58)	7.16 (0.55)	7.90 (0.75)	14.98 (1.10)

Table 2. Rates of water absorption in water repellent treated long specimens (15x2x2cm). Subscripts after R and W indicate percent solution concentration of resin and wax.

A. Corsican pine : before cycling

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.14 (0.02)	0.35 (0.04)	0.54 (0.10)	0.86 (0.09)	1.03 (0.18)	1.50 (0.20)	1.86 (0.25)	2.36 (0.16)	2.70 (0.14)	3.00 (0.28)	3.32 (0.32)	3.62 (0.18)	6.29 (0.41)
R_{11}	0.09 (0.02)	0.22 (0.04)	0.58 (0.05)	0.62 (0.05)	0.85 (0.20)	1.32 (0.24)	1.68 (0.30)	1.97 (0.28)	2.39 (0.30)	2.82 (0.32)	3.34 (0.26)	3.53 (0.30)	5.94 (0.58)
R_{12}	0.05 (0.02)	0.18 (0.03)	0.26 (0.04)	0.44 (0.05)	0.58 (0.05)	0.92 (0.12)	1.28 (0.16)	1.47 (0.26)	1.93 (0.26)	2.32 (0.18)	2.73 (0.20)	3.03 (0.22)	5.93 (0.78)
R_{15}	0.05 (0.02)	0.09 (0.03)	0.20 (0.05)	0.34 (0.05)	0.42 (0.10)	0.54 (0.08)	0.66 (0.12)	0.89 (0.14)	1.18 (0.12)	1.38 (0.12)	1.76 (0.22)	1.99 (0.23)	5.25 (0.54)
R_{20}	0.00 (0.00)	0.05 (0.01)	0.09 (0.03)	0.18 (0.04)	0.33 (0.04)	0.49 (0.09)	0.58 (0.10)	0.86 (0.12)	1.10 (0.14)	1.36 (0.22)	1.50 (0.18)	1.65 (0.26)	4.23 (0.48)
$R_{10}W_1$	0.02 (0.01)	0.10 (0.02)	0.14 (0.02)	0.18 (0:03)	0.24 (0.04)	0.32 (0.04)	0.42 (0.07)	0.52 (0.10)	0.61 (0.10)	0.78 (0.12)	0.85 (0.10)	0.96 (0.18)	3.11 (0.40)
$R_{10}W_2$	0.00 (0.00)	0.06 (0.02)	0.13 (0.02)	0.16 (0103)	0.18 (0.05)	0.26 (0.05)	0.34 (0.06)	0.48 (0.06)	0.56 (0.08)	0.71 (0.08)	0.77 (0.15)	0.84 (0.12)	2.81 (0.22)
$R_{10}W_5$	0.00 (0.00)	0.02 (0.01)	0.03 (0.01)	0.04 (0.01)	0.10 (0.02)	0.20 (0.04)	0.28 (0.06)	0.41 (0.05)	0.48 (0.06)	0.54 (0.05)	0.58 (0.06)	0.62 (0.13)	2.38 (0.20)
$R_{10}W_{10}$	0.00 (0.00)	0.00 (0.00)	0.02 (0.01)	0.04 (0.02)	0.05 (0.02)	0.08 (0.02)	0.12 (0.04)	0.20 (0.04)	0.24 (0.04)	0.28 (0.04)	0.32 (0.06)	0.36 (0.08)	1.51 (0.23)

Table 2 cont'd

B. Corsican pine : after 5 weathering cycles

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.15 (0.07)	0.37 (0.09)	0.71 (0.12)	1.08 (0.24)	1.27 (0.17)	1.78 (0.20)	2.30 (0.32)	2.88 (0.38)	3.36 (0.44)	3.92 (0.52)	4.67 (0.48)	5.25 (0.45)	8.76 (0.75)
R_{11}	0.18 (0.03)	0.26 (0.04)	0.60 (0.08)	0.89 (0.08)	1.23 (0.10)	1.55 (0.12)	2.07 (0.18)	2.65 (0.28)	3.25 (0.26)	3.82 (0.28)	4.55 (0.34)	5.02 (0.48)	8.34 (0.54)
R_{12}	0.15 (0.05)	0.25 (0.05)	0.48 (0.14)	0.56 (0.16)	0.83 (0.10)	1.24 (0.18)	1.62 (0.20)	2.02 (0.24)	2.56 (0.26)	3.08 (0.36)	3.94 (0.36)	4.40 (0.48)	8.00 (0.60)
R_{15}	0.10 (0.02)	0.18 (0.03)	0.38 (0.05)	0.55 (0.08)	0.76 (0.12)	1.00 (0.10)	1.28 (0.16)	1.66 (0.20)	2.18 (0.28)	2.74 (0.20)	3.22 (0.36)	3.76 (0.44)	7.19 (0.66)
R_{20}	0.09 (0.02)	0.20 (0.05)	0.32 (0.05)	0.58 (0.06)	0.78 (0.10)	1.10 (0.12)	1.35 (0.20)	1.55 (0.18)	1.80 (0.20)	2.28 (0.16)	2.69 (0.21)	3.00 (0.20)	6.16 (0.71)
$R_{10}W_1$	0.07 (0.02)	0.12 (0.02)	0.20 (0.05)	0.36 (0.06)	0.52 (0.08)	0.69 (0.10)	0.82 (0.12)	0.89 (0.10)	0.94 (0.14)	1.02 (0.12)	1.18 (0.14)	1.33 (0.15)	4.40 (0.28)
$R_{10}W_2$	0.06 (0.02)	0.08 (0.02)	0.12 (0.03)	0.22 (0.05)	0.36 (0.08)	0.48 (0.08)	0.66 (0.10)	0.80 (0.16)	0.92 (0.16)	1.08 (0.20)	1.12 (0.18)	1.15 (0.15)	3.50 (0.52)
$R_{10}W_5$	0.02 (0.01)	0.05 (0.01)	0.10 (0.02)	0.18 (0.03)	0.34 (0.05)	0.43 (0.06)	0.65 (0.08)	0.72 (0.10)	0.86 (0.10)	0.92 (0.12)	0.97 (0.12)	1.02 (0.12)	2.83 (0.20)
$R_{10}W_{10}$	0.00 (0.00)	0.05 (0.01)	0.09 (0.03)	0.11 (0.02)	0.15 (0.03)	0.25 (0.05)	0.38 (0.06)	0.46 (0.08)	0.50 (0.10)	0.54 (0.10)	0.56 (0.12)	0.58 (0.10)	2.78 (0.25)

Table 2 cont'd

C. Corsican pine : after 10 weathering cycles

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.24 (0.06)	0.48 (0.12)	0.86 (0.15)	1.08 (0.18)	1.33 (0.22)	1.82 (0.18)	2.17 (0.22)	2.58 (0.27)	3.10 (0.26)	3.86 (0.38)	4.60 (0.43)	5.13 (0.77)	8.28 (0.58
R_{11}	0.28 (0.04)	0.51 (0.05)	0.88 (0.08)	1.01 (0.10)	1.31 (0.12)	1.72 (0.20)	2.12 (0.23)	2.49 (0.22)	3.29 (0.25)	3.97 (0.27)	4.44 (0.38)	5.03 (0.96)	7.70 (0.38)
R_{12}	0.25	0.37	0.60	0.82	1.13	1.58	2.00	2.45	2.93	3.32	3.61	4.17 (0.22)	6.91 (0.17)
R_{15}	0.22 (0.04)	0.35 (0.05)	0.65 (0.05)	0.75 (0.06)	1.03 (0.08)	1.41 (0.10)	1.63 (0.12)	1.99 (0.12)	2.34 (0.22)	2.71 (0.33)	3.11 (0.35)	3.56 (0.54)	6.79 (0.49)
R_{20}	0.20 (0.04)	0.32 (0.04)	0.62 (0.06)	0.74 (0.08)	1.01 (0.12)	1.27 (0.10)	1.50 (0.14)	2.01 (0.12)	2.30 (0.15)	2.52 (0.17)	2.75 (0.20)	2.93 (0.25)	6.33 (0.65)
$R_{10}W_1$	0.12 (0.02)	0.18 (0.04)	0.27 (0.05)	0.34 (0.06)	0.46 (0.06)	0.68 (0.08)	0.84 (0.10)	0.95 (0.12)	1.01 (0.15)	1.16 (0.14)	1.31 (0.15)	1.47 (0.18)	3.85 (0.33)
$R_{10}W_2$	0.07 (0.01)	0.12 (0.02)	0.19 (0.04)	0.28 (0.05)	0.46 (0.05)	0.62 (0.09)	0.78 (0.10)	0.86 (0.14)	1.00 (0.10)	1.12 (0.16)	1.24 (0.12)	1.33 (0.14)	3.87 (0.35)
$R_{10}W_5$	0.05 (0.01)	0.10 (0.02)	0.20 (0.02)	0.25 (0.03)	0.33 (0.04)	0.47 (0.05)	0.53 (0.05)	0.58 (0.06)	0.62 (0.06)	0.71 (0.10)	0.82 (0.09)	0.91 (0.09)	2.28 (0.08)
$R_{10}W_{10}$	0.05 (0.01)	0.10 (0.02)	0.18 (0.02)	0.25 (0.03)	0.30 (0.05)	0.35 (0.05)	0.43 (0.06)	0.50 (0.05)	0.58 (0.13)	0.63 (0.15)	0.68 (0.14)	0.71 (0.18)	2.13 (0.26)

Table 2 cont'd

D. Corsican pine : after 20 weathering cycles

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.28 (0.04)	0.65 (0.08)	0.95 (0.10)	1.35 (0.12)	1.62 (0.18)	2.22 (0.25)	2.60 (0.22)	2.95 (0.15)	3.30 (0.27)	3.52 (0.34)	3.90 (0.43)	4.37 (0.54)	8.27 (1.06)
R_{11}	0.29 (0.04)	0.62 (0.04)	0.91 (0.12)	1.33 (0.10)	1.61 (0.16)	2.21 (0.18)	2.57 (0.20)	2.90 (0.28)	3.25 (0.30)	3.47 (0.32)	3.80 (0.44)	4.24 (0.52)	7.55 (1.24)
R_{12}	0.30 (0.05)	0.57 (0.08)	0.80 (0.08)	1.30 (0.10)	1.60 (0.20)	2.12 (0.23)	2.55 (0.32)	2.90 (0.35)	3.10 (0.20)	3.32 (0.41)	3.57 (0.46)	3.85 (0.69)	6.84 (0.82)
R_{15}	0.31 (0.05)	0.58 (0.08)	0.78 (0.10)	1.06 (0.12)	1.28 (0.13)	1.68 (0.12)	1.96 (0.18)	2.28 (0.26)	2.45 (0.24)	2.84 (0.32)	3.29 (0.45)	3.63 (0.56)	6.22 (0.93)
R_{20}	0.24 (0.04)	0.42 (0.07)	0.77 (0.12)	1.01 (0.22)	1.23 (0.20)	1.44 (0.24)	1.66 (0.32)	1.90 (0.24)	2.11 (0.25)	2.32 (0.31)	2.63 (0.32)	2.85 (0.41)	5.19 (0.62)
$R_{10}W_1$	0.10 (0.01)	0.22 (0.04)	0.28 (0.05)	0.43 (0.05)	0.49 (0.07)	0.71 (0.08)	0.85 (0.10)	0.92 (0.13)	0.98 (0.14)	1.06 (0.13)	1.11 (0.18)	1.20 (0.20)	3.70 (0.73)
$R_{10}W_2$	0.08 (0.01)	0.12 (0.02)	0.20 (0.04)	0.28 (0.04)	0.38 (0.05)	0.47 (0.05)	0.60 (0.06)	0.73 (0.07)	0.79 (0.08)	0.87 (0.10)	0.97 (0.08)	1.09 (0.06)	3.07 (0.42)
$R_{10}W_5$	0.08 (0.02)	0.12 (0.03)	0.20 (0.03)	0.22 (0.05)	0.32 (0.05)	0.42 (0.06)	0.52 (0.09)	0.63 (0.12)	0.78 (0.14)	0.82 (0.08)	0.94 (0.12)	1.02 (0.14)	2.49 (0.25)
$R_{10}W_{10}$	0.03 (0.01)	0.11 (0.02)	0.14 (0.02)	0.16 (0.04)	0.22 (0.03)	0.35 (0.05)	0.44 (0.07)	0.52 (0.08)	0.58 (0.12)	0.66 (0.16)	0.69 (0.15)	0.73 (0.17)	2.10 (0.18)

Table 2 cont'd

E. European beech : before weathering

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.01 (0.01)	0.03 (0.01)	0.05 (0.01)	0.08 (0.02)	0.16 (0.02)	0.22 (0.02)	0.32 (0.01)	0.42 (0.05)	0.49 (0.04)	0.59 (0.02)	0.65 (0.02)	0.70 (0.05)	2.26 (0.29)
R_{11}	0.01 (0.01)	0.01 (0.01)	0.06 (0.01)	0.10 (0.01)	0.12 (0.01)	0.17 (0.02)	0.23 (0.04)	0.34 (0.03)	0.38 (0.06)	0.44 (0.05)	0.51 (0.05)	0.59 (0.07)	1.85 (0.12)
R_{12}	0.01 (0.01)	0.03 (0.02)	0.10 (0.04)	0.11 (0.03)	0.13 (0.02)	0.18 (0.04)	0.25 (0.04)	0.33 (0.05)	0.37 (0.05)	0.42 (0.06)	0.49 (0.05)	0.56 (0.04)	1.83 (0.40)
R_{15}	0.00 (0.00)	0.03 (0.01)	0.05 (0.01)	0.07 (0.01)	0.14 (0.02)	0.16 (0.04)	0.19 (0.02)	0.22 (0.03)	0.26 (0.04)	0.33 (0.04)	0.41 (0.05)	0.48 (0.05)	1.54 (0.27)
R_{20}	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.09 (0.02)	0.14 (0.02)	0.16 (0.03)	0.18 (0.03)	0.24 (0.04)	0.27 (0.03)	0.32 (0.05)	0.38 (0.05)	0.41 (0.06)	1.24 (0.30)
$R_{10}W_1$	0.00 (0.00)	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.08 (0.02)	0.13 (0.03)	0.16 (0.04)	0.20 (0.02)	0.24 (0.03)	0.30 (0.04)	0.36 (0.04)	0.39 (0.04)	1.15 (0.15)
$R_{10}W_2$	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.04 (0.01)	0.06 (0.02)	0.11 (0.03)	0.16 (0.03)	0.21 (0.02)	0.25 (0.04)	0.29 (0.03)	0.34 (0.03)	0.38 (0.05)	1.17 (0.17)
$R_{10}W_5$	0.02 (0.01)	0.02 (0.01)	0.06 (0.02)	0.09 (0.03)	0.11 (0.02)	0.13 (0.03)	0.16 (0.04)	0.20 (0.02)	0.24 (0.02)	0.29 (0.03)	0.34 (0.03)	0.38 (0.03)	1.16 (0.13)
$R_{10}W_{10}$	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.06 (0.02)	0.10 (0.02)	0.16 (0.03)	0.20 (0.04)	0.25 (0.05)	0.28 (0.04)	0.32 (0.05)	1.08 (0.11)

Table 2 cont'd

F. European beech : after 5 weathering cycles

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.59 (0.05)	1.04 (0.07)	1.40 (0.12)	1.91 (0.20)	2.49 (0.23)	3.61 (0.26)	4.40 (0.24)	5.22 (0.19)	5.80 (0.26)	6.30 (0.30)	6.70 (0.36)	7.19 (0.42)	12.31 (0.60)
R_{11}	0.54 (0.10)	0.95 (0.12)	1.28 (0.20)	1.62 (0.16)	1.95 (0.22)	2.80 (0.13)	3.48 (0.18)	4.11 (0.21)	4.70 (0.22)	5.25 (0.17)	5.82 (0.24)	6.25 (0.26)	11.48 (0.33)
R_{12}	0.53 (0.06)	0.95 (0.10)	1.25 (0.12)	1.67 (0.16)	2.01 (0.19)	2.80 (0.18)	3.43 (0.22)	4.06 (0.30)	4.54 (0.29)	5.05 (0.41)	5.50 (0.39)	6.04 (0.48)	10.88 (0.33)
R_{15}	0.44 (0.05)	0.81 (0.10)	1.08 (0.18)	1.45 (0.16)	1.70 (0.18)	2.45 (0.22)	2.79 (0.28)	3.25 (0.21)	3.60 (0.30)	3.96 (0.31)	4.27 (0.34)	4.52 (0.37)	9.00 (0.36)
R_{20}	0.40 (0.06)	0.81 (0.08)	1.02 (0.08)	1.38 (0.10)	1.64 (0.10)	2.18 (0.14)	2.50 (0.12)	2.89 (0.18)	3.14 (0.16)	3.37 (0.21)	3.62 (0.07)	3.95 (0.23)	7.73 (0.66)
$R_{10}W_1$	0.14 (0.04)	0.20 (0.05)	0.27 (0.10)	0.32 (0.10)	0.47 (0.06)	0.63 (0.07)	0.77 (0.10)	0.91 (0.09)	1.04 (0.12)	1.18 (0.11)	1.26 (0.18)	1.39 (0.22)	3.39 (0.36)
$R_{10}W_2$	0.09 (0.03)	0.14 (0.04)	0.20 (0.05)	0.28 (0.06)	0.32 (0.06)	0.46 (0.10)	0.55 (0.12)	0.67 (0.16)	0.76 (0.15)	0.88 (0.11)	0.99 (0.20)	1.13 (0.31)	2.12 (0.35)
$R_{10}W_5$	0.05 (0.01)	0.10 (0.02)	0.12 (0.02)	0.14 (0.03)	0.17 (0.03)	0.32 (0.10)	0.40 (0.08)	0.47 (0.10)	0.52 (0.12)	0.57 (0.16)	0.65 (0.13)	0.74 (0.20)	2.01 (0.21)
$R_{10}W_{10}$	0.04 (0.01)	0.08 (0.02)	0.10 (0.02)	0.16 (0.02)	0.21 (0.03)	0.26 (0.05)	0.32 (0.07)	0.41 (0.08)	0.46 (0.10)	0.50 (0.10)	0.55 (0.08)	0.63 (0.10)	1.72 (0.30)

Table 2 cont'd

G. European beech : after 10 weathering cycles

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.70 (0.05)	1.40 (0.10)	1.85 (0.14)	2.24 (0.15)	2.65 (0.18)	3.53 (0.23)	4.06 (0.34)	4.62 (0.32)	5.07 (0.40)	5.52 (0.42)	5.98 (0.48)	6.52 (0.58)	11.83 (0.63)
R_{11}	0.67 (0.06)	1.41 (0.09)	1.81 (0.12)	2.23 (0.15)	2.67 (0.11)	3.57 (0.14)	4:08 (0.22)	4.60 (0.21)	5.11 (0.34)	5.55 (0.35)	5.87 (0.45)	6.22 (0.57)	10.40 (0.76)
R_{12}	0.50 (0.05)	1.14 (0.07)	1.60 (0.08)	1.96 (0.06)	2.35 (0.12)	3.06 (0.22)	3.45 (0.31)	3.86 (0.23)	4.23 (0.19)	4.53 (0.33)	4.82 (0.31)	5.20 (0.37)	9.23 (0.58)
R_{15}	0.49 (0.09)	1.11 (0.07)	1.47 (0.10)	1.77 (0.12)	2.08 (0.08)	2.75 (0.07)	3.23 (0.11)	3.48 (0.12)	3.82 (0.16)	4.25 (0.14)	4.70 (0.22)	5.08 (0.28)	9.19 (0.49)
R_{20}	0.32 (0.04)	0.79 (0.07)	1.13 (0.08)	1.38 (0.15)	1.63 (0.14)	2.21 (0.10)	2.60 (0.14)	2.98 (0.22)	3.37 (0.22)	3.75 (0.21)	4.06 (0.29)	4.39 (0.28)	9.13 (0.52)
$R_{10}W_1$	0.07 (0.02)	0.29 (0.05)	0.41 (0.08)	0.50 (0.12)	0.61 (0.11)	0.80 (0.12)	0.89 (0.15)	1.01 (0.19)	1.09 (0.22)	1.16 (0.28)	1.30 (0.32)	1.48 (0.39)	3.93 (0.31)
$R_{10}W_2$	0.07 (0.02)	0.20 (0.02)	0.24 (0.04)	0.27 (0.05)	0.35 (0.05)	0.49 (0.08)	0.60 (0.10)	0.71 (0.12)	0.80 (0.08)	0.89 (0.11)	0.98 (0.15)	1.17 (0.14)	3.22 (0.47)
$R_{10}W_5$	0.00 (0.00)	0.09 (0.03)	0.14 (0.04)	0.16 (0.05)	0.18 (0.05)	0.33 (0.05)	0.40 (0.09)	0.47 (0.10)	0.56 (0.12)	0.65 (0.14)	0.72 (0.12)	0.80 (0.12)	2.13 (0.13)
$R_{10}W_{10}$	0.00 (0.00)	0.07 (0.02)	0.09 (0.02)	0.11 (0.02)	0.13 (0.03)	0.24 (0.04)	0.29 (0.05)	0.33 (0.05)	0.37 (0.05)	0.41 (0.07)	0.46 (0.06)	0.59 (0.10)	1.73 (0.18)

Table 2 cont'd

H. European beech : after 20 weathering cycles

Treating solution	Soaking time (minutes) and rates of water absorption (1 standard deviation), %												
	1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	0.85 (0.05)	1.49 (0.10)	1.92 (0.14)	2.43 (0.18)	2.74 (0.22)	3.10 (0.17)	3.43 (0.26)	3.80 (0.20)	4.18 (0.22)	4.61 (0.30)	4.95 (0.37)	5.30 (0.38)	8.95 (0.56)
R_{11}	0.78 (0.12)	1.46 (0.17)	1.89 (0.14)	2.31 (0.19)	2.65 (0.21)	3.17 (0.27)	3.40 (0.29)	3.72 (0.34)	4.03 (0.23)	4.34 (0.28)	4.62 (0.34)	4.74 (0.43)	8.46 (0.32)
R_{12}	0.74 (0.15)	1.18 (0.08)	1.53 (0.18)	2.07 (0.17)	2.62 (0.18)	3.16 (0.22)	3.32 (0.20)	3.68 (0.26)	4.00 (0.22)	4.29 (0.40)	4.58 (0.42)	4.90 (0.46)	8.23 (0.44)
R_{15}	0.72 (0.08)	1.28 (0.07)	1.65 (0.12)	2.04 (0.14)	2.48 (0.14)	2.92 (0.20)	3.30 (0.22)	3.53 (0.30)	3.81 (0.33)	4.06 (0.35)	4.26 (0.38)	4.33 (0.44)	7.74 (0.33)
R_{20}	0.75 (0.08)	1.22 (0.15)	1.56 (0.18)	2.10 (0.20)	2.46 (0.22)	2.88 (0.28)	3.14 (0.35)	3.41 (0.32)	3.63 (0.30)	3.85 (0.38)	4.07 (0.40)	4.15 (0.42)	7.03 (0.54)
$R_{10}W_1$	0.12 (0.03)	0.23 (0.03)	0.41 (0.08)	0.60 (0.10)	0.81 (0.12)	1.19 (0.16)	1.43 (0.11)	1.68 (0.13)	1.82 (0.12)	1.93 (0.10)	1.99 (0.22)	2.04 (0.27)	4.48 (0.38)
$R_{10}W_2$	0.07 (0.02)	0.20 (0.03)	0.33 (0.06)	0.54 (0.08)	0.65 (0.08)	0.87 (0.10)	1.08 (0.08)	1.17 (0.12)	1.24 (0.18)	1.37 (0.16)	1.49 (0.24)	1.67 (0.32)	3.23 (0.43)
$R_{10}W_5$	0.05 (0.01)	0.07 (0.02)	0.09 (0.02)	0.15 (0.02)	0.25 (0.04)	0.38 (0.05)	0.42 (0.08)	0.49 (0.10)	0.55 (0.12)	0.68 (0.10)	0.77 (0.11)	0.86 (0.19)	1.83 (0.28)
$R_{10}W_{10}$	0.02 (0.01)	0.04 (0.01)	0.07 (0.01)	0.13 (0.02)	0.17 (0.05)	0.35 (0.04)	0.39 (0.06)	0.46 (0.07)	0.53 (0.07)	0.60 (0.07)	0.67 (0.08)	0.75 (0.08)	1.58 (0.15)

Table 3. Effect of heat-treatment on the water absorption of control 15cm long sticks before and after cycling (4 replicates)

		Soaking time (minutes) and rate of water absorption (1 stand. dev.) %								
Species	No. of cycles	15m	30m	45m	60m	75m	90m	105m	120m	720m
Pine	0	5.56 (0.67)	7.75 (0.78)	9.64 (1.51)	11.17 (1.80)	12.58 (1.77)	14.79 (2.01)	16.76 (2.26)	19.22 (3.00)	27.88 (1.92)
	5	6.88 (0.48)	10.16 (0.46)	12.82 (1.81)	14.96 (2.06)	16.69 (2.48)	18.10 (2.75)	19.79 (3.32)	21.96 (3.62)	30.08 (6.58)
	10	7.53 (0.54)	11.22 (1.05)	13.79 (1.09)	15.84 (1.09)	16.84 (1.68)	18.95 (2.48)	20.48 (3.07)	21.94 (2.18)	33.64 (5.22)
	20	8.11 (1.62)	12.26 (2.36)	15.26 (3.02)	17.30 (3.35)	19.31 (3.73)	20.30 (3.97)	21.56 (4.43)	22.71 (4.92)	34.39 (5.66)
Beech	0	1.69 (0.31)	2.57 (0.46)	3.20 (0.60)	3.74 (0.70)	4.34 (0.80)	4.64 (0.84)	4.87 (0.82)	5.42 (1.0)	10.36 (1.16)
	5	1.94 (0.14)	2.82 (0.26)	4.06 (0.28)	5.01 (0.31)	5.69 (0.48)	6.27 (0.52)	6.86 (0.49)	7.42 (0.57)	10.69 (0.81)
	10	2.42 (0.24)	3.69 (0.29)	4.82 (0.29)	5.89 (0.43)	6.90 (0.39)	7.63 (0.31)	8.23 (0.63)	8.73 (0.58)	14.35 (0.76)
	20	2.80 (0.31)	3.92 (0.28)	5.12 (0.38)	6.22 (0.49)	7.18 (0.53)	7.91 (0.43)	8.67 (0.58)	9.01 (0.64)	14.89 (1.32)

Table 4. Time to half/quarter swell of wafer specimens cut along depth of treatment from variously treated cycled and uncycled long specimens (3 replicates)

A. Corsican pine : Time to half swell*: Before cycling

Treating solution**	Time to half/quarter swell (1 standard deviation),minutes						
	Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	5.27 (1.16)	3.35 (0.25)	2.4 (14.0)	2.3 (0.26)	1.47 (0.15)	0.80 (0.20)	0.63 (0.15)
R_{11}	6.47 (0.77)	4.4 (0.60)	3.6 (1.0)	2.3 (0.20)	1.53 (0.27)	0.80 (0.20)	0.83 (0.11)
R_{12}	7.36 (1.30)	5.2 (0.65)	4.4 (0.46)	2.87 (0.51)	1.93 (0.5)	1.37 (0.11)	1.03 (0.25)
R_{15}	8.87 (1.10)	6.47 (1.8)	4.67 (0.15)	2.97 (0.8)	2.00 (0.6)	1.73 (0.5)	1.2 (1.1)
R_{20}	9.53 (0.87)	7.90 (0.20)	5.43 (0.38)	3.17 (0.20)	2.63 (0.25)	1.90 (0.3)	1.40 (0.17)
$R_{10}-W_1$	44.0 (3.0)	33.8 (3.2)	22.07 (40.0)	16.3 (2.3)	12.0 (2.0)	8.3 (1.0)	5.8 (0.28)
$R_{10}-W_2$	66.3 (8.3)	46.3 (6.6)	31.3 (2.5)	22.0 (2.6)	14.67 (2.0)	9.3 (1.5)	7.8 (0.76)
$R_{10}-W_5$	166.0 (7.5)	137.6 (7.5)	122.6 (5.0)	101.6 (10.0)	86.0 (7.0)	66.0 (15.0)	42.0 (4.6)
$R_{10}-W_{10}$	228.0 (37.0)	185.0 (16.7)	139.6 (10.9)	110.0 (10.4)	95.6 (6.0)	75.6 (11.0)	63.0 (7.5)

* Time to half swell for untreated control wafers = 0.6 minute

** Subscripts after R and W indicate percentage of resin and wax

Table 4 cont'd

B. Corsican pine : Time to half swell : After 5 weathering cycles

Treating solution	Time to half/quarter swell (1 standard deviation),minutes						
	Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	3.9 (0.5)	3.3 (0.15)	2.7 (0.4)	2.4 (0.5)	1.8 (0.6)	0.87 (0.46)	0.8 (0.36)
R_{11}	5.08 (0.78)	4.23 (0.51)	3.4 (0.3)	2.23 (0.2)	1.6 (0.11)	0.8 (0.05)	0.8 (0.1)
R_{12}	6.14 (0.4)	5.0 (0.7)	4.1 (0.23)	2.8 (0.17)	1.7 (0.17)	1.6 (0.34)	1.3 (0.28)
R_{15}	6.97 (0.2)	5.6 (0.47)	4.7 (0.2)	3.2 (0.57)	2.2 (0.25)	1.3 (0.36)	1.3 (0.37)
R_{20}	8.0 (1.1)	6.27 (0.58)	5.4 (0.05)	4.37 (0.41)	3.43 (0.56)	2.0 (0.4)	1.3 (0.4)
$R_{10}-W_1$	35.8 (5.0)	30.0 (4.6)	21.6 (1.7)	17.4 (3.2)	11.0 (2.0)	6.3 (1.5)	4.7 (0.87)
$R_{10}-W_2$	55.8 (5.8)	41.2 (2.2)	27.5 (5.9)	19.13 (4.8)	16.9 (4.3)	11.1 (1.4)	8.1 (1.1)
$R_{10}-W_5$	149.5 (16.0)	145.0 (15.5)	126.8 (13.7)	107.0 (13.0)	90.1 (11.8)	67.5 (5.8)	52.8 (4.6)
$R_{10}-W_{10}$	203.0 (13.0)	178.0 (7.0)	146.2 (8.9)	111.5 (10.0)	89.7 (1.0)	70.5 (2.3)	63.67 (6.6)

Table 4 (cont'd)

C. Corsican pine : Time to half swell : After 10 weathering cycles

Treating solution	Time to half/quarter swell (1 standard deviation), minutes Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	3.93 (0.61)	3.47 (0.41)	2.83 (0.15)	2.13 (0.20)	1.5 (0.41)	0.77 (0.15)	0.76 (0.05)
R_{11}	4.9 (0.6)	3.87 (0.05)	3.03 (0.20)	2.32 (0.28)	1.33 (0.38)	1.03 (0.15)	0.76 (0.05)
R_{12}	6.3 (1.2)	5.46 (0.53)	4.43 (0.60)	3.7 (0.78)	2.43 (0.38)	1.27 (0.25)	1.0 (0.2)
R_{15}	6.7 (0.98)	5.53 (0.32)	4.8 (0.5)	3.9 (0.36)	2.5 (0.20)	1.5 (0.5)	1.3 (0.35)
R_{20}	8.06 (2.2)	7.0 (0.66)	5.4 (0.58)	4.76 (0.45)	3.6 (0.53)	2.37 (0.63)	1.46 (0.15)
R_{10}-W_1	35.5 (1.8)	31.8 (1.9)	19.0 (2.0)	13.9 (0.9)	10.66 (1.5)	7.8 (1.7)	6.3 (1.5)
R_{10}-W_2	45.1 (3.8)	40.0 (2.64)	30.2 (3.4)	17.8 (1.07)	14.0 (0.87)	11.0 (2.0)	7.7 (1.5)
R_{10}-W_5	138.0 (9.0)	138.0 (6.5)	123.6 (5.5)	104.0 (10.5)	80.3 (8.5)	63.5 (7.5)	53.8 (5.6)
R_{10}-W_{10}	182.0 (9.0)	179.0 (24.9)	168.2 (17.4)	120.0 (10.0)	96.3 (7.4)	67.3 (8.5)	60.0 (13.0)

Table 4 (cont'd)

D. Corsican pine : Time to half swell : After 20 weathering cycles

Treating solution	Time to half/quarter swell (1 standard deviation), minutes						
	Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	3.77 (0.66)	3.8 (0.85)	2.9 (0.26)	2.4 (0.20)	1.7 (0.26)	1.2 (0.2)	8.0 (0.15)
R_{11}	4.5 (0.43)	4.7 (0.5)	3.37 (0.38)	2.8 (0.40)	2.1 (0.25)	1.56 (0.20)	0.96 (0.05)
R_{12}	6.03 (0.6)	5.5 (0.73)	3.9 (0.15)	3.2 (0.2)	2.3 (0.1)	1.46 (0.49)	1.0 (0.2)
R_{15}	6.0 (0.36)	6.0 (0.32)	4.16 (0.60)	3.4 (0.4)	2.2 (0.2)	1.5 (0.3)	1.06 (0.25)
R_{20}	6.4 (0.26)	6.5 (0.7)	5.6 (0.56)	4.4 (0.49)	3.3 (0.45)	2.2 (0.32)	1.2 (0.30)
$R_{10}-W_1$	30.5 (3.27)	30.7 (2.5)	20.7 (2.5)	13.9 (2.5)	10.0 (0.45)	7.5 (0.7)	6.26 (0.64)
$R_{10}-W_2$	41.5 (2.29)	40.3 (3.05)	29.0 (1.72)	19.16 (1.75)	14.66 (2.08)	10.1 (2.06)	7.16 (0.72)
$R_{10}-W_5$	127.0 (11.5)	128.0 (15.3)	116.6 (14.6)	93.0 (4.58)	75.6 (8.73)	62.3 (14.0)	59.0 (11.1)
$R_{10}-W_{10}$	180.6 (15.0)	182.2	169.0 (9.7)	133.0 (4.04)	88.7 (6.0)	6.6 (10.4)	64.5 (6.9)

Table 4 cont'd

E. European beech : Time to quarter swell* : Before cycling

Treating solution	Time to half/quarter swell (1 standard deviation), minutes						
	Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	31.25 (1.39)	22.3 (2.0)	19.46 (0.40)	16.4 (1.2)	15.7 (0.85)	13.0 (0.25)	11.4 (0.30)
R_{11}	32.6 (2.5)	24.2 (3.0)	20.7 (2.1)	17.6 (2.0)	16.5 (2.0)	14.0 (0.25)	12.0 (1.0)
R_{12}	33.7 (2.3)	25.4 (2.1)	21.2 (1.25)	18.6 (1.15)	17.8 (1.8)	14.4 (1.25)	13.0 (1.44)
R_{20}	37.3 (4.25)	25.7 (2.0)	22.8 (0.86)	18.8 (0.76)	17.6 (1.5)	15.0 (0.53)	13.8 (0.51)
$R_{10}-W_1$	45.0 (4.36)	33.6 (5.13)	27.8 (5.75)	25.0 (7.2)	19.9 (5.55)	16.7 (2.37)	14.3 (3.3)
$R_{10}-W_2$	46.3 (7.2)	35.0 (4.58)	28.2 (1.6)	25.8 (2.8)	19.9 (2.1)	17.1 (3.2)	14.1 (1.15)
$R_{10}-W_5$	49.9 (3.1)	38.5 (2.78)	29.3 (4.93)	26.8 (4.16)	21.6 (1.5)	18.7 (1.5)	15.0 (1.5)
$R_{10}-W_{10}$	96.6 (20.1)	56.0 (10.1)	43.7 (6.65)	29.9 (5.87)	24.3 (3.13)	19.6 (0.53)	15.2 (0.58)

* Time to quarter swell for untreated control wafers = 2.5 minutes

Table 4 cont'd

F. European beech : Time to quarter swell : After 5 weathering cycles

Treating solution	Time to half/quarter swell (1 standard deviation), minutes						
	Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	17.56 (1.35)	21.16 (2.36)	17.7 (1.5)	14.3 (1.15)	10.2 (1.0)	9.8 (0.59)	7.9 (0.38)
R_{11}	17.70 (0.80)	23.10 (0.85)	29.6 (1.5)	17.3 (1.5)	14.3 (1.10)	11.7 (1.09)	8.4 (0.32)
R_{12}	18.6 (1.44)	23.86 (3.12)	20.8 (2.2)	18.1 (2.0)	16.8 (1.32)	14.0 (1.02)	10.7 (0.88)
R_{15}	19.7 (2.08)	24.66 (2.60)	22.2 (1.25)	18.3 (1.55)	17.0 (1.22)	15.6 (2.29)	11.8 (1.75)
R_{20}	23.7 (2.93)	30.06 (3.4)	23.84 (2.57)	20.2 (1.50)	18.8 (1.10)	16.3 (1.04)	14.2 (0.82)
$R_{10}W_1$	25.4 (0.6)	34.0 (4.35)	27.7 (1.5)	22.8 (1.23)	20.0 (1.08)	16.92 (2.06)	15.0 (2.18)
$R_{10}W_2$	26.76 (1.72)	36.86 (3.6)	28.76 (1.75)	24.1 (2.05)	22.08 (2.90)	18.1 (1.85)	16.4 (1.68)
$R_{10}W_5$	31.8 (3.07)	38.7 (4.0)	29.8 (1.70)	26.0 (2.05)	23.15 (3.0)	19.86 (1.57)	17.68 (0.97)
$R_{10}W_{10}$	48.2 (4.36)	45.8 (5.2)	42.0 (4.3)	35.6 (3.0)	28.0 (2.28)	22.5 (2.18)	20.0 (1.26)

Table 4 cont'd

G. European beech : Time to quarter swell : After 10 weathering cycles

Treating solution	Time to half/quarter swell (1 standard deviation),minutes						
	Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	9.43 (1.6)	19.33 (2.66)	20.1 (1.15)	16.6 (0.60)	13.7 (0.88)	10.2 (1.04)	7.9 (0.76)
R_{11}	10.3 (1.2)	20.2 (1.9)	20.1 (1.15)	17.4 (0.67)	14.13 (1.02)	12.76 (2.85)	11.2 (1.27)
R_{12}	11.56 (1.6)	21.0 (2.18)	21.0 (1.8)	19.4 (1.63)	15.7 (0.96)	13.8 (0.77)	11.9 (1.6)
R_{15}	12.89 (1.46)	23.5 (2.5)	22.3 (1.5)	20.7 (1.64)	18.2 (1.7)	15.6 (1.97)	12.7 (1.4)
R_{20}	13.10 (2.23)	26.86 (1.87)	23.8 (1.8)	21.2 (1.75)	20.3 (0.76)	16.5 (2.0)	14.3 (2.25)
$R_{10}W_1$	17.2 (1.28)	29.8 (1.82)	27.5 (1.87)	24.5 (1.25)	20.8 (1.49)	17.0 (0.75)	15.2 (0.80)
$R_{10}W_2$	18.7 (1.8)	31.2 (3.35)	27.8 (1.26)	25.56 (1.6)	21.4 (0.93)	18.4 (1.4)	16.8 (0.76)
$R_{10}W_5$	22.42 (2.1)	35.9 (4.0)	30.7 (3.3)	28.4 (1.6)	24.4 (2.12)	20.3 (1.9)	18.6 (1.78)
$R_{10}W_{10}$	33.5 (3.08)	44.8 (2.62)	39.3 (2.70)	32.1 (2.6)	25.6 (2.10)	22.8 (1.39)	19.3 (1.5)

Table 4 cont'd

H. European beech : Time to quarter swell : After 20 weathering cycles

Treating solution	Time to half/quarter swell (1 standard deviation),minutes						
	Specimen number and position along depth of treatment from treated end (mm)						
	1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
R_{10}	4.8 (0.45)	18.06 (3.17)	18.2 (2.9)	16.0 (2.9)	14.0 (2.28)	10.5 (1.3)	7.6 (0.65)
R_{11}	7.6 (2.0)	19.8 (3.22)	18.3 (5.8)	16.2 (2.2)	15.0 (1.5)	13.1 (1.6)	9.7 (1.5)
R_{12}	8.2 (2.6)	20.16 (2.9)	19.2 (3.1)	17.3 (2.5)	15.8 (0.64)	13.9 (1.0)	11.4 (1.7)
R_{15}	9.56 (2.0)	22.3 (2.7)	20.86 (2.0)	18.76 (1.1)	16.46 (0.76)	13.98 (0.9)	12.1 (1.8)
R_{20}	10.3 (1.66)	24.6 (1.2)	22.10 (1.27)	19.6 (1.44)	17.7 (2.36)	14.5 (1.5)	13.8 (1.25)
$R_{10}W_1$	12.3 (2.0)	27.8 (1.89)	26.5 (1.5)	22.6 (1.76)	19.2 (1.69)	16.56 (2.51)	15.0 (2.5)
$R_{10}W_2$	14.7 (1.4)	30.2 (1.85)	26.9 (1.3)	22.8 (2.16)	21.4 (1.5)	18.2 (1.07)	14.4 (2.5)
$R_{10}W_5$	18.2 (1.82)	31.7 (2.5)	28.0 (3.54)	25.16 (3.5)	23.3 (2.6)	20.1 (2.46)	16.56 (1.9)
$R_{10}W_{10}$	19.8 (2.0)	37.4 (1.89)	32.5 (1.75)	29.24 (1.76)	25.7 (1.69)	22.6 (2.51)	20.9 (1.5)

APPENDIX II

Table 1. Water Absorption of Water Repellent Treated Corsican Pine Long Sticks Before Cycling (3 Replicates)

Treatment (minute)	Water Repellent %	Soaking Period (minutes) and Water Absorption ± Standard Deviation, %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
½ (dip)	10 Resin	0.14 (0.10)	0.38 (0.12)	0.56 (0.12)	0.88 (0.10)	1.20 (0.20)	1.70 (0.22)	1.92 (0.18)	2.54 (0.22)	2.92 (0.24)	3.34 (0.30)	3.80 (0.36)	4.22 (0.42)	8.28 (0.50)
½ (vac)		0.14 (0.02)	0.32 (0.04)	0.51 (0.12)	0.76 (0.09)	0.95 (0.20)	1.38 (0.22)	1.78 (0.26)	2.18 (0.22)	2.56 (0.24)	3.02 (0.28)	3.42 (0.32)	3.54 (0.36)	7.28 (0.42)
1 (vac)		0.09 (0.02)	0.22 (0.04)	0.38 (0.04)	0.60 (0.08)	0.81 (0.08)	1.22 (0.20)	1.56 (0.22)	1.86 (0.28)	2.21 (0.30)	2.69 (0.32)	3.13 (0.30)	3.62 (0.36)	7.07 (0.38)
3 (vac)		0.07 (0.01)	0.25 (0.02)	0.39 (0.07)	0.50 (0.07)	0.75 (0.09)	0.90 (0.14)	1.08 (0.13)	1.30 (0.13)	1.58 (0.16)	1.71 (0.18)	1.87 (0.20)	2.30 (0.20)	6.65 (0.34)
5 (vac)		0.05 (0.01)	0.21 (0.02)	0.31 (0.05)	0.45 (0.04)	0.69 (0.05)	0.84 (0.10)	1.03 (0.08)	1.24 (0.07)	1.55 (0.14)	1.73 (0.18)	1.86 (0.23)	2.21 (0.28)	6.42 (0.49)
10 (vac)		0.04 (0.02)	0.21 (0.02)	0.30 (0.09)	0.43 (0.10)	0.53 (0.08)	0.76 (0.13)	1.00 (0.10)	1.20 (0.14)	1.30 (0.11)	1.60 (0.12)	1.80 (0.15)	2.10 (0.10)	5.02 (0.38)
½ (dip)	10 Resin + 10 Wax	0.05 (0.01)	0.13 (0.02)	0.15 (0.03)	0.16 (0.02)	0.18 (0.05)	0.28 (0.05)	0.34 (0.05)	0.52 (0.06)	0.62 (0.09)	0.75 (0.08)	0.83 (0.10)	0.90 (0.12)	3.41 (0.38)
½ (vac)		0.02 (0.01)	0.13 (0.01)	0.13 (0.02)	0.15 (0.02)	0.21 (0.03)	0.26 (0.05)	0.39 (0.05)	0.47 (0.07)	0.56 (0.08)	0.74 (0.12)	0.80 (0.10)	0.85 (0.18)	2.69 (0.26)
1 (vac)		0.00 (0.00)	0.00 (0.00)	0.03 (0.01)	0.10 (0.02)	0.20 (0.04)	0.23 (0.06)	0.35 (0.05)	0.45 (0.07)	0.50 (0.09)	0.62 (0.14)	0.70 (0.12)	0.75 (0.12)	2.52 (0.24)
3 (vac)		0.00 (0.00)	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.09 (0.02)	0.21 (0.05)	0.31 (0.06)	0.40 (0.06)	0.57 (0.09)	0.60 (0.10)	0.64 (0.12)	0.68 (0.12)	2.04 (0.16)
5 (vac)		0.00 (0.00)	0.00 (0.00)	0.02 (0.01)	0.05 (0.01)	0.07 (0.05)	0.19 (0.06)	0.28 (0.06)	0.39 (0.10)	0.45 (0.08)	0.48 (0.10)	0.52 (0.12)	0.55 (0.12)	1.70 (0.16)
10 (vac)		0.00 (0.00)	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.09 (0.02)	0.18 (0.03)	0.25 (0.05)	0.34 (0.07)	0.34 (0.10)	0.35 (0.08)	0.42 (0.10)	0.47 (0.12)	1.40 (0.20)

Table 1 continued: Water Absorption After 5 Cycles (Corsican Pine)

Treatment (minute)	Water Repellent %	Soaking Period (minutes) and Water Absorption ± Standard Deviation, %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
½ (dip)	R_{10}	0.39 (0.09)	0.87 (0.15)	1.44 (0.18)	2.05 (0.20)	2.68 (0.12)	3.62 (0.30)	4.36 (0.16)	6.18 (0.24)	7.65 (0.22)	8.59 (0.23)	9.57 (0.33)	10.48 (0.36)	21.87 (0.67)
½ (vac)		0.40 (0.12)	0.67 (0.14)	0.90 (0.10)	1.25 (0.12)	1.66 (0.15)	2.28 (0.16)	2.97 (0.15)	3.69 (0.22)	4.40 (0.28)	5.04 (0.36)	5.65 (0.41)	6.30 (0.48)	15.02 (0.82)
1 (vac)		0.36 (0.10)	0.62 (0.08)	0.88 (0.22)	1.00 (0.18)	1.37 (0.21)	1.96 (0.25)	2.58 (0.30)	3.23 (0.33)	3.84 (0.41)	4.40 (0.28)	4.95 (0.36)	5.60 (0.44)	14.53 (1.05)
3 (vac)		0.35 (0.10)	0.58 (0.15)	0.84 (0.14)	1.03 (0.10)	1.32 (0.16)	1.66 (0.20)	2.44 (0.27)	3.01 (0.23)	3.50 (0.19)	3.95 (0.30)	4.51 (0.35)	5.15 (0.38)	13.45 (0.63)
5 (vac)		0.25 (0.05)	0.49 (0.08)	0.78 (0.10)	1.01 (0.18)	1.24 (0.12)	1.47 (0.16)	1.66 (0.23)	2.64 (0.28)	3.36 (0.29)	4.04 (0.45)	4.42 (0.39)	4.98 (0.67)	12.62 (0.81)
10 (vac)		0.14 (0.08)	0.35 (0.10)	0.68 (0.11)	0.90 (0.23)	1.20 (0.16)	1.38 (0.20)	1.57 (0.15)	2.23 (0.35)	2.81 (0.42)	3.41 (0.46)	3.91 (0.52)	4.68 (0.41)	10.66 (1.86)
½ (dip)	$R_{10}W_{10}$	0.06 (0.02)	0.42 (0.05)	0.66 (0.10)	0.78 (0.13)	1.12 (0.14)	1.46 (0.18)	1.83 (0.20)	2.26 (0.22)	3.01 (0.32)	3.42 (0.28)	3.68 (0.36)	4.05 (0.41)	9.87 (0.67)
½ (vac)		0.06 (0.02)	0.30 (0.10)	0.57 (0.14)	0.68 (0.08)	1.06 (0.12)	1.34 (0.22)	1.68 (0.28)	2.02 (0.12)	2.54 (0.30)	2.77 (0.26)	3.26 (0.32)	3.62 (0.31)	8.02 (0.61)
1 (vac)		0.05 (0.01)	0.22 (0.10)	0.48 (0.10)	0.66 (0.15)	0.80 (0.14)	1.16 (0.12)	1.40 (0.18)	1.81 (0.17)	2.05 (0.15)	2.29 (0.22)	2.67 (0.17)	3.10 (0.17)	6.40 (0.34)
3 (vac)		0.05 (0.01)	0.15 (0.03)	0.27 (0.05)	0.47 (0.08)	0.65 (0.10)	0.72 (0.10)	1.17 (0.12)	1.24 (0.14)	1.73 (0.14)	2.08 (0.19)	2.20 (0.16)	2.26 (0.18)	4.62 (0.26)
5 (vac)		0.05 (0.01)	0.05 (0.01)	0.20 (0.05)	0.24 (0.04)	0.38 (0.08)	0.56 (0.10)	0.62 (0.12)	0.88 (0.12)	0.96 (0.13)	1.16 (0.10)	1.38 (0.18)	1.70 (0.24)	3.85 (0.22)
10 (vac)		0.00 (0.00)	0.03 (0.01)	0.17 (0.05)	0.23 (0.05)	0.26 (0.08)	0.45 (0.10)	0.47 (0.12)	0.51 (0.10)	0.60 (0.13)	0.67 (0.10)	0.76 (0.12)	1.12 (0.12)	3.07 (0.18)

Table 1 continued: Water Absorption After 10 Cycles (Corsican Pine)

Treatment (minute)	Water Repellent %	Soaking Period (minutes) and Water Absorption ± Standard Deviation, %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
½ (dip)	R_{10}	0.42 (0.12)	1.37 (0.17)	1.83 (0.16)	2.24 (0.14)	3.18 (0.22)	4.64 (0.22)	5.43 (0.23)	6.61 (0.27)	7.67 (0.28)	8.56 (0.34)	9.59 (0.49)	10.75 (0.67)	22.84 (1.18)
½ (vac)		0.40 (0.10)	0.90 (0.16)	1.15 (0.20)	1.52 (0.21)	1.76 (0.24)	2.16 (0.26)	2.80 (0.30)	3.62 (0.42)	4.94 (0.43)	4.94 (0.48)	5.88 (0.50)	6.45 (0.47)	14.98 (0.82)
1 (vac)		0.38 (0.12)	0.66 (0.12)	0.94 (0.20)	1.28 (0.19)	1.68 (0.20)	2.14 (0.22)	2.61 (0.26)	3.25 (0.31)	3.88 (0.32)	4.45 (0.32)	5.05 (0.42)	5.78 (0.48)	14.60 (1.70)
3 (vac)		0.32 (0.10)	0.60 (0.14)	0.84 (0.15)	1.13 (0.18)	1.40 (0.22)	1.68 (0.22)	2.42 (0.18)	2.98 (0.17)	3.72 (0.28)	4.36 (0.32)	4.77 (0.41)	5.30 (0.52)	13.38 (1.08)
5 (vac)		0.28 (0.08)	0.54 (0.15)	0.77 (0.12)	1.08 (0.10)	1.26 (0.14)	1.54 (0.14)	2.20 (0.18)	2.66 (0.22)	3.23 (0.21)	3.95 (0.26)	4.48 (0.19)	4.92 (0.28)	12.70 (0.67)
10 (vac)		0.20 (0.05)	0.47 (0.10)	0.68 (0.12)	0.95 (0.12)	1.21 (0.15)	1.40 (0.20)	2.00 (0.25)	2.42 (0.22)	3.01 (0.22)	3.58 (0.40)	4.06 (0.28)	4.62 (0.44)	10.89 (0.77)
½ (dip)	$R_{10}W_{10}$	0.16 (0.05)	0.62 (0.08)	0.95 (0.17)	1.23 (0.16)	1.53 (0.17)	2.04 (0.11)	2.44 (0.12)	2.91 (0.22)	3.28 (0.20)	3.72 (0.23)	4.15 (0.23)	4.42 (0.24)	10.39 (0.55)
½ (vac)		0.14 (0.05)	0.58 (0.12)	1.08 (0.12)	1.34 (0.16)	1.63 (0.16)	1.80 (0.15)	2.02 (0.20)	2.28 (0.20)	2.28 (0.26)	3.03 (0.22)	3.42 (0.28)	3.65 (0.36)	8.21 (0.82)
1 (vac)		0.06 (0.03)	0.18 (0.08)	0.37 (0.10)	0.96 (0.18)	1.28 (0.16)	1.42 (0.10)	1.87 (0.14)	2.06 (0.12)	2.44 (0.14)	2.88 (0.13)	3.12 (0.17)	3.37 (0.22)	6.80 (0.88)
3 (vac)		0.05 (0.01)	0.10 (0.05)	0.19 (0.06)	0.28 (0.10)	0.40 (0.08)	0.67 (0.10)	0.92 (0.12)	1.16 (0.11)	1.49 (0.12)	1.85 (0.14)	2.18 (0.17)	2.48 (0.20)	4.82 (0.42)
5 (vac)		0.03 (0.01)	0.04 (0.01)	0.09 (0.03)	0.19 (0.05)	0.24 (0.05)	0.40 (0.08)	0.68 (0.10)	0.97 (0.10)	1.10 (0.09)	1.26 (0.12)	1.60 (0.12)	1.94 (0.14)	4.60 (0.40)
10 (vac)		0.00 (0.00)	0.04 (0.00)	0.08 (0.01)	0.16 (0.02)	0.24 (0.05)	0.31 (0.04)	0.44 (0.10)	0.71 (0.10)	0.83 (0.11)	1.11 (0.08)	1.48 (0.12)	1.56 (0.16)	3.18 (0.43)

Table 1 continued: Water Absorption After 20 Cycles (Corsican Pine)

Treatment (Minute)	Water Repellent %	Soaking Period (minutes) and Water Absorption ± Standard Deviation, %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
½ (dip)	R_{10}	0.61 (0.14)	1.31 (0.11)	1.73 (0.14)	2.28 (0.20)	3.26 (0.22)	4.69 (0.25)	5.50 (0.37)	6.67 (0.47)	7.78 (0.40)	8.69 (0.44)	9.65 (0.48)	10.85 (0.52)	22.90 (1.35)
½ (vac)		0.44 (0.12)	o.82 (0.18)	1.20 (0.20)	1.48 (0.26)	1.88 (0.30)	2.30 (0.34)	2.87 (0.32)	3.60 (0.40)	4.32 (0.43)	4.92 (0.48)	5.72 (0.50)	6.48 (0.48)	15.08 (0.88)
1 (vac)		0.38 (0.18)	0.58 (0.10)	0.97 (0.10)	1.30 (0.24)	1.64 (0.21)	2.28 (0.24)	3.00 (0.21)	3.61 (0.23)	4.05 (0.30)	4.44 (0.35)	5.21 (0.38)	6.14 (0.42)	14.81 (0.83)
3 (vac)		0.31 (0.10)	0.54 (0.10)	0.77 (0.11)	0.98 (0.12)	1.18 (0.15)	1.63 (0.13)	2.02 (0.18)	2.52 (0.30)	3.15 (0.14)	3.88 (0.23)	4.65 (0.28)	5.34 (0.33)	13.85 (0.68)
5 (vac)		0.27 (0.05)	0.49 (0.14)	0.72 (0.14)	0.90 (0.10)	1.07 (0.19)	1.48 (0.21)	1.87 (0.22)	2.43 (0.22)	2.99 (0.25)	3.69 (0.20)	4.22 (0.26)	4.91 (0.28)	12.70 (0.56)
10 (vac)		0.24 (0.10)	0.40 (0.16)	0.65 (0.16)	0.86 (0.18)	1.04 (0.15)	1.36 (0.17)	1.74 (0.18)	2.32 (0.25)	2.79 (0.21)	3.42 (0.25)	4.17 (0.38)	4.57 (0.40)	10.86 (0.68)
½ (dip)	$R_{10}W_{10}$	0.25 (0.10)	0.42 (0.15)	0.78 (0.17)	1.13 (0.16)	1.44 (0.17)	1.74 (0.21)	1.94 (0.22)	2.24 (0.22)	2.49 (0.20)	2.98 (0.23)	3.42 (0.25)	3.82 (0.24)	9.30 (0.55)
½ (vac)		0.14 (0.05)	0.38 (0.12)	0.75 (0.12)	1.08 (0.16)	1.34 (0.16)	1.63 (0.15)	1.87 (0.20)	2.02 (0.20)	2.28 (0.26)	2.66 (0.22)	3.03 (0.28)	3.45 (0.36)	8.20 (0.80)
1 (vac)		0.08 (0.02)	0.20 (0.08)	0.37 (0.10)	0.82 (0.18)	1.28 (0.16)	1.42 (0.10)	1.80 (0.14)	1.98 (0.12)	2.20 (0.14)	2.60 (0.13)	2.43 (0.17)	3.20 (0.22)	6.82 (0.84)
3 (vac)		0.05 (0.01)	0.10 (0.05)	0.19 (0.06)	0.28 (0.10)	0.40 (0.08)	0.67 (0.10)	0.92 (0.12)	1.16 (0.11)	1.49 (0.12)	1.85 (0.14)	2.18 (0.17)	2.45 (0.20)	4.96 (0.42)
5 (vac)		0.03 (0.01)	0.04 (0.01)	0.09 (0.03)	0.19 (0.05)	0.24 (0.10)	0.40 (0.08)	0.68 (0.10)	0.97 (0.12)	1.10 (0.09)	1.26 (0.12)	1.60 (0.12)	1.94 (0.14)	4.80 (0.40)
10 (vac)		0.00 (0.00)	0.04 (0.00)	0.08 (0.01)	0.16 (0.02)	0.24 (0.05)	0.31 (0.08)	0.44 (0.10)	0.71 (0.10)	0.83 (0.11)	1.11 (0.08)	1.48 (0.12)	1.56 (0.16)	3.48 (0.43)

Table 2 Water Absorption of Water Repellent Treated Beech Long Specimens (3 Replicates) Before Cycling (10% Resin = R_{10} and 10% Resin + 10% Wax = $R_{10}W_{10}$)

Water Repellent %	Quantity (ml)	Soaking Period (minute) and Water Absorption ± Standard Deviation, %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	1	0.06 (0.02)	0.12 (0.03)	0.16 (0.05)	0.21 (0.06)	0.28 (0.08)	0.52 (0.10)	0.70 (0.10)	0.94 (0.12)	1.10 (0.10)	1.30 (0.13)	1.48 (0.12)	1.65 (0.10)	3.66 (0.40)
	2	0.06 (0.02)	0.10 (0.02)	0.13 (0.03)	0.20 (0.05)	0.24 (0.04)	0.38 (0.06)	0.56 (0.08)	0.71 (0.10)	0.82 (0.10)	0.98 (0.12)	1.18 (0.10)	1.40 (0.12)	3.05 (0.48)
	3	0.05 (0.01)	0.08 (0.02)	0.12 (0.03)	0.18 (0.04)	0.20 (0.05)	0.32 (0.05)	0.40 (0.08)	0.58 (0.06)	0.66 (0.06)	0.78 (0.08)	0.92 (0.10)	1.12 (0.10)	2.70 (0.44)
	5	0.04 (0.01)	0.08 (0.02)	0.10 (0.02)	0.14 (0.04)	0.20 (0.04)	0.26 (0.05)	0.28 (0.05)	0.50 (0.06)	0.58 (0.08)	0.66 (0.08)	0.80 (0.08)	0.98 (0.10)	2.21 (0.37)
$R_{10}W_{10}$	1	0.04 (0.01)	0.05 (0.01)	0.08 (0.02)	0.12 (0.02)	0.14 (0.03)	0.18 (0.04)	0.22 (0.06)	0.34 (0.05)	0.42 (0.05)	0.50 (0.08)	0.68 (0.10)	0.76 (0.10)	1.84 (0.46)
	2	0.02 (0.01)	0.04 (0.01)	0.06 (0.02)	0.08 (0.02)	0.10 (0.02)	0.16 (0.04)	0.22 (0.05)	0.30 (0.05)	0.40 (0.06)	0.52 (0.08)	0.62 (0.08)	0.70 (0.08)	1.11 (0.20)
	3	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.08 (0.02)	0.10 (0.02)	0.15 (0.03)	0.20 (0.05)	0.26 (0.05)	0.34 (0.06)	0.44 (0.08)	0.52 (0.10)	0.62 (0.12)	1.18 (0.18)
	5	0.00 (0.00)	0.00 (0.00)	0.02 (0.01)	0.04 (0.01)	0.06 (0.01)	0.08 (0.02)	0.14 (0.02)	0.22 (0.02)	0.30 (0.05)	0.34 (0.05	0.38 (0.06)	0.48 (0.08)	1.02 (0.15)

Table 2 continued: Water Absorption After 5 Cycles (European Beech)

Water Repellent %	Quantity (ml)	Soaking Period (minute) and Water Absorption ± Standard Deivation, %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	1	0.34 (0.01)	0.78 (0.18)	1.30 (0.07)	1.66 (0.20)	2.04 (0.11)	2.58 (0.25)	3.20 (0.29)	3.88 (0.18)	4.35 (0.17)	4.93 (0.37)	5.10 (0.07)	5.49 (0.34)	11.52 (2.13)
	2	0.27 (0.08)	0.50 (0.12)	0.89 (0.17)	1.13 (0.21)	1.43 (0.22)	1.96 (0.19)	2.48 (0.18)	2.88 (0.35)	3.53 (0.25)	3.89 (0.26)	4.23 (0.09)	4.43 (0.21)	9.65 (0.22)
	3	0.27 (0.09)	0.49 (0.09)	0.83 (0.18)	0.98 (0.13)	1.27 (0.17)	1.75 (0.40)	2.19 (0.20)	2.60 (0.35)	3.04 (0.23)	3.46 (0.16)	3.79 (0.10)	3.83 (0.12)	9.00 (0.25)
	5	0.21 (0.00)	0.41 (0.02)	0.67 (0.02)	1.02 (0.05)	1.21 (0.12)	1.55 (0.12)	1.90 (0.15)	2.13 (0.07)	2.40 (0.17)	2.69 (0.10)	2.78 (0.15)	2.96 (0.14)	6.41 (0.33)
$R_{10}W_{10}$	1	0.14 (0.04)	0.27 (0.05)	0.63 (0.16)	0.71 (0.13)	0.84 (0.21)	1.07 (0.07)	1.39 (0.11)	1.57 (0.12)	1.79 (0.08)	2.01 (0.14)	2.25 (0.05)	2.40 (0.09)	6.00 (0.13)
	2	0.14 (0.05)	0.27 (0.08)	0.32 (0.09)	0.46 (0.07)	0.80 (0.18)	0.89 (0.12)	1.13 (0.10)	1.33 (0.12)	1.48 (0.11)	1.60 (0.09)	1.70 (0.17)	1.77 (0.16)	4.30 (0.48)
	3	0.08 (0.02)	0.12 (0.03)	0.33 (0.03)	0.37 (0.03)	0.43 (0.05)	0.56 (0.06)	0.64 (0.05)	0.73 (0.11)	0.91 (0.10)	0.97 (0.06)	1.05 (0.06)	1.14 (0.11)	2.87 (0.29)
	5	0.03 (0.02)	0.06 (0.02)	0.11 (0.02)	0.15 (0.03)	0.21 (0.04)	0.27 (0.03)	0.35 (0.03)	0.40 (0.03)	0.46 (0.01)	0.52 (0.04)	0.60 (0.06)	0.72 (0.08)	2.28 (0.30)

Table 2 continued: Water Absorption After 10 Cycles (European Beech)

Water Repellent %	Quantity (ml)	Soaking Period (minute) and Water Absorption ± Standard Deviation, %												
		1	3	5	10	15	30	45	60	75	90	105	120	720
R_{10}	1	0.39 (0.09)	0.84 (0.21)	1.28 (0.12)	1.69 (0.22)	2.10 (0.10)	2.86 (0.13)	3.58 (0.12)	4.12 (0.34)	4.71 (0.35)	5.15 (0.06)	5.61 (0.36)	6.14 (0.23)	11.90 (0.35)
	2	0.48 (0.06)	0.88 (0.06)	1.42 (0.10)	1.80 (0.11)	2.25 (0.03)	2.90 (0.21)	3.48 (0.13)	4.08 (0.37)	4.48 (0.21)	4.91 (0.12)	5.43 (0.22)	5.83 (0.22)	11.70 (0.24)
	3	0.44 (0.13)	0.81 (0.12)	1.35 (0.15)	1.66 (0.13)	2.02 (0.22)	2.64 (0.18)	3.25 (0.15)	3.82 (0.20)	4.25 (0.22)	4.82 (0.21)	5.33 (0.19)	5.78 (0.24)	11.16 (0.43)
	5	0.35 (0.05)	0.80 (0.09)	1.18 (0.13)	1.63 (0.23)	1.96 (0.10)	2.58 (0.23)	3.15 (0.14)	3.63 (0.17)	4.07 (0.30)	4.69 (0.03)	5.11 (0.33)	5.60 (0.23)	10.99 (0.40)
$R_{10}W_{10}$	1	0.21 (0.04)	0.29 (0.04)	0.48 (0.05)	0.66 (0.05)	0.84 (0.10)	1.30 (0.16)	1.53 (0.06)	1.70 (1.20)	2.00 (0.09)	2.39 (0.24)	2.49 (0.26)	2.78 (0.20)	7.08 (0.24)
	2	0.16 (0.04)	0.27 (0.07)	0.33 (0.06)	0.47 (0.07)	0.52 (0.07)	0.80 (0.17)	0.89 (0.11)	1.09 (0.08)	1.17 (0.09)	1.38 (0.09)	1.53 (0.09)	1.91 (0.14)	4.54 (0.20)
	3	0.13 (0.05)	0.16 (0.02)	0.22 (0.04)	0.31 (0.04)	0.39 (0.04)	0.53 (0.07)	0.67 (0.06)	0.73 (0.08)	0.81 (0.08)	0.93 (0.06)	1.04 (0.05)	1.10 (0.05)	2.92 (0.19)
	5	0.09 (0.02)	0.12 (0.02)	0.18 (0.04)	0.29 (0.05)	0.34 (0.04)	0.49 (0.05)	0.56 (0.08)	0.65 (0.04)	0.80 (0.09)	0.83 (0.09)	0.90 (0.08)	0.95 (0.06)	2.57 (0.25)

Table 2 continued: Water Absorption After 20 Cycles (European Beech)

Water Repellent %	Quantity (ml)	Soaking Period (minute) and Water Absorption ± Standard Deviation, %												
		1	3	5	10	15	30	45	60	75	90	105.	120	720
R_{10}	1	0.65 (0.03)	1.28 (0.06)	1.62 (0.17)	2.09 (0.26)	2.58 (0.08)	3.30 (0.20)	3.70 (0.17)	4.15 (0.16)	4.63 (0.14)	4.98 (0.19)	5.32 (0.18)	5.58 (0.20)	11.42 (0.38)
	2	0.51 (0.08)	1.05 (0.12)	1.38 (0.10)	1.82 (0.08)	2.14 (0.16)	2.81 (0.08)	3.32 (0.20)	3.73 (0.31)	3.99 (0.59)	4.70 (0.19)	5.07 (0.18)	5.41 (0.10)	11.24 (0.42)
	3	0.51 (0.09)	1.09 (0.05)	1.44 (0.04)	1.87 (0.15)	2.17 (0.16)	2.72 (0.35)	3.37 (0.17)	3.75 (0.27)	4.22 (0.08)	4.69 (0.13)	5.01 (0.05)	5.30 (0.13)	10.92 (0.47)
	5	0.52 (0.09)	1.08 (0.14)	1.43 (0.13)	1.87 (0.09)	2.19 (0.17)	2.77 (0.28)	3.49 (0.14)	3.74 (0.26)	4.32 (0.07)	4.69 (0.21)	5.05 (0.07)	5.33 (0.11)	10.50 (0.30)
$R_{10}W_{10}$	1	0.17 (0.03)	0.35 (0.03)	0.48 (0.05)	0.67 (0.14)	0.90 (0.11)	1.24 (0.13)	1.49 (0.11)	1.63 (0.14)	1.97 (0.20)	2.24 (0.14)	2.45 (0.12)	2.63 (0.17)	6.29 (0.38)
	2	0.10 (0.00)	0.32 (0.13)	0.48 (0.06)	0.62 (0.02)	0.68 (0.07)	1.05 (0.13)	1.26 (0.13)	1.36 (0.07)	1.58 (0.04)	1.69 (0.02)	1.79 (0.08)	1.99 (0.10)	4.96 (0.16)
	3	0.06 (0.02)	0.15 (0.04)	0.23 (0.03)	0.40 (0.05)	0.52 (0.06)	0.60 (0.06)	0.86 (0.11)	0.96 (0.03)	1.09 (0.05)	1.18 (0.07)	1.27 (0.05)	1.43 (0.12)	3.65 (0.13)
	5	0.04 (0.00)	0.05 (0.01)	0.08 (0.02)	0.24 (0.02)	0.34 (0.07)	0.47 (0.04)	0.59 (0.03)	0.63 (0.04)	0.78 (0.02)	0.81 (0.01)	0.87 (0.02)	0.90 (0.01)	2.57 (0.20)

Table 3 Gravimetric Estimation of Extracted Resin Deposit Along Depth of Treatment in Corsican Pine Long Specimens After Various Weathering Cycles (Mean of 3 Replicates)

Treating period (min)	No. of Cycles	Specimen nos. (and position from treated end, mm) and quantity of extractives (gm)						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
½ (dip)	0	0.0522	0.0106	0.0028	0.0028	0.0015	0.0013	0.0010
½ (vac)		0.0855	0.0262	0.0226	0.0208	0.0207	0.0208	0.0165
1 (vac)		0.0963	0.0311	0.0258	0.0242	0.0234	0.0246	0.0236
3 (vac)		0.1103	0.0498	0.0338	0.0328	0.0304	0.0296	0.0279
5 (vac)		0.1382	0.0608	0.0477	0.0445	0.0388	0.0396	0.0371
10 (vac)		0.1466	0.0694	0.0483	0.0489	0.0418	0.0390	0.0379
½ (dip)	5	0.0458	0.0103	0.0097	0.0060	0.0051	0.0046	
½ (vac)		0.0772	0.0266	0.0228	0.0177	0.0150	0.0151	
1 (vac)		0.0802	0.0331	0.0301	0.0229	0.0197	0.0184	
3 (vac)		0.0943	0.0538	0.0409	0.0345	0.0308	0.0300	
5 (vac)		0.1090	0.0583	0.0433	0.0353	0.0320	0.0317	
10 (vac)		0.1143	0.0638	0.0564	0.0519	0.0462	0.0433	
½ (dip)	10	0.0493	0.0191	0.0158	0.0121	0.0087	0.0098	
½ (vac)		0.0699	0.0303	0.0181	0.0175	0.0168	0.0120	
1 (vac)		0.0805	0.0385	0.0300	0.0213	0.0200	0.0186	
3 (vac)		0.0929	0.0507	0.0413	0.0398	0.0337	0.0329	
5 (vac)		0.1124	0.0635	0.0483	0.0416	0.0384	0.0358	
10 (vac)		0.1157	0.0671	0.0510	0.0421	0.0396	0.0389	
½ (dip)	20	0.0453	0.0169	0.0135	0.0104	0.0055	0.0056	
½ (vac)		0.0645	0.0307	0.0193	0.0190	0.0174	0.0160	
1 (vac)		0.0822	0.0386	0.0239	0.0228	0.0194	0.0192	
3 (vac)		0.0909	0.0474	0.0417	0.0322	0.0278	0.0285	
5 (vac)		0.1018	0.0597	0.0497	0.0420	0.0365	0.0330	
10 (vac)		0.1177	0.0639	0.0535	0.0453	0.0420	0.0385	

Table 3 continued: Estimation of Resin-Wax In Pine

Treating period (min)	No. of Cycles	Specimen nos. (and position from treated end, mm) and quantity of extractives (gm)						
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)	7(51)
½ (dip)	0	0.0713	0.0207	0.0115	0.0113	0.0120	0.0102	0.0113
½ (vac)		0.0900	0.0383	0.0332	0.0254	0.0196	0.0108	0.0108
1 (vac)		0.1188	0.0586	0.0521	0.0464	0.0324	0.0190	0.0175
3 (vac)		0.1405	0.0658	0.0599	0.0570	0.0536	0.0489	0.0425
5 (vac)		0.1773	0.0881	0.0649	0.0555	0.0524	0.0513	0.0439
10 (vac)		0.1780	0.0879	0.0652	0.0571	0.0529	0.0520	0.0444
½ (dip)	5	0.0593	0.0211	0.0105	0.0103	0.0076	0.0073	
½ (vac)		0.0761	0.0390	0.0300	0.0243	0.0146	0.0105	
1 (vac)		0.0914	0.0590	0.0493	0.0405	0.0341	0.0219	
3 (vac)		0.1178	0.0683	0.0543	0.0529	0.0484	0.0439	
5 (vac)		0.1335	0.0793	0.0602	0.0525	0.0504	0.0475	
10 (vac)		0.1404	0.0870	0.0640	0.0553	0.0504	0.0495	
½ (dip)	10	0.0567	0.0191	0.0111	0.0100	0.0087	0.0099	
½ (vac)		0.0766	0.0371	0.0309	0.0243	0.0163	0.0137	
1 (vac)		0.0906	0.0557	0.0443	0.0380	0.0262	0.0221	
3 (vac)		0.1060	0.0623	0.0546	0.0525	0.0504	0.0469	
5 (vac)		0.1259	0.0805	0.0601	0.0557	0.0510	0.0514	
10 (vac)		0.1313	0.0829	0.0639	0.0560	0.0500	0.0490	
½ (dip)	20	0.0553	0.0194	0.0087	0.0075	0.0062	0.0067	
½ (vac)		0.0759	0.0347	0.0297	0.0224	0.0130	0.0114	
1 (vac)		0.0848	0.0539	0.0458	0.0369	0.0321	0.0193	
3 (vac)		0.1077	0.0624	0.0564	0.0528	0.0485	0.0442	
5 (vac)		0.1222	0.0789	0.0637	0.0517	0.0508	0.0454	
10 (vac)		0.1288	0.0861	0.0640	0.0519	0.0526	0.0472	

Table 4. Gravimetric Estimation of Extracted Resin Deposit Along Depth of Treatment in European Beech Long Specimens After Various Weathering Cycles (Mean of 3 Replicates)

Water Repellent (ml)	No. of Cycles	Specimen nos. and position (mm) from treated end and extractives (gm)					
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)
1	0	0.0890	0.0318	0.0117	0.0106	0.0055	0.0055
2		0.1144	0.0504	0.0308	0.0244	0.0193	0.0158
3		0.1301	0.0660	0.0354	0.0293	0.0209	0.0179
5		0.1398	0.6950	0.0491	0.0336	0.0233	0.0189
1	5	0.0804	0.0282	0.0107	0.0109	0.0043	0.0043
2		0.1111	0.0413	0.0244	0.0155	0.0114	0.0103
3		0.1220	0.0664	0.0305	0.0191	0.0149	0.0115
5		0.1290	0.0688	0.0441	0.0249	0.0185	0.0168
1	10	0.0770	0.0286	0.0104	0.0072	0.0045	0.0040
2		0.1092	0.0395	0.0234	0.0153	0.0122	0.0103
3		0.1195	0.0610	0.0313	0.0206	0.0142	0.0142
5		0.1288	0.0670	0.0422	0.0243	0.0179	0.0147
1	20	0.0784	0.0250	0.0122	0.0077	0.0053	0.0057
2		0.1054	0.0421	0.0222	0.0138	0.0112	0.0100
3		0.1150	0.0627	0.0307	0.0205	0.0141	0.0165
5		0.1299	0.0669	0.0405	0.0242	0.0174	0.0142
		Estimation of Resin-Wax in European Beech					
1	0	0.0988	0.0559	0.0439	0.0274	0.0211	0.0164
2		0.0999	0.0680	0.0564	0.0454	0.0355	0.0301
3		0.1293	0.0908	0.0705	0.0543	0.0472	0.0395
5		0.1319	0.1016	0.0865	0.0706	0.0610	0.0515

Table 4 continued: Estimation of Resin-Wax in European Beech

Water Repellent (ml)	No. of Cycles	Specimen nos. and position (mm) from treated end and extractives (gm)					
		1(3)	2(11)	3(19)	4(27)	5(35)	6(51)
1	5	0.0842	0.0537	0.0423	0.0251	0.0209	0.0148
2		0.0908	0.0680	0.0576	0.0453	0.0370	0.0294
3		0.1218	0.0907	0.0706	0.0575	0.0472	0.0393
5		0.1250	0.1023	0.0879	0.0724	0.0588	0.0509
1	10	0.0785	0.0529	0.0392	0.0244	0.0205	0.0133
2		0.0910	0.0649	0.0560	0.0449	0.0348	0.0270
3		0.1125	0.0969	0.0732	0.0559	0.0467	0.0389
5		0.1225	0.1014	0.0875	0.0718	0.0567	0.0504
1	20	0.0756	0.0539	0.0400	0.0225	0.0214	0.0154
2		0.0908	0.0651	0.0543	0.0442	0.0340	0.0280
3		0.1116	0.0902	0.0722	0.0542	0.0461	0.0371
5		0.1256	0.1026	0.0883	0.0714	0.0566	0.0501

Table 5. Contact Angle of Water on Films on Glass Slides made by Extracted Resin-Wax From Treated and Variously Cycled Specimens. Corsican Pine Specimens (3 Replicates)

Treatment (min)	No. of Cycles	Contact Angle (mean and range in degrees) and specimen nos. (position in mm from the treated end)					
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)
½ (dip	0	105 (102-106)	108 (107-109)	56 (55-57)	53 (48-55)	52 (51-53)	51 (50-52
½ (vac)		104 (98-107)	107 (107-108)	107 (106-109)	108 (107-110)	107 (105-110)	106 (105-108)
1 (vac)		106 (104-108)	108 (106-111)	107 (106-109)	110 (109-111)	107 (106-108)	102 (96-105)
3 (vac)		107 (104-110)	106 (103-109)	102 (98-106)	108 (107-110)	108 (105-110)	109 (108-110)
5 (vac)		105 (100-110)	107 (107-108)	107 (106-108)	106 (103-110)	106 (104-108)	110 (109-111)
10 (vac)		109 (109-110)	109 (109-110)	110 (109-111)	110 (109-110)	110 (109-110)	106 (105-107)
½ (dip)	5	102 (101-103)	106 (105-107)	*	*	*	*
½ (vac)		110 (109-110)	112 (110-113)	112 (111-113)	110 (110-111)	60 (56-63)	39 (38-45)
1 (vac)		111 (110-111)	111 (110-112)	110 (109-111)	110 (109-110)	112 (111-113)	112 (112-113)
3 (vac)		110 (108-112)	110 (109-111)	110 (109-110)	111 (109-113)	108 (108-109)	110 (109-111)
5 (vac)		104 (103-105)	104 (103-105)	108 (107-109)	108 (107-109)	109 (107-109)	110 (110-111)
10 (vac)		107 (105-108)	109 (108-110)	109 (108-109)	108 (107-108)	108 (107-109)	108 (108-109)
½ (dip)	10	107 (105-108)	110 (109-111)	65 (64-66)	*	*	*
½ (vac)		108 (106-109)	107 (106-108)	103 (101-105)	*	*	*
1 (vac)		108 (106-109)	107 (107-108)	103 (101-105)	106 (104-108)	108 (107-109)	108 (107-109)
3 (vac)		110 (108-111)	110 (109-111)	104 (103-107)	107 (106-108)	105 (103-107)	110 (108-111)

Table 5 continued:

Treatment (min)	No. of Cycles	Contact Angle (mean and range in degrees) and specimen nos. (position in mm from the treated end)					
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)
5 (vac)	10	105 (104-107)	109 (108-109)	110 (109-111)	110 (109-111)	110 (109-110)	109 (109-110)
10 (vac)		108 (107-109)	109 (109-110)	109 (108-110)	109 (108-110)	109 (109-110)	109 (108-109)
½ (dip)	20	108 (107-109)	*	*	*	*	*
½ (vac)		100 (98-103)	110 (108-111)	110 (108-111)	*	*	*
1 (vac)		110 (108-111)	110 (109-111)	108 (106-110)	110 (108-111)	109 (110-111)	107 (106-108)
3 (vac)		107 (106-109)	108 (107-109)	107 (107-108)	108 (107-109)	107 (106-108)	108 (107-109)
5 (vac)		103 (102-105)	107 (106-108)	106 (105-108)	108 (106-109)	106 (105-107)	106 (105-107)
10 (vac)		106 (104-108)	104 (101-106)	105 (101-108)	105 (103-107)	106 (105-108)	107 (106-109)

Contact Angle of European Beech Specimens (3 Replicates)

Treatment (ml)	No of Cycles	Contact Angle and Range					
1	0	107 (106-107)	106 (106-107)	106 (105-107)	105 (104-106)	101 (99-102)	57 (54-60)
2		107 (106-107)	103 (102-104)	104 (103-104)	100 (99-101)	100 (96-101)	97 (96-98)
3		105 (104-106)	104 (104-105)	104 (103-105)	105 (104-105)	104 (104-105)	105 (105-106)
5		104 (103-105)	107 (106-107)	104 (102-105)	107 (106-107)	105 (104-105)	106 (105-107)
1	5	107 (106-108)	109 (107-110)	110 (109-111)	108 (107-108)	108 (107-109)	109 (108-110)
2		110 (109-110)	109 (109-110)	109 (106-111)	110 (109-111)	110 (109-110)	110 (109-111)
3		109 (108-110)	109 (108-109)	109 (109-110)	110 (109-110)	110 (108-112)	110 (109-111)
5		112 (110-113)	109 (108-110)	110 (109-111)	107 (106-109)	110 (108-111)	111 (110-111)

Table 5 continued:

Treatment (ml)	No. of Cycles	Contact Angle and Range					
		1(3)	2(11)	3(19)	4(27)	5(35)	6(43)
1	10	110 (110-111)	110 (110-111)	110 (110-111)	111 (110-112)	110 (108-111)	111 (110-112)
2		110 (108-112)	109 (109-111)	109 (108-111)	110 (109-111)	112 (111-114)	110 (108-111)
3		110 (109-110)	108 (107-109)	107 (106-109)	110 (108-111)	111 (109-112)	111 (110-112)
5		108 (107-109)	109 (107-111)	109 (107-111)	108 (106-109)	107 (107-108)	109 (108-110)
1	20	107 (106-108)	109 (107-110)	110 (109-111)	108 (107-110)	108 (107-110)	109 (107-110)
2		110 (109-111)	109 (108-109)	108 (106-109)	110 (109-110)	110 (109-111)	110 (110-111)
3		110 (108-111)	110 (108-111)	109 (109-110)	110 (109-110)	110 (108-112)	110 (109-111)
5		112 (110-113)	109 (108-111)	110 (109-111)	107 (106-108)	110 (108-111)	111 (110-112)

* Could not be measured because of rapidly spreading nature.