Removal of solvent from swollen wood

Ashton, H. E.

Wood Science, 6, 4, pp. 368-374, 1974-04

National Research Council Canada
Conseil national de recherches Canada

REMOVAL OF SOLVENT FROM SWOLLEN WOOD

BY

H. E. ASHTON

REPRINTED FROM
WOOD SCIENCE
VOL. 6, NO. 4, APRIL 1974
P. 368-374

RESEARCH PAPER NO. 614
OF THE
DIVISION OF BUILDING RESEARCH

OTTAWA

PRICE 10 CENTS

NRCC 14227

LA SEPARATION D'UN SOLVANT D'UN ECHANTILLON DE BOIS GONFLE

SOMMAIRE

On analyse la séparation de solvants polaires de quatre essences au moyen des changements de volume et de poids. Des blocs gonflés sont exposés à une humidité relative de 100% et de 50%, à un séchage au four, puis au vide à plusieurs reprises. Pour un des solvants, on utilise aussi la séparation de l'eau. Le solvant se dégage le plus rapidement du pin, le plus lentement du Douglas vert. La pyridine s'évapore rapidement et le diméthylformamide assez rapidement. Le sulfoxyde de diméthyle et la méthylpyrrolidone sont partiellement retenus après le séchage au four.

Removal of Solvent From Swollen Wood

H. E. Ashton

ABSTRACT. The removal of polar solvents previously proposed as swelling agents for wood was followed by means of weight and volume changes. The degree of swelling and quantities of dimethyl sulfoxide, dimethylformamide, N-methyl pyrrolidone, and pyridine left in yellow birch, beech, white pine, and Douglas-fir after exposure for various times to evaporation at 100 and 50 percent relative humidities, ovendrying, and vacuum were determined. For the most strongly held solvent, water extraction was also used. Pine was found to release solvents most quickly and fir most slowly. Pyridine evaporated rapidly and dimethylformamide fairly rapidly at 50 percent RH, but even after ovendrying, 2 to 4 percent by weight of these solvents was retained except in pine. Eleven to 19 percent dimethylsulfoxide and methyl pyrrolidone was retained in birch and beech after ovendrying, and application of moderate vacuum had little effect on the retention. Preliminary evaporation at 100 percent RH is unnecessary, and evaporation at 50 percent RH is not practical with the slower solvents. Beech, which swells rapidly, is prone to cracking. Sufficient material is extracted from birch to cause volumetric shrinkage. Treatment of white pine with dimethylformamide appears to be the most practical system.

Chemical reaction with cellulose hydroxyl groups is one way of dimensionally stabilizing wood. Because the hydroxyl groups occur on polymer molecules which are part of larger micelles, they are not readily available for reaction. As a result, the conditions required to carry out a chemical reaction with the hydroxyl groups are, in many cases, so severe that the wood structure is damaged. The author proposed swelling wood with polar organic solvents to make the hydroxyls more readily available to reactants and to catalyze the desired reactions.[1]

In that previous paper, the effectiveness of polar organic solvents in swelling wood was studied. It was found that the selected solvents caused greater swelling than would be expected from water; consequently, they could be used as media in which to carry out chemical reactions with the cellulose hydroxyl groups of wood. Following treatment it would be necessary to remove whichever solvent was used and recover it to make the process economically feasible and to render the reacted wood suitable for handling. This present paper reports studies on the removal of the polar solvents from swollen but unreacted wood. It is expected that solvent would be more readily removed from treated wood for two reasons: hydrogen bonding to hydroxyl groups would be reduced through reaction, and physical entrapment would be less in the swollen state.

Procedure

The woods studied were yellow birch, beech, white pine, and Douglas-fir. The solvents used to swell them were dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl pyrrolidone (MP), and pyridine. The preparation of the wood blocks and solvents, the immersion process, and the measurement of the dimensions have all been described previously.[1]

After maximum swelling had been reached, the excess solvent was blotted from the surface and the blocks were weighed. The

[1]Ashton, H. E. 1973. The swelling of wood in polar organic solvents. Wood Sci. 6(2):159-166.

The author is Research Officer, Materials Section, Division of Building Research, National Research Council of Canada, Ottawa, Canada. The author acknowledges the assistance of R. C. Seeley and L. R. Dubois who weighed and measured the wood blocks. This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division. It was received for publication in January 1973.

solvents were then allowed to evaporate from the blocks under several drying conditions; the block weights and dimensions were measured at intervals. Because all the samples had not been immersed in solvent for the same length of time, the drying schedule was not the same in all cases. Evaporation first took place at 100 percent and then at 50 percent relative humidity (RH). The intention was to prevent rapid solvent evaporation from the surface, which might cause checking because the interior would still be swollen.

To allow evaporation at 100 percent RH, the blocks were placed in a desiccator containing distilled water in the bottom. The desiccator was kept in a room maintained at 23±2°C (73.5 ±3.5°F). Since the water was not stirred, the humidity was probably somewhat below saturation. For drying at 50 percent RH the blocks were stood on end on the bench in a conditioned room which was designed for an RH of 50 ±2 percent RH. As the room was large and well ventilated, evaporated solvent was dispersed rapidly.

Following the 50 percent RH conditioning, the blocks were ovendried for 24 hours in a common laboratory oven set at 105 ±2°C (221 ±3.5°F). After heating, the samples were cooled in a desiccator containing phosphorous pentoxide. Generally the blocks were weighed within a few hours, but in one case they were left in the desiccator over a weekend. The blocks were evacuated in the same desiccator by connecting it to a vacuum pump and evacuating the system to 28 inches when the pump was shut off. When the vacuum decreased to 25 inches after 1 or 2 days, the pump was turned over again until the higher vacuum was restored. The vacuum referred to later as 25 inches actually fluctuated between 25 and 28 inches.

The first group of samples to attain equilibrium swelling was left in the solvents for a week before weighing. When they were subsequently dried according to the schedule, it was found that more than half the MP originally absorbed was retained in the wood after a total of 16 days' gradual drying. Similarly, yellow birch contained more than 20 percent DMF and pyridine, and beech more than 20 percent DMF of the weight absorbed. Only white pine that had been immersed in these last two solvents contained less than 10 percent solvent. Ovendrying twice and storing over P_2O_5 reduced the weight pickup to below 4 percent in most cases. It did not, however, remove the last 10 to 20 percent of MP except from the white pine.

The blocks were then subjected to a vacuum of 25 inches mercury for various times, but this treatment had little effect on retained weight. Finally the birch, beech, and pine blocks that had been immersed in MP and still contained, respectively, 18, 12, and 4 percent of the amount originally absorbed were soaked in water for a week. They were then redried at 100 percent and 50 percent RH and in a vacuum. Other samples in the first and second groups were not subjected to this procedure.

The immersion period required for Douglas-fir to reach maximum swelling in DMSO, MP, and pyridine had been considerably longer than for the other wood-solvent combinations.

TABLE 1. — *Weight of solvent absorbed (percent of ovendry weight).*

Length of immersion	Species	Solvent			
		Dimethyl formamide	Dimethyl sulfoxide	Methyl pyrrolidone	Pyridine
49 days	Yellow birch	102.7	—	103.3	100.2
	Beech	114.4	—	118.0	121.1
	White pine	207.0	—	192.5	208.4
	Douglas-fir	125.2	—	—	—
58 days	Yellow birch	—	110.9	—	—
	Beech	—	123.4	—	—
	White pine	—	232.5	—	—
92 days	Douglas-fir	—	161.6	134.3	132.0

Consequently by the time the fir samples were removed from these solvents, it was known that two ovendrying periods and possibly soaking in water were necessary to remove most of the DMSO and MP. As a result they were only subjected to drying at 50 percent RH.

Results and Discussion

The dimensional and weight changes of the wood blocks during the various drying stages were calculated as mean percent volumetric change and mean percent of original weight increase. The latter was used because calculating weight increase as percent of the ovendry weight reflects mainly the specific gravity of the wood. For example, in 49 days the 2- by 1- by 1-inch blocks of pine absorbed about 23.9 g of MP and the same size birch blocks about 0.3 g more. On percent of ovendry weight, the values are 192 percent for pine and 103 percent for birch; this suggests a greater difference between them than in fact exists. The percent solvent originally absorbed is given in Table 1.

The volumetric and percent weight changes are plotted in Figures 1 to 5. It can be seen that when the wood blocks were exposed to near 100 percent RH after solvent immersion, they all picked up some additional weight except for those containing pyridine. The volume, however, tended to decrease, in most cases only slightly. The added water resulted in slight shrinkage, confirming the conclusion of the first paper that the three solvents have a greater effectiveness than water in swelling wood.

It is also evident that evaporation of the solvents at 50 percent RH was a relatively slow process other than where the solvent was pyridine or the wood was pine. At this drying condition, decrease in weight occurred faster than volumetric shrinkage. Most of the blocks remained close to their final maximum volume for the first 3 to 4 days, while their weight decreased during this period. Volumetric shrinkage only became significant after 13 to 14 days' drying at 50 percent RH, apart from all woods in pyridine, birch in DMF, and fir in DMSO. The slowest solvent to evaporate at 50

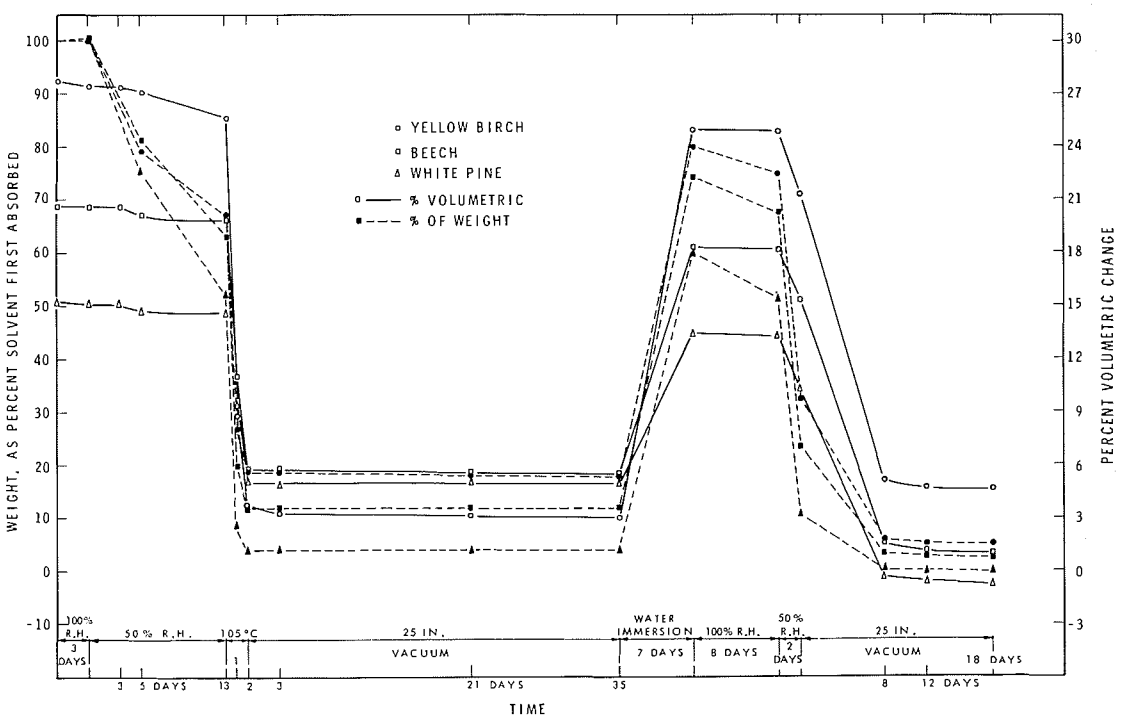

Figure 1. — Volume and weight changes during evaporation of methyl pyrrolidone.

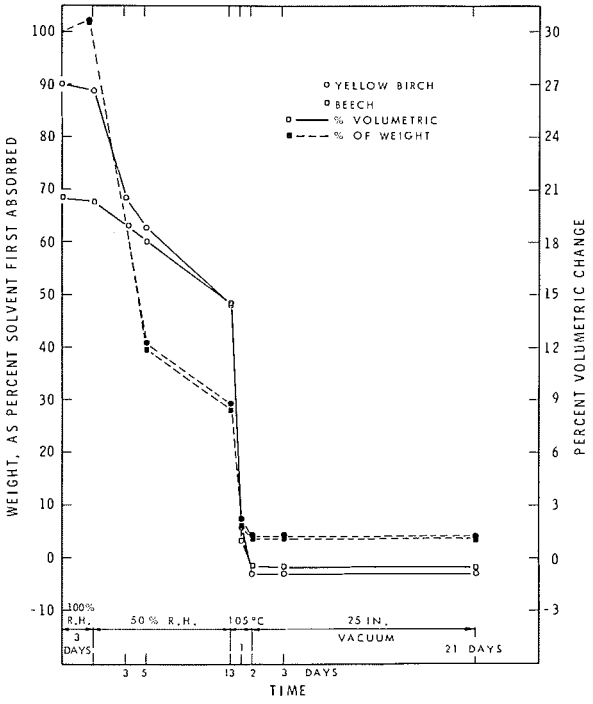

Figure 2. — Volume and weight changes during evaporation of dimethyl formamide.

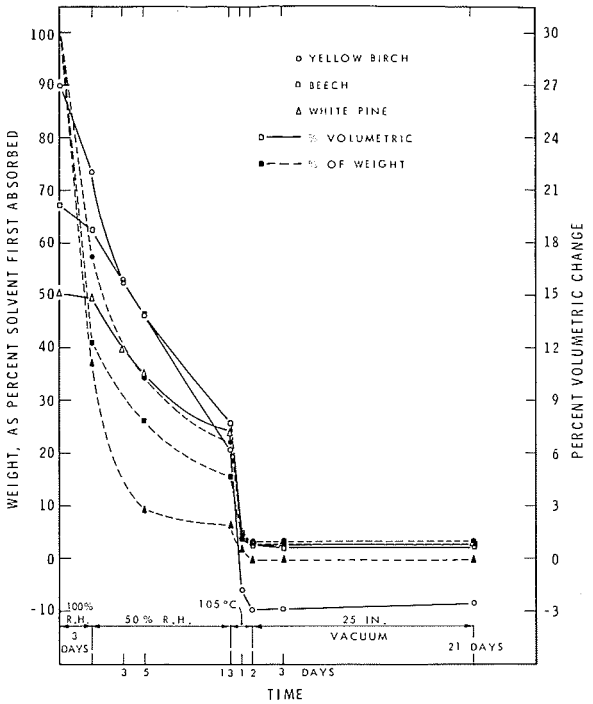

Figure 4. — Volume and weight changes during evaporation of pyridine.

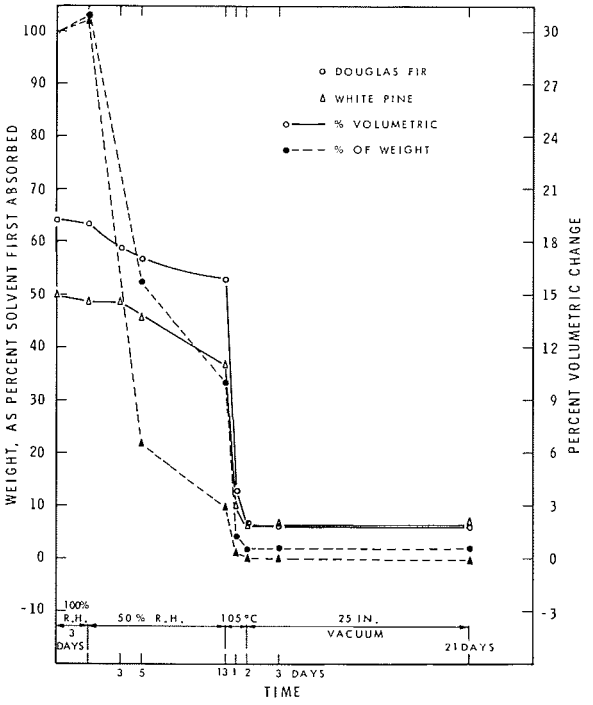

Figure 3. — Volume and weight changes during evaporation of dimethyl formamide.

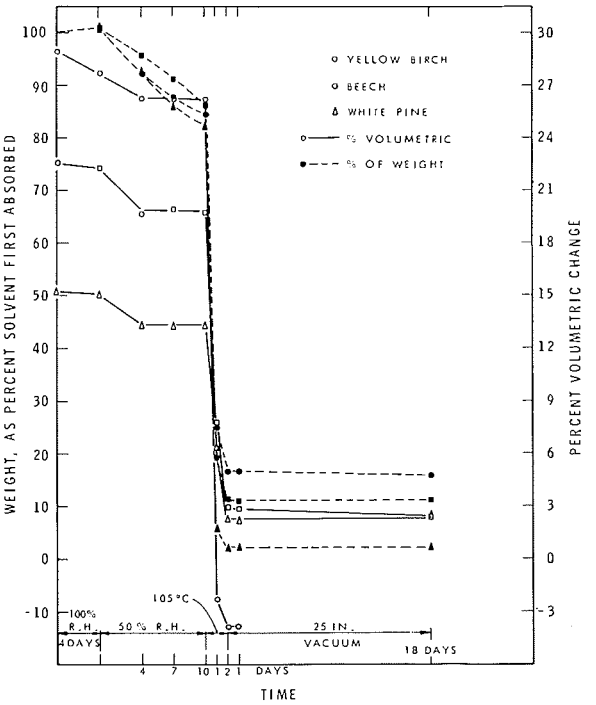

Figure 5. — Volume and weight changes of wood during evaporation of dimethyl sulfoxide.

percent RH was MP when considered on a volume basis, but DMSO was slowest on a weight basis.

The figures also show that ovendrying caused a considerable drop in both weight and volume. Pine that had been immersed in DMF and pyridine returned to its original weight although there was still some slight swelling. Birch and beech retained from 2.5 to 4 percent of these two solvents, but the volumes were less than the original. Pine in DMSO and MP as well as fir in DMF retained from 2 to 4 percent excess weight with corresponding swelling after ovendrying. Birch retained 17 to 19 percent DMSO and MP, and beech about 12 percent of these solvents. After two periods of ovendrying, MP was retained in the respective samples to a greater extent than DMSO both on a weight and a volume basis.

Continued heating might have removed the last of the retained solvent. However, it was considered that 3 days' heating at 105°C (221°F) might not be a practical process so two other methods were investigated.

First, a vacuum of 25 inches of mercury was applied. This method did not significantly change the weights or volumes of the blocks even over longer periods.

Second, because MP had been the solvent most resistant to removal by ovendrying, the birch, beech, and pine samples containing it were soaked in water for a week to see if the material could be extracted. It can be seen in Figure 1 that the woods did not swell as much in water as in the solvents. This difference may be due to the lower swelling effect of water, the much shorter immersion period, or a combination of both factors. The weight gain was also less, ranging from 60 to 80 percent of the weight of solvent previously absorbed. On subsequent exposure to near 100 percent RH, the blocks lost weight instead of gaining as they had done when saturated with solvent. Again the volume decreased slightly at this condition. At 50 percent RH, drying also occurred much faster than previously with both weights and volumes considerably lower after 2 days than they were after 13 days when solvent was being removed.

The first application of vacuum to the water-soaked blocks reduced the weights to less than those measured immediately before immersion. It is difficult to judge whether continued drying at 50 percent RH may have been just as effective in producing the losses in weight. Volumetrically the beech and pine also decreased below the presoaked condition, but the birch was more swollen than before immersion in water. Perhaps a mixture of water and MP has a greater swelling effect on birch. Exposure to the vacuum for an additional 10 days resulted in only minor gravimetric and volumetric decreases. At the end of the test the beech still retained about 2.5 percent of the weight and about 5 percent of the volume attained under equilibrium swelling in MP. Pine had slightly decreased and birch moderately increased compared with the original ovendried weights and dimensions.

The results from the Douglas-fir samples that had been measured more frequently while drying at 50 percent RH are shown in Fig. 6. For ease of comparison the volumetric changes are

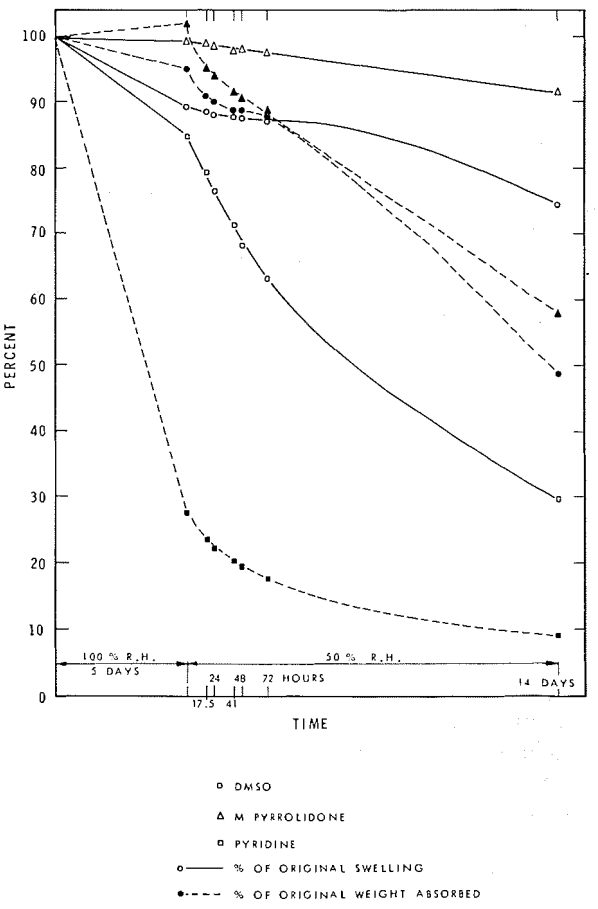

Figure 6. — Solvent removal from Douglas-fir.

plotted here as percent of the values reached at maximum swelling. Again it is obvious that pyridine evaporated much more quickly than the other solvents and that high humidity did not noticeably retard its evaporation.

MP evaporated from fir at a uniform rate by weight after the first overnight period at 50 percent RH. By contrast, the volumetric swelling remained fairly constant for the first 2 to 3 days and showed a significant decrease only over the last 11-day period. Unexpectedly, the fir blocks containing DMSO decreased volumetrically as well as gravimetrically during the 5 days at 100 percent RH.

During the swelling tests it had been noted that most of the beech blocks developed checks, especially on the tangential faces. After the first set of blocks had been ovendried for 24 hours, they were examined visually to see whether any cracks or checks remained. Neither the pine nor birch showed any noticeable effects of the swelling and shrinking processes. Although beech had swollen volumetrically less than birch, blocks that had been immersed in DMSO had deep cracks on the tangential faces. The samples that had cracked on swelling in DMF showed only a few small end grain checks on drying. One beech block had cracked in pyridine and one in MP but neither showed any evidence of this on drying. Nevertheless, the application of solvent swelling to dried beech may not be possible since it appears prone to develop cracks that would be visible if the wood were permanently distended. If chemical treatment of beech is considered desirable, it would probably be necessary to start with green wood and remove the water by solvent drying.[2]

Conclusions

Pyridine evaporated relatively quickly from wood when exposed to atmospheres of 100 and 50 percent RH. Dimethylformamide (DMF), which swells wood quickly, evaporated fairly rapidly at 50 percent RH. About 30 percent of the DMF originally absorbed remained after 13 days, except for white pine where only 10 percent was retained. Methyl pyrrolidone (MP) and dimethyl sulfoxide (DMSO) were strongly held, and it is questionable whether permanent swelling of the wood by chemical reaction would have much effect on their retention.

Judging by weight losses, pine released solvents more quickly than the other woods and in most cases was swollen less after drying at 50 percent RH. This agrees with the generally low swelling resistance coefficients obtained in the previous work. Evaporation was usually a little faster from beech than from birch, but this was probably due to the cracks in the former. As with swelling, fir was the slowest to release solvent in the one comparable case.

Ovendrying was required to remove most of the remainder of the two solvents, which evaporated quickly, and the bulk of the more strongly held solvents. Between 11 and 19 percent of MP and DMSO was left in birch and beech after two 24-hour heating periods. From 2 to 4 percent of these solvents was left in pine, and the same quantity of DMF and pyridine remained in all woods except pine, which returned essentially to original weight when heated.

Extraction would be required to remove strongly held solvents, and water was generally effective with MP. Although no tests were run, it is suggested that a low-boiling water-soluble solvent such as acetone or methanol might be more effective than water in removing the last of the retained polar compounds. The proposed solvents have been used to decrease markedly the time to remove water from green timber[2] and should act similarly with polar solvents.

Preliminary exposure to 100 percent RH is an unnecessary step in removing solvents from swollen wood. Evaporation at 50 percent RH is not practical with DMSO or MP. Application of a moderate vacuum was not effective in removing the last of any of the solvents.

The conclusions of the previous paper are reinforced by this study as to the best solvent, the ease of treating white pine and the difficulties in treating Douglas-fir. As well as swelling wood most rapidly, DMF was the second fastest to evaporate and is not as obnoxious to handle as pyridine. This study also adds to the previous adverse conclusion that DMSO, while causing the greatest equilibrium swelling, requires pressure or vacuum impregnation to bring it about in a reasonable time. It was found here that an extraction

[2]Seth, K. K., and A. B. Anderson. 1965. Solvent drying of California redwood with methanol. Forest Prod. J. 15(7):297-301.

process would be needed to remove it from the wood.

One result of this study that adversely affects the previous work is the observation that beech, which swells most rapidly, checks most readily. The rapid swelling is probably enhanced by checking. Additional work would be needed to show whether beech can be swollen satisfactorily with polar solvents.

After swelling in solvent and subsequent drying, the radial and tangential dimensions of birch were generally smaller than originally. Either sufficient solvent-soluble material was extracted or there was partial collapse of the cells causing permanent shrinkage.

The greatest chance for successful treatment of wood appears to be with a process comprising swelling white pine with DMF, reaction of the hydroxyl groups with the desired chemical reagent, washing with additional DMF to recover unreacted reagent, and subsequent heating to remove the solvent.