

# INDUCED SHRINKAGE AND STRUCTURAL REORGANISATION IN AMMONIA-TREATED WOOD OF CORSICAN PINE<sup>1</sup>

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## ABSTRACT

The ammonia-induced shrinkage of Corsican pine wood (*Pinus nigra* var. *calabrica*) was determined over a wide range of temperature, from the melting point ( $-78$  C) to above the critical temperature ( $132$  C) of liquid anhydrous ammonia. The swelling of wood was also measured but over a slightly more limited temperature range. The observed swelling and induced shrinkage of wood are explained in terms of two principal mechanisms: crimping and internal swelling of latewood and collapse of earlywood fibres. Confirmation of these mechanisms was provided by electron microscopy studies. Wood is most effectively plasticized between  $-5$  and  $-33$  C and this would seem to be the optimum temperature range for treating wood.

*Keywords:* *Pinus nigra* var. *calabrica*, ammonia treatments, cell-wall crimping, internal swelling, collapse, plasticization, ray parenchyma, shrinkage, anatomy.

## INTRODUCTION

Treatment of wood with liquid anhydrous ammonia is a very mild chemical process, resulting in the formation of amides, amines, and ammonium salts within the wood and in the transformation of the crystalline cellulose lattice from cellulose I to cellulose III (Lewin and Roldan 1971). However, the same treatment also results in drastic physical changes in the structure of wood.

The solvent characteristics of ammonia resemble those of water and comparisons are invariably made of the relative effects of treating wood with water and with ammonia. However, the principal differences between the two solvents should be noted (Jolly and Hallada 1965; Parham 1971a). The excellent solvent characteristics of water depend almost exclusively on its very high dipole moment and its ability to form hydrogen bonds, whereas the solvent characteristics of ammonia are equally dependent on its somewhat weaker hydrogen bonding capacity, due to its lower dipole moment, and on its significant dispersion forces. The latter makes ammonia a more appropriate solvent for large, nonpolar organic molecules. Further, the basic character of ammonia means that carboxylic acids, alcohols, and phenols (all of which possess acidic hydrogen atoms) are highly soluble in ammonia (in many cases it is difficult to distinguish the effects of basicity from the effects of hydrogen bonding). These characteristics make ammonia a much superior solvent for lignin than is water. Further, ammonia is able to hydrogen bond with the entire cellulosic fraction of the cell wall, penetrating and swelling even the crystalline microfibrils. Thus ammonia can completely penetrate wood fibres at the molecular level, separating the molecular chains and

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causing the wood to become plastic, to soften, and to swell; but, because the ammonia adsorption process is essentially physical rather than chemical it is reversible, and the wood regains its original rigidity and other physical characteristics when the ammonia is evaporated.

The effect of ammonia on the physical structure of wood was first noted by Stamm (1955). The softening or plasticizing of wood, accompanied by only the mildest of chemical reactions, indicated that such a treatment could be used by industry as an alternative process to the steam bending of wood (Schuerch 1964; Davidson 1969). It could be used to densify and mould low quality wood for the manufacture of such items as gears, bearings, consumer products, as well as mine timbers (Bersinsh 1971). Pulping experiments using liquid ammonia under pressure (O'Connor 1972) and treatments of bisulphite pulps (Kibblewhite and Kerr 1978; Kerr et al. 1978) also suggest that ammonia might have an important role to play in this industry. In every case the essential feature is that the wood is processed while it is in a plasticized state and that all species of wood can be treated in a similar manner.

There is one major difference between the behaviour of wood in water and in ammonia. Generally on redrying water-swollen wood the wood returns to its original oven-dry dimensions, whereas ammonia-swollen wood shrinks to below its original oven-dry size. In this paper dimensional changes are based on the original oven-dry state of wood, and therefore:

Swelling in ammonia (or water) = swelling from the original oven-dry state to the fully swollen state

Ammonia-induced shrinkage = shrinkage below the original oven-dry state.

The general objective of the present work was to observe the response of a single species of wood (Corsican pine, *Pinus nigra* var. *calabrica*) to a comprehensive series of liquid anhydrous ammonia treatments covering a very wide range of temperature in order to identify the optimum conditions for treating wood.

#### EXPERIMENTAL

Small blocks of Corsican pine sapwood measuring 15 mm in the longitudinal and tangential directions were machined on the radial faces to exactly four annual rings: usually, the radial thickness was close to 15 mm ( $\pm 5$  mm maximum variation). The blocks were water-saturated to relieve any stresses produced during machining and then oven-dried at 105 C for three days, after which they were weighed and their dimensions measured. Over 400 specimens were required.

Collection of the main items of data was designed around a completely randomized block (Bailey 1959). Nine specimens were treated at a time at one of eight temperatures, each treatment being duplicated five times. Each set of blocks was retreated for a second and a third time at the same temperature. The temperatures chosen were  $-78$ ,  $-33$ ,  $-5$ ,  $25$ ,  $55$ ,  $85$ ,  $115$  and  $145$  C.  $-78$  and  $-33$  C correspond to the melting and boiling points, respectively, of ammonia.

Basically the treatment consisted of immersing the oven-dried blocks in ammonia at  $-33$  C, adjusting the temperature to the desired value and leaving for a further twenty-four hours. The liquid ammonia was then decanted off and the absorbed/adsorbed ammonia allowed to evaporate at a controlled rate before

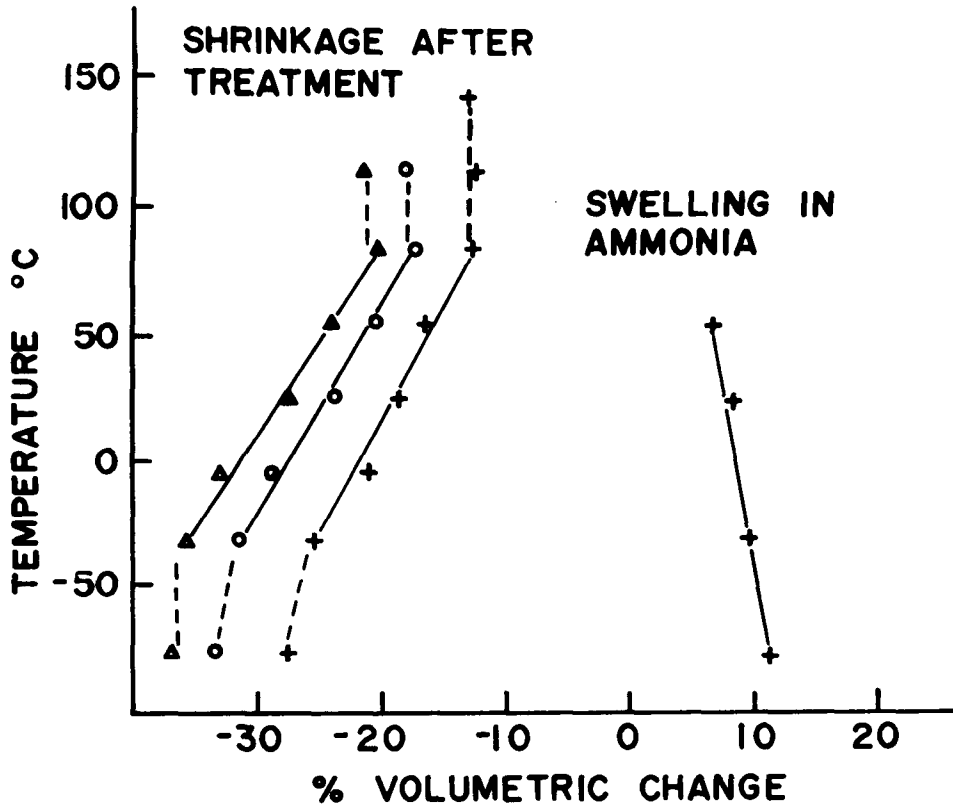


FIG. 1. Percentage volumetric change relative to the original oven-dry volume during ammonia treatment at various temperatures.

- + First cycle
- o Second cycle
- Δ Third cycle

placing the blocks in an oven at 105 C for three days. Finally the weights and dimensions of the blocks were remeasured. Two factors influenced the choice of treatment schedule. First, twenty-four hours was considered to be long enough to ensure complete plasticization of the wood (Green and Koch 1971). Second, the rate of evaporation was restricted to ensure that there was sufficient heat flow into the blocks to offset the latent heat of evaporation of the ammonia without cooling the wood: calculations indicated that the rate of release of gas should not

TABLE I. The swelling of wood in ammonia.<sup>a</sup>

T °C	Tangential		Radial		Longitudinal		Volumetric mean % swelling	Level of significance between temperatures
	Mean % swelling	SD	Mean % swelling	SD	Mean % swelling	SD		
55	7.2	1.29	1.1	0.41	-2.1	0.33	6.6	10%
25	9.4	0.58	1.6	0.54	-2.3	0.56	8.3	10%
-33	11.7	0.72	1.6	0.56	-3.5	0.18	9.8	10%
-78	11.3	0.68	2.9	0.32	-2.5	0.45	11.4	—

<sup>a</sup> Volumetric swelling of Corsican pine in water at 25 C is 12.8 ± 0.78%.

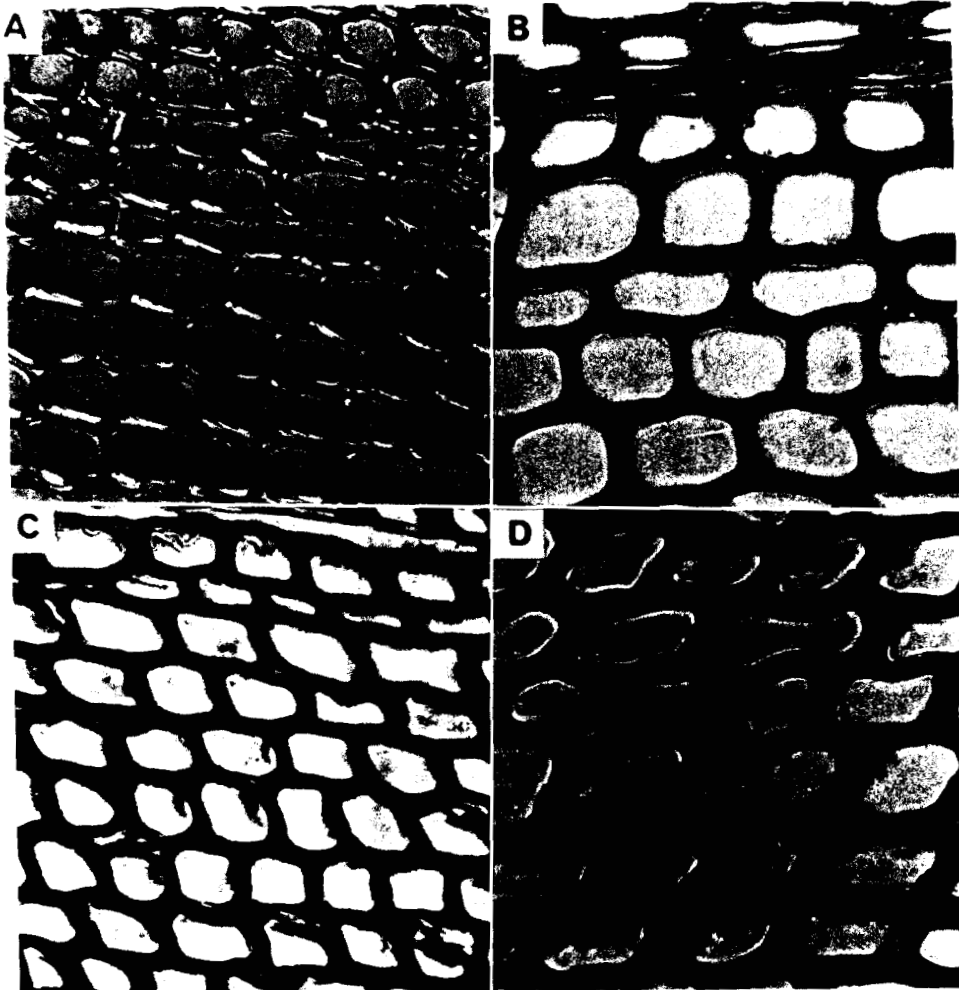


FIG. 2. Earlywood after one cycle of ammonia treatment.

- A. Untreated control. ( $\times 500$ )
- B. Treated at 85 C. ( $\times 750$ )
- C. Treated at 25 C. ( $\times 500$ )
- D. Treated at -33 C. ( $\times 750$ )

exceed  $1 \text{ ml s}^{-1}$  as measured by a flow meter at atmospheric pressure. For temperatures above  $-33 \text{ C}$  a stainless steel pressure vessel was needed to maintain the ammonia as a liquid above its boiling point.

The swollen dimensions of wood in liquid ammonia were measured in a second pressure vessel which was fitted at each end with 22-mm-thick sight-glasses, using a metal flange and polythene 'O' ring to provide a pressure seal. Measurements were restricted to temperatures at or below  $55 \text{ C}$ . Only two blocks were treated at a time. Each block rested on a flat metal tray and was held against one of the sight-glasses by a small spring so the dimensions of one face of each block could be measured with a travelling microscope; only two dimensions per specimen could be measured for each treatment.

TABLE 2. *The induced shrinkage of wood in ammonia.*

T °C	Cycle	Tangential		Radial		Longitudinal		Volumetric mean % shrinkage	Level of significance between temperatures*
		Mean % shrinkage	SD	Mean % shrinkage	SD	Mean % shrinkage	SD		
145	1st	—	—	—	—	—	—	13.5	NS
115	1st	6.9	0.30	4.4	0.31	2.0	0.20	12.8	NS
	2nd	10.2	0.30	6.8	0.30	2.6	0.58	18.5	NS
	3rd	12.1	0.50	8.3	0.64	2.7	0.88	21.6	NS
85	1st	7.0	0.65	4.7	0.34	1.4	0.06	12.9	1%
	2nd	9.6	0.83	6.8	0.56	1.9	0.10	17.5	1%
	3rd	11.6	1.10	8.2	0.66	2.3	0.18	20.6	1%
55	1st	9.0	0.52	6.9	0.29	1.6	0.32	16.5	1%
	2nd	11.4	0.51	8.8	0.53	2.2	0.28	20.8	1%
	3rd	13.1	0.54	10.1	0.32	2.5	0.26	24.2	1%
25	1st	10.4	0.54	8.1	0.61	1.4	0.25	19.0	1%
	2nd	13.6	0.04	11.3	0.61	2.1	0.24	23.9	1%
	3rd	15.1	0.79	12.7	0.76	2.4	0.31	27.5	1%
-5	1st	11.4	0.28	9.9	1.21	1.3	0.17	21.4	1%
	2nd	16.2	1.30	13.8	1.14	1.9	0.23	29.2	5%
	3rd	18.0	1.47	16.2	1.39	2.2	0.22	33.1	1%
-33	1st	12.6	0.91	12.5	0.89	3.0	0.15	25.7	5%
	2nd	16.1	0.34	15.8	0.69	3.8	0.19	31.8	10%
	3rd	18.6	1.47	18.1	0.60	4.3	0.18	36.0	NS
-78	1st	13.7	1.02	13.1	0.61	3.4	0.33	27.5	—
	2nd	16.4	2.05	17.3	1.45	4.0	0.26	33.6	—
	3rd	17.6	1.46	18.6	1.62	4.5	0.34	37.0	—

\* The level of significance between adjacent temperatures at the same treatment cycle is tabulated under the higher of the two temperatures.

## RESULTS

*Dimensional and weight changes*

The swelling of wood in ammonia (Table 1) and the subsequent induced shrinkage (Table 2) as related to temperature are shown in Fig. 1.

Data on the swelling of wood in ammonia are somewhat limited as they were not a primary objective of the research and refer to only a single treatment cycle.

TABLE 3. *% Weight loss over three successive cycles of ammonia treatment.*

T °C	1 Cycle		2 Cycles		3 Cycles	
	Mean % weight loss	Sign. between temps.	Mean % weight loss	Sign. between temps.	Mean % weight loss	Sign. between temps.
115	1.2	1%	2.2	5%	3.2	5%
85	3.6	NS	4.0	NS	4.9	NS
55	3.2	NS	4.6	NS	5.6	NS
25	3.8	10%	5.8	NS	6.1	NS
-5	2.6	NS	4.7	5%	5.0	10%
-33	1.7	10%	2.6	5%	3.5	1%
-78	0.3		0.5		0.9	
SD	1.10		1.26		1.29	

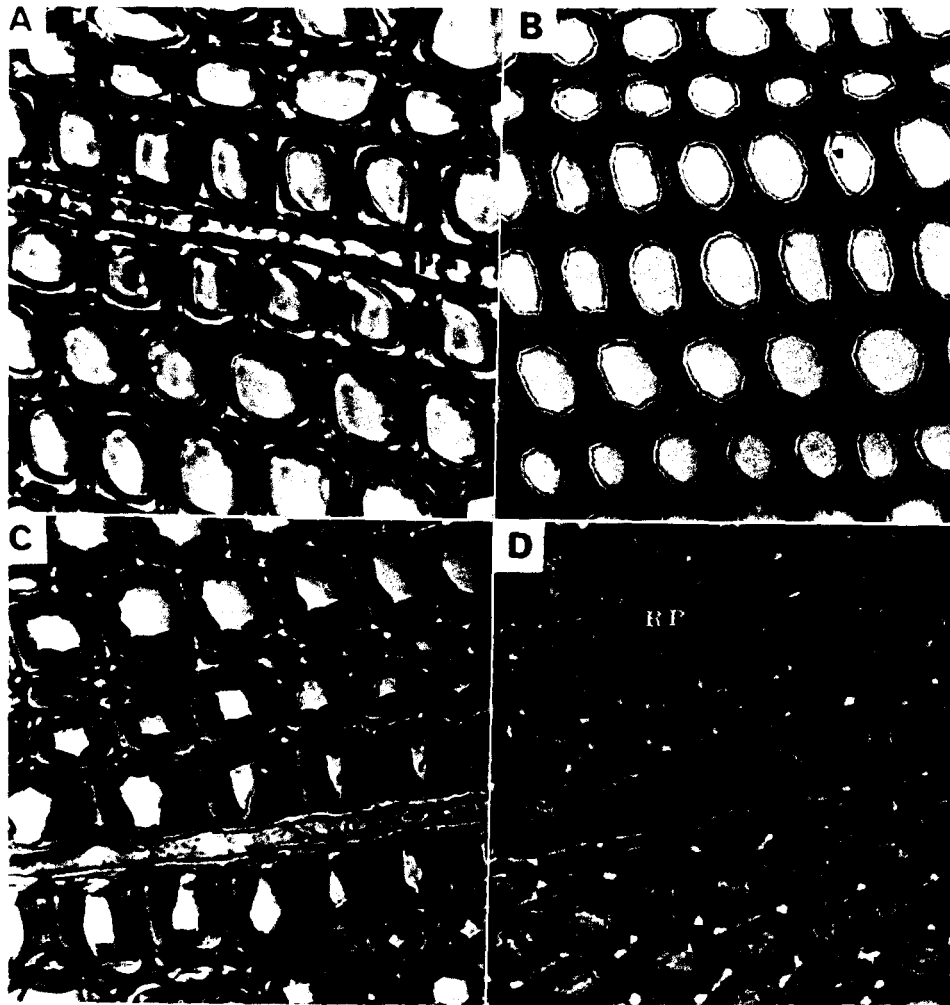


FIG. 3. Latewood after one cycle of ammonia treatment.

A. Untreated control. ( $\times 750$ )

B. Treated at 115 C. ( $\times 750$ )

C. Treated at 55 C. ( $\times 750$ )

D. Treated at -33 C. ( $\times 750$ )

Symbol: RP = Ray parenchyma.

FIG. 4. Ultrastructural changes in earlywood after one cycle of ammonia treatment.

A. TEM untreated control. ( $\times 22,500$ )

B. SEM untreated control. ( $\times 4,600$ )

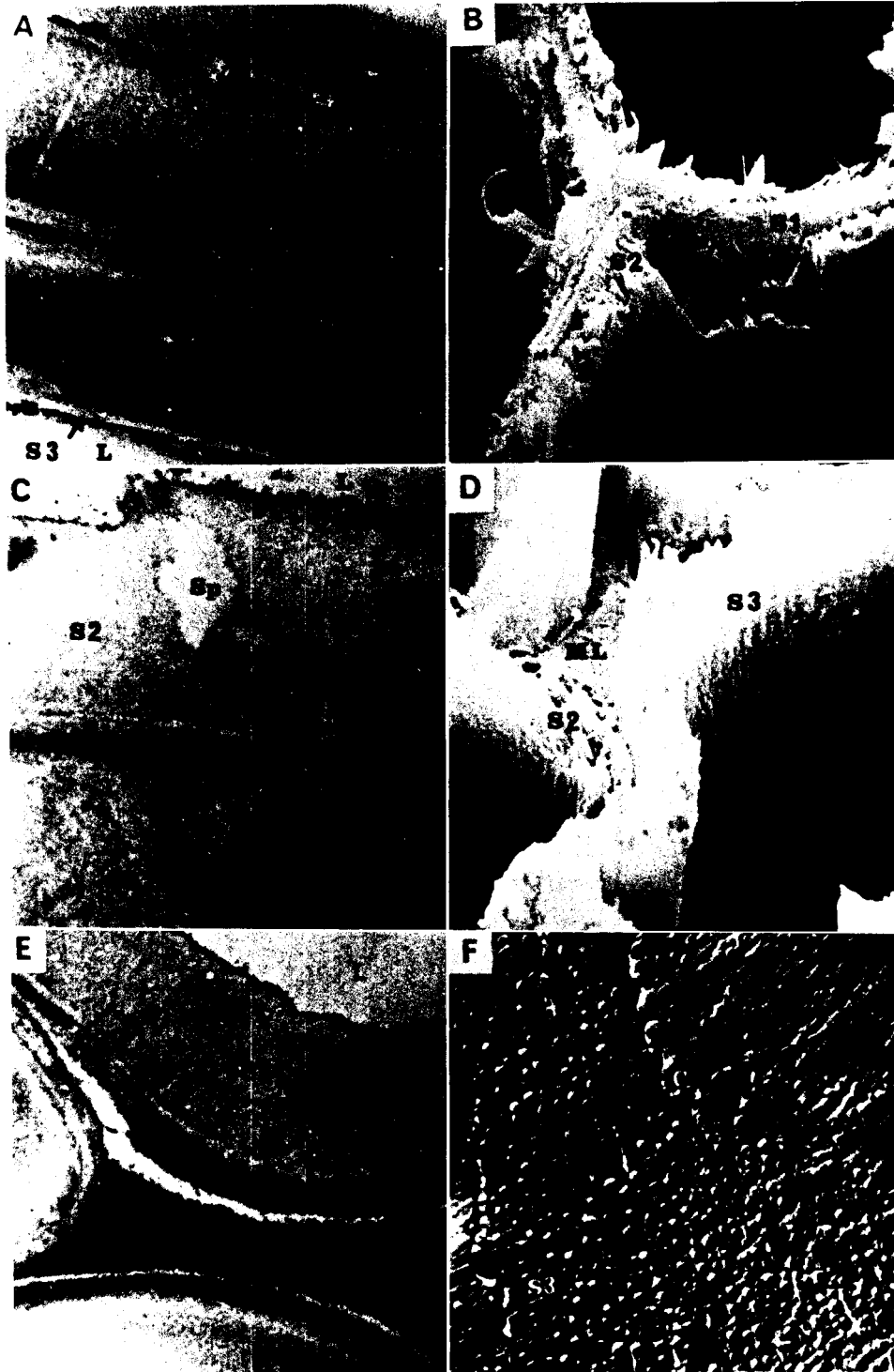
C. TEM treated at 85 C. ( $\times 22,500$ )

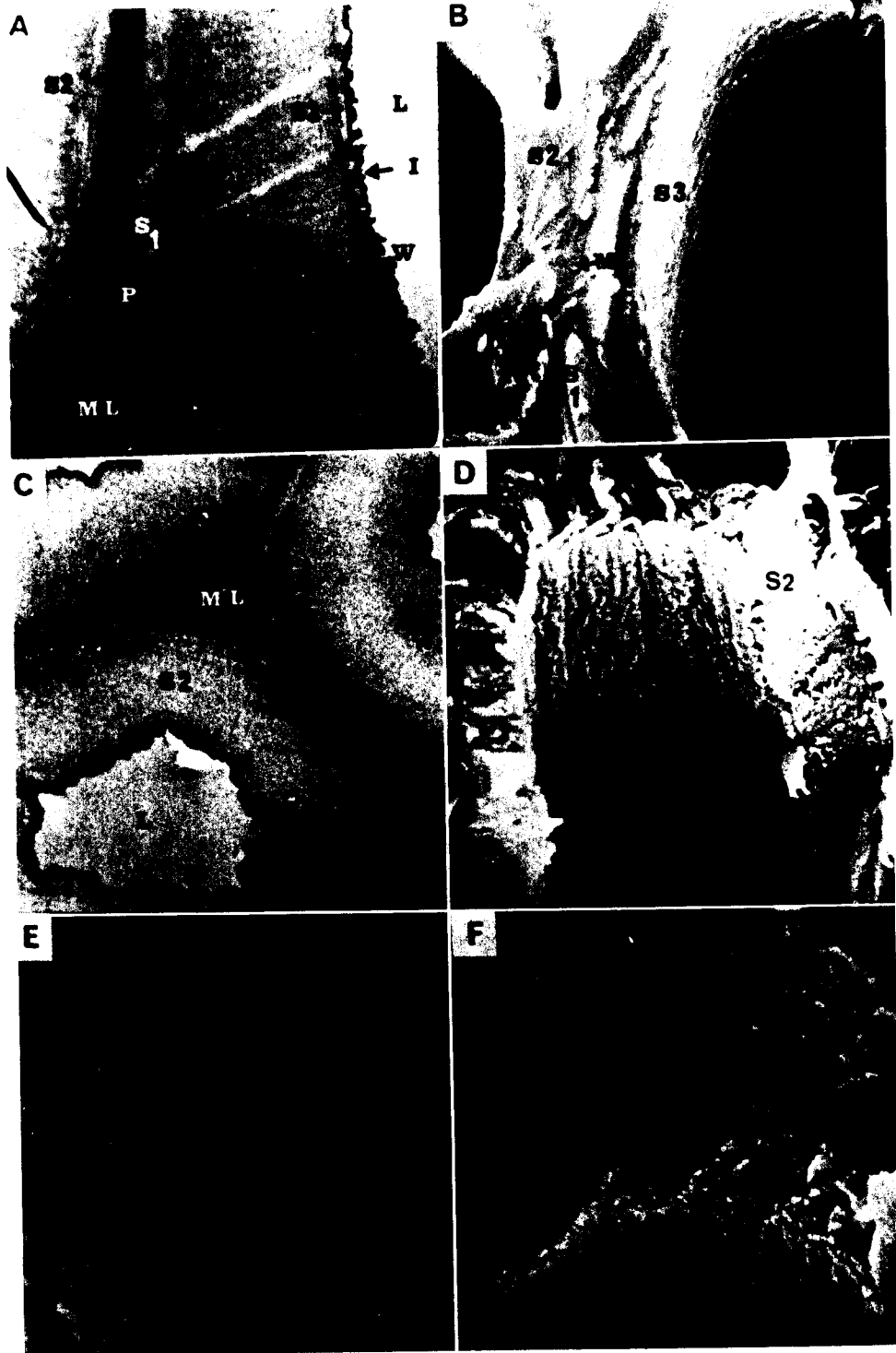
D. SEM treated at 25 C. ( $\times 6,000$ )

E. TEM treated at 55 C. ( $\times 22,500$ )

F. Replication of lumen surface treated at 85 C. ( $\times 13,500$ )

Symbols:  $S_1$ ,  $S_2$ ,  $S_3$  = layers of the secondary wall; L = Lumen; ML = Middle lamella; Sp = splitting; C = cracking.







Even so, it is clear that volumetric swelling between  $-78$  and  $55$  C decreases regularly with increasing temperature.

Ammonia-induced shrinkage of wood after treatment at temperatures between  $-33$  C and  $85$  C also decreased regularly with increasing temperature, but there is no significant difference between the induced shrinkage at and above  $85$  C for all three treatment cycles and by the third cycle there is no significant difference between shrinkage at  $-33$  and  $-78$  C. The linear regression equations for the percentage induced volumetric shrinkage ( $y$ ) versus temperature in  $^{\circ}\text{C}$  ( $x$ ) between  $-33$  C and  $85$  C for each cycle are shown below:

Cycle	Regression equation	Correlation coefficient
1	$y = 208 - 9.6x$	0.993
2	$y = 220 - 7.9x$	0.995
3	$y = 235 - 7.4x$	0.995.

The loss in weight occurring over three cycles of ammonia treatment is shown in Table 3. The weight loss increased from a low value at  $-78$  C to a maximum near  $25$  C, beyond which point the weight loss fell off again. Further losses occurred during retreatment.

A maximum density increase for oven-dry wood of about 37% occurred after three cycles at  $-78$  C; an increase from the original value of  $470 \text{ kg/m}^3$  to  $640 \text{ kg/m}^3$ .

#### *Structural changes*

Changes in the structure and ultrastructure of the wood were observed using the light microscope and both the scanning electron microscope (SEM) and transmission electron microscope (TEM). The scanning electron microscope proved a particularly useful tool since it enabled the wood to be viewed in 3 dimensions with the minimum of preparation (Coles 1973). All involved the use of fairly standard techniques. (For more information see Coles 1973, 1974.) More detailed observations of the surface detail of the tissue were made using platinum-shadowed replicas prepared from dry wood. A two stage process was employed using a plastic film as an intermediate. Radial surfaces were used since this surface yields the most information.

Additional information was gained from the examination of transverse sections. These were cut from water saturated tissue for viewing in the light microscope and ultra thin sections were cut from similar tissue after suitable staining and embedding for viewing in the transmission electron microscope. Sectioning can

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FIG. 5. Ultrastructural changes in latewood after one cycle of ammonia treatment.

- A. TEM untreated control. ( $\times 13,500$ )
- B. SEM untreated control. ( $\times 4,700$ )
- C. TEM treated at  $85$  C. ( $\times 5,600$ )
- D. SEM treated at  $55$  C. ( $\times 4,700$ )
- E. TEM treated at  $25$  C. ( $\times 9,000$ )
- F. SEM treated at  $25$  C. ( $\times 11,200$ )

Symbols: P = Primary wall; I = Incrustations; W = Warts (other symbols as in Fig. 4).

introduce artifacts into the specimens but when used in conjunction with other techniques yields some particularly useful information. From the many sections examined and particularly on comparison with results obtained from the scanning electron microscope the variations in structure shown are thought to be true variations induced by the ammonia treatment.

Restructuring following ammonia treatment is summarized in a series of photographs that attempt to illustrate the effect of temperature and of repeated treatment on earlywood (EW) and latewood (LW) tracheids and on radial wood tissue.

Figures 2 and 3 compare the structure of EW and LW after a single treatment cycle as a function of treatment temperature. Evidence of restructuring of the wood is particularly noticeable at low temperatures. There is evidence of widespread buckling and collapse in the EW, while in the LW the lumens become shrunken and crimped in contrast with the rounded, smooth lumens of the controls.

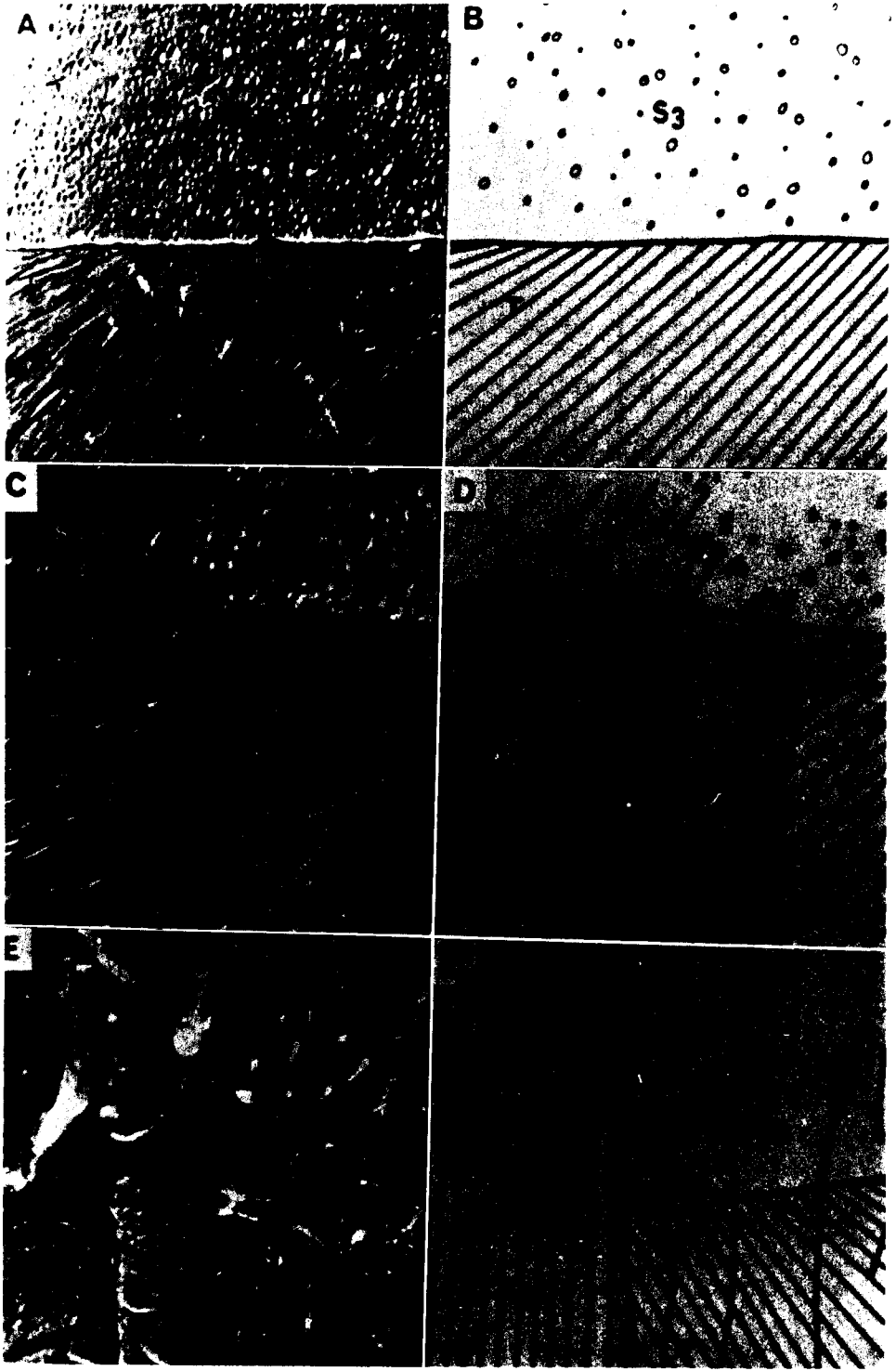
Figures 4 to 7 illustrate the effect of ammonia treatment on ultrastructural organization, as revealed by electron microscopy.

Buckling and collapse of the EW cell walls can be quite marked if the treatment temperature is low (Fig. 4D), whereas cell-wall crimping is slight, or even absent in very thin-walled material, being confined to cell corners. At higher treatment temperatures ( $\geq 55$  C) evidence of buckling and crimping is slight, but there are signs of delamination of the cell walls. Delamination occurs at the middle lamella/primary wall boundary (Fig. 4E), at the  $S_1/S_2$  boundary (Fig. 4C), or by splitting across the cell wall (Fig. 4C). The thicker-walled EW tends to delaminate near the ML whilst very thin-walled EW can split across the  $S_2$  layer. A fine system of cracks and fissures is often revealed on the lumen surface after high temperature treatment (Fig. 4F). There is little evidence of crimping, even at low temperatures where it is difficult to distinguish from minute compression failures (Dinwoodie 1968; Pentoney 1966).

In untreated LW the cell walls are thick and the lumens are rounded (Fig. 5A and B). There are indications that considerable internal swelling occurs during ammonia treatment and the walls become heavily crimped in the direction of the fibre axis (Fig. 5C and D). This folding is even observed in the cell corners of the  $S_1$  layer (Fig. 5F). The fine detail of crimping in the SEM photographs does not show up as well in the TEM sections, probably because these have to be cut from water-saturated specimens. The SEM pictures suggest that ammonia-treated wood fractures differently (compare Fig. 5B with 5D and F).

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- FIG. 6. Replication of radially split surfaces using acetyl cellulose film shadowed with platinum.
- A. Untreated earlywood control. ( $\times 5,600$ )
  - B. Schematic representation of A.
  - C. Earlywood ammonia treated at 25 C. ( $\times 13,500$ )
  - D. Schematic representation of C.
  - E. Latewood ammonia treated at 25 C. ( $\times 22,500$ )
  - F. Schematic representation of E.

Symbols: T = transition layer (other symbols as in Fig. 4). The  $S_3$  as labelled includes the overlying warty layer.



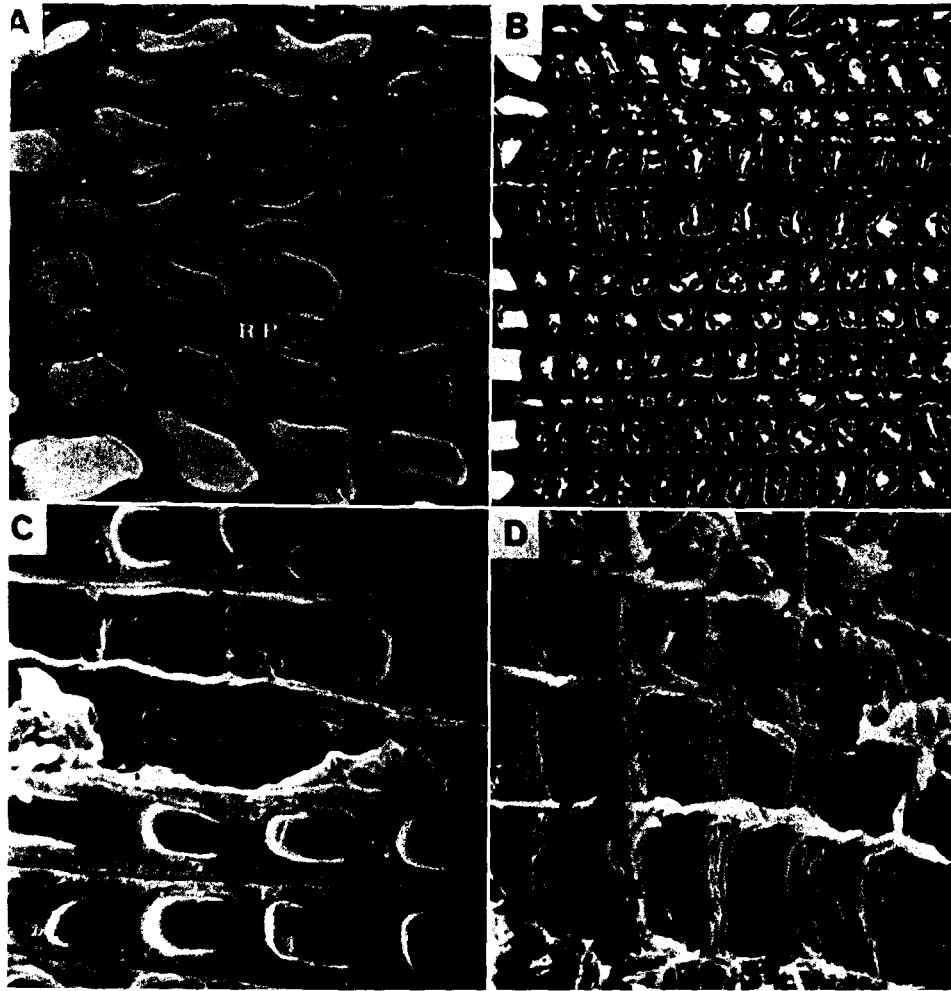


FIG. 7. A. Treated earlywood (3 cycles) at  $-33\text{ C}$ . ( $\times 750$ )  
 B. Treated latewood (3 cycles) at  $-33\text{ C}$ . ( $\times 500$ )  
 C. SEM radially split sample looking into ray parenchyma of untreated latewood control. ( $\times 1,000$ )  
 D. SEM radially split sample looking into ray parenchyma of ammonia treated latewood at  $25\text{ C}$  for one cycle. ( $\times 1,000$ )

Figure 6 attempts to illustrate the relationship between cell-wall crimping of the lumen surface and the  $S_2$  layer. The sketches (Fig. 6B, D and F) on the right hand side of Fig. 6 are intended to represent schematically photographs of the replicas (A, C and E). In Fig. 6E the the  $S_3$  layer of a latewood tracheid is shown in the top right hand portion of the photograph: the  $S_3$  layer is heavily crimped and encrusted. On the left hand side the  $S_3$  has been peeled away revealing the  $S_2$  layer. Crimping of the cell wall lies parallel to the microfibrils of the  $S_2$  layer. A similar situation is illustrated in the thin-walled earlywood, although cell-wall crimping is only slight (Fig. 6C). Here only the  $S_3$  and  $S_2/S_3$  transition layer are

exposed, but the crimping runs across the photograph in the same direction as one would suppose the unexposed  $S_2$  microfibrils to lie.

After three treatment cycles the restructuring resembles that observed after one cycle, although it is intensified (Fig. 7A and B). Structural reorganization of the radial tissue of treated wood appears to be determined by the behaviour of the longitudinal tracheids. In EW the tracheids buckle and collapse forcing the ray tissue to meander from side to side, clearly shown in Fig. 7A. In LW the tracheids become shrunken and crimped, forcing the ray tissue to fold in a concertina-like fashion (Fig. 7D). This illustrates the passive response of the ray tissue to restructuring of the longitudinal wood tracheids: if ray tissue were to show its own response to ammonia treatment, the folding would be more constant along the entire ray length since ray tissue differs little between EW and LW zones. Parham (1971b) only observed explosion artifacts of ray parenchyma cell walls. Almost certainly our success is due to the slow controlled rate of ammonia evaporation after treatment.

#### INTERPRETATION OF THE SWELLING AND SHRINKAGE PHENOMENA

Ammonia swells wood beyond its green, water-swollen state. Under these conditions the swelling pressure stretches the P and  $S_1$  microfibrils (these are in tension) and at the same time causes significant internal swelling (the  $S_3$  layer is under compression) (Stamm 1955). Pollisco et al. (1971) suggest that it is the internal swelling of wood in ammonia and the subsequent evaporation of the ammonia that causes the ammonia-induced shrinkage of wood. Figure 8 portrays the sequence of events. Ammonia is initially adsorbed by the lumen lining ( $S_3$  and warty layer) and the cell wall swells into the lumen (Stage 2). No external swelling is postulated because the outer region (near the middle lamella) is still rigid, since ammonia has not yet diffused through the cell wall to soften and plasticize that region. Plasticization proceeds through the cell wall ( $S_3$  to ML) allowing further internal swelling and then some external swelling to occur. The cell wall is now completely plasticized (Stage 3). The opposite situation develops during evaporation. Ammonia escapes from the wood through the interconnecting lumen system and the lumen lining is the first part of the cell wall to lose its plasticity. The bulk of the cell wall is still swollen occupying a significant part of the original lumen volume, which means that the  $S_3$  layer is held in a crimped position while it regains its rigidity (Stage 4). All subsequent shrinkage is direct inwards, towards the lumen, since the inner layers of the wall are now rigid and they force the more plastic outer layers to shrink inwards towards them (Stage 5), causing an overall decrease in wood volume.

A second hypothesis to explain ammonia-induced shrinkage applies principally to low density species. Stamm (1955) interpreted the exceptionally large induced shrinkage of balsa in terms of collapse and buckling of the cell walls into the lumens. Such collapse can occur during evaporation if the capillary forces exceed the compressive strength of the ammonia-softened cell walls. This theory is consistent with the observation that collapse did not occur in thin sections of balsa where all the fibres were severed (Stamm 1955).

A third possible model is postulated by Pentoney (1966). He suggests that the induced shrinkage results from the coiling tendency of linear polysaccharides when they are released from imperfect lattice restraints by the adsorbed ammonia.

In his model the effect of coiling was supposed to be most pronounced in the P, S<sub>1</sub> and S<sub>3</sub> layers since a reduction in the mean end-to-end length of the molecules would lead to a decrease in cell and lumen diameter.

The experimental work reported in this paper indicates that all three mechanisms (with certain important modifications) have a part to play in ammonia-induced swelling and shrinkage of wood.

#### DISCUSSION

##### *The swelling of wood*

The physical phenomenon causing wood to swell in water or ammonia is related to hydrogen bonding (Stamm and Tarkow 1950), and the strength of hydrogen bonding decreases as the temperature increases (Pimental and McClellan 1960). Consequently, the fibre saturation point, the sorptive capacity of the cell wall for water and the volumetric swelling of wood in water are observed to decrease with increasing temperature (Skaar 1972; Stamm 1964). Hence, by analogy, the decrease in the external volumetric swelling of the wood in ammonia with increasing temperature is readily explicable (Fig. 1).

On swelling in ammonia the longitudinal dimension actually decreases in length. This is similar in magnitude to the decrease after ammonia evaporation<sup>4</sup> (Tables 1 and 2). We suggest that both are caused by changes in the cellulose structure when cellulose I is swollen to form ammonia-cellulose. This restructuring remains after evaporation when ammonia-cellulose is transformed to cellulose III. The longitudinal shrinkage could be due to a reduction in microfibril length and thus tracheid length caused by the coiling of cellulose chains of the S<sub>2</sub> layer in the ammonia-swollen state (Pentoney 1966). Such an effect would be most noticeable during the first treatment cycle. The longitudinal shrinkage data for the second and third treatment cycles confirm that little further longitudinal shrinkage occurs. Hess and Gundermann (1937) noted that two swelling complexes can be formed, ammonia-cellulose I above about -30 to -20 C and ammonia-cellulose II below this transformation temperature. The slightly greater longitudinal shrinkage obtained at -33 and -78 C might be due to the formation of ammonia-cellulose II rather than ammonia-cellulose I.

##### *The ammonia-induced shrinkage of wood*

Results reported here agree with data of earlier workers which, however, covered a narrower temperature range (Stamm 1955; Pollisco et al. 1971; Parham et al. 1972). Corsican pine, in common with other woods, shows an induced volumetric shrinkage after ammonia treatment. In general, the induced volumetric shrinkage decreases through all three treatment cycles as the ammonia treatment temperature increases (Fig. 1 and Table 2): we ignore for the moment data obtained below -33 and above 85 C.

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<sup>4</sup> The longitudinal shrinkage when wood is swollen in ammonia exceeds the oven-dry ammonia induced shrinkage (1st treatment cycle) at 55, 25 and -33 C but not at -78 C. Dr. R. W. Meyer has commented that at the higher temperatures this longitudinal contraction in ammonia, relative to the ammonia treated oven-dry state, might be analogous to a Poisson effect due to the extensive lateral swelling. At -78 C the ammonia swollen wood may not be fully plasticized (see later) and swells and shrinks less than would be predicted by extrapolation of data from higher temperatures.

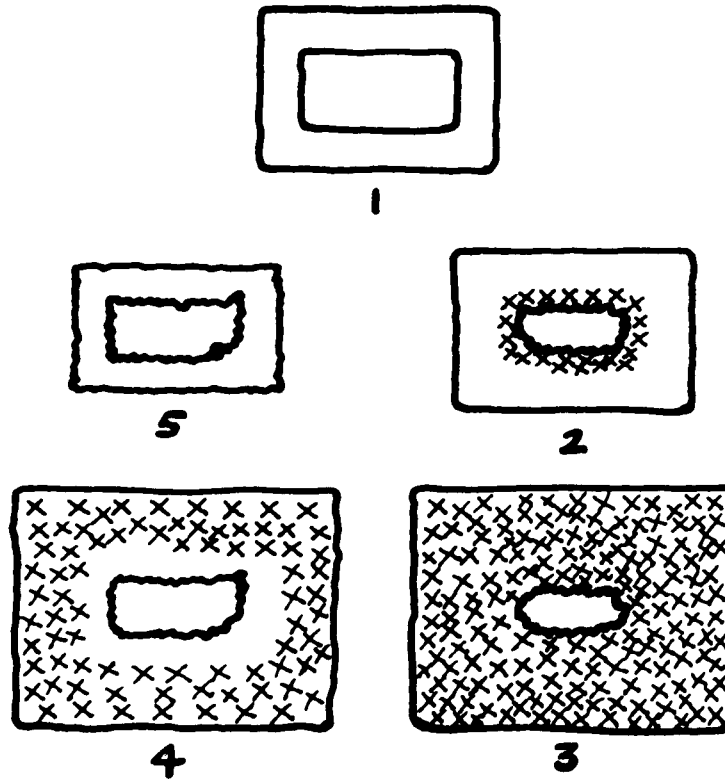


FIG. 8. Internal swelling and shrinkage of wood (xxx denotes swollen ammonia-plasticized state).  
 Stage 1. Latewood before ammonia treatment.  
 Stage 2. Ammonia only adsorbed near the lumen causing internal swelling.  
 Stage 3. Whole cell wall swollen and plasticized.  
 Stage 4. Ammonia desorbed near the lumen causing adjacent cell-wall material to regain its rigidity.  
 Stage 5. All ammonia lost. Cell now shrunken with crimped lumen.

We suggest that cell-wall collapse (Stamm 1955) that is confined to EW (Fig. 2 and 4), together with cell-wall crimping and internal swelling (Pollisco et al. 1971) which is observed mainly in LW (Fig. 3 and 5), causes the induced transverse shrinkage of wood. A clear distinction exists between the restructuring occurring in EW and LW, and confirms earlier observations (Coles 1973). These two mechanisms, together with the cellulose coiling model of Pentoney (1966), causing longitudinal shrinkage, account for the observed ammonia-induced volumetric shrinkage.

The collapse and buckling of EW in ammonia differ in one important respect from that which is observed during kiln-drying of certain woods. With ammonia treatment collapse is more severe at low temperatures (Fig. 2), whereas with kiln-drying, collapse is more severe at high temperatures. Factors determining the probability of collapse are the same in both instances. They are the surface tension of the liquid which, together with the size of the pit membrane apertures, controls the liquid or capillary tensile force and the compressive strength of the

cell wall, which determines the magnitude of the capillary force that the fibre can withstand. With ammonia treatment the increasing severity of collapse in EW at lower temperatures suggests that surface tension ultimately controls the process, since the surface tension increases with decreasing temperature, from a value of zero at the critical temperature of 132 C to  $2 \text{ N} \cdot \text{m}^{-2}$  at 50 C and to  $4 \text{ N} \cdot \text{m}^{-2}$  at the melting point of  $-78 \text{ C}$ . There is no evidence of collapse in LW, presumably because the compressive strength of the thick cell walls always exceeds the tensile capillary force within the ammonia. With kiln-drying, collapse is governed by the plasticity of the cell walls, which increases with increasing temperature (Goring 1963; Bolton et al. 1974) rather than by the surface tension of water.

Internal swelling and cell-wall crimping, running in the direction of the  $S_2$  (Fig. 6C and E), are only pronounced in thick-walled tracheids, in LW (Fig. 5) and in the cell corners of some EW tracheids (Fig. 4D). Parham (1971b) has already published TEM photographs of crimping in the cell corners of EW tracheids of loblolly pine after vapour phase ammoniation at 25 C and 1 MPa. Our own observations are consistent with that study. There are two reasons for the minimal amount of crimping in EW. First, the thin-walled EW will not swell significantly, so any internal swelling and crimping that do occur in the ammonia swollen state are likely to be small. Second, the key point in the theory of Pollisco et al. (1971) is that there is a large difference in plasticity across the cell wall during the early stages of evaporation (Fig. 8, Stage 4). This is true for thick-walled LW but not for EW. If we assume that the initial rate of ammonia evaporation from the lumen surface is the same in both EW and LW, then the ammonia concentration *gradient* within the wall adjacent to the lumen must also be similar. By the time the  $S_3$  layer has lost its ammonia and become rigid, the rest of the EW wall will also have lost much of its ammonia and will be rapidly de-swelling and losing plasticity—the little crimping and internal swelling that existed in the ammonia-swollen state will be lost—whereas in the thick-walled LW much of the wall will still be swollen, forcing the  $S_3$  to become set in a crimped position. It seems likely that differing rates of ammonia evaporation at this critical stage will influence the amount of crimping. However, in these experiments the rate of evaporation was kept constant.

It is unfortunate that previous workers have failed to control and measure the rate of ammonia evaporation after treatment. We believe this will affect significantly the extent of crimping (more severe at high evaporation rates) and collapse (slightly more severe at high evaporation rates: the specimen must cool to provide latent heat for evaporation of liquid ammonia and the surface tension of the ammonia will increase).

The extent of swelling within the cell wall will dictate the amount of internal and external swelling and thus the intensity of crimping. The external swelling data (Fig. 1) suggest that the degree of cell-wall swelling in ammonia increases with decreasing temperature. This would also be expected by analogy with the behaviour of wood in water. Consequently crimping and lumen shrinkage in LW will be more noticeable at low temperatures. This is observed (Fig. 3).

The induced volumetric shrinkage above 85 C is greater than that predicted by extrapolation from lower temperatures (Fig. 1). There is no obvious reason for this. Collapse is less likely at high temperatures, since surface tension is very small. Crimping is also less effective, as there should be little cell-wall swelling.



Indeed, at the critical temperature, 132 C, there can be no collapse (surface tension is zero) and minimal swelling (only monomolecular adsorption is possible) (Stamm 1964; Brunauer et al. 1938). Treatment history provides the most plausible explanation. The pressure vessel containing the wood samples was filled with ammonia at  $-33$  C and placed in a water/oil bath at the required temperature for 24 hours. During the warm-up period the wood will attempt to adjust to the localized, instantaneous treatment conditions and some internal swelling and cell-wall restructuring may occur that would not have occurred had the vessel been filled with ammonia at the final treatment temperature. For example, if the cell wall was extensively swollen during the early stages of the conditioning period, i.e., at  $-33$  C, the cell wall would de-swell—even when immersed in liquid ammonia—as the localized temperature gradually rose towards the final treatment temperature (Fig. 1). The effect of heating to the final temperature is similar to Stage 4 in Fig. 8. Treatment history can affect only the crimping and lumen shrinkage mechanism as collapse occurs during evaporation when the ammonia is at the water/oil bath temperature. Consequently, at these elevated temperatures, the induced volumetric shrinkage is almost entirely due to crimping and lumen shrinkage. There is evidence of such structural reorganization at high temperatures in LW (Fig. 3B and Fig. 5C) but little sign of collapse in EW (Fig. 2B).

The induced volumetric shrinkage at  $-78$  C is less than that predicted by extrapolation from higher temperatures. This could be associated with a thermal softening point of the ammonia-swollen wood in the temperature range of  $-5$  to  $-33$  C: this same temperature range is also associated with a transition between two ammonia-cellulose complexes, as noted earlier. Evidence of thermal softening above  $-33$  C is easily demonstrated (Schuerch 1964). Wood soaked in ammonia at  $-33$  C remains brittle and snaps on attempted bending, whereas if allowed to warm up slightly it bends with ease. Because the cell wall is not fully plasticized below the thermal softening temperature, the amount of cell-wall restructuring that can occur is limited and thus the degree of crimping and lumen shrinkage is less than predicted. In EW the fibres will be stronger than expected and less susceptible to collapse under capillary tension, although even at these low temperatures EW is sufficiently plastic for some collapse to occur.

An interesting point that seems to be associated with the occurrence of a thermal softening point is the behaviour of the dry ammonia-treated wood on subsequent water soaking and drying. Upon water soaking and drying, the wood that has been treated in ammonia at high temperatures suffers further induced shrinkage presumably due to the weakening effect of the structural changes, but wood that has been treated at low temperatures actually shows recovery. The change-over point occurs at an interpolated value of  $-10$  C, within the suggested range of the thermal softening temperature. It would seem that below this temperature the wood is more rigid and restructuring is less complete and thus partly reversible upon water soaking (Coles 1974).

Parham et al. (1972) have commented on the low T/R ammonia-induced shrinkage ratios as compared to the usual T/R shrinkage ratios of green wood. For example, loblolly pine treated with gaseous ammonia at 25 C and 1 MPa pressure gave a ratio of 0.838 as against their value of 1.38 for the wood-water system at 25 C. From our Table 2 one can calculate the ammonia induced T/R shrinkage

ratios which range from 1.57 at 115 C (1st cycle) to 0.95 at -78 C (2nd and 3rd cycles). However, unlike previous workers, we do not feel such comparisons are fair as they do not compare like with like. It seems preferable to calculate the T/R shrinkage ratio from the ammonia swollen state (Table 1) to the ammonia-induced shrinkage value after the first treatment cycle (Table 2). In this case the T/R ratio becomes  $2.1 \pm 0.2$ ,  $2.0 \pm 0.2$ ,  $1.7 \pm 0.2$  and  $1.6 \pm 0.1$  at 55, 25, -33 and -78 C, respectively. These ratios are not particularly low compared to those generally observed in the wood-water system: Coles (1974) determined a T/R ratio for untreated Corsican pine in water at only 25 C: the ratio was 2.63.

Corsican pine suffers a weight loss after ammonia treatment that is broadly comparable with that determined by Yan and Purves (1956) for spruce wood. The weight loss is thought to show two effects with temperature. An increase in temperature enhances the solubility of the low molecular weight wood components, causing a loss in weight but at the same time it enhances the chemical reaction of the ammonia with wood and thus the fixation of the ammonia causing a weight gain. In consequence the weight loss reaches a maximum of about 4% at 25 C (Table 3). The loss of low molecular weight fractions of lignin and hemicellulose from the cell wall must also contribute to the induced shrinkage of wood in ammonia.

Wood samples darken considerably following ammonia treatment. This is particularly noticeable at high treatment temperatures. Schuerch and Davidson (1971) have examined this phenomenon in some detail and have suggested a means of control.

#### CONCLUSIONS

Corsican pine, in common with other woods, shows an induced shrinkage after ammonia treatment that decreases with increasing temperature. Structural studies show that this is primarily due to crimping and internal swelling in the latewood and collapse in the earlywood. The optimum temperature for processing wood would appear to be about -20 C to -10 C (just above the thermal softening temperature). At lower temperatures the incomplete plasticity of the wood limits the amount of bending, compression, or moulding that is possible. Above this temperature the degree of swelling of the cell wall decreases and, most important, the necessary treatment pressure increases steadily.

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