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SWELLING OF WOOD¹

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The Phenomenon of Swelling

There are three essential characteristics of the phenomenon of swelling; namely, (1) that the solid material increases in both dimensions and weight with an accompanying thermal change as a result of the taking up of another phase, (2) that the combined phases become and remain homogeneous in a microscopic sense, and (3) that the cohesion of the solid is reduced but not eliminated.

The phenomenon of swelling is characteristic of all elastic colloidal materials but differs somewhat for different types of materials. Gelatin, for example, can swell to the point where the cohesion of the solid becomes negligible; that is, it shows a gradual transition from a swollen to a dispersed condition. Cellulosic materials, on the other hand, show no such property in ordinary swelling agents. The cohesion of the solid structure is under practically all conditions sufficiently great to limit the distention of the solid and imbibing of liquids. Cellulosic materials also show a definitely oriented structure that gives rise to differences in the dimensional swelling in the three structural directions and they lack the amphoteric property that makes gelatin readily responsive to pH changes. Cellulosic materials differ from gelatin still further in that they exhibit a coarse capillary structure that is capable of taking up liquids without accompanying swelling as well as the characteristic capillary structure of swelling. This fact greatly complicates the measurement of the swelling of cellulosic materials. The swelling of gelatin can be followed by weight changes alone. This can be done for cellulosic materials only with the greatest precautions as only the true adsorption is accompanied by swelling. For example, a piece of wood can take up about 30 percent of water on the basis of the weight of the dry wood with accompanying swelling. When immersed in water it may take up from 150 to 300 percent more water in the coarse capillary structure without any further swelling taking place. So-called swelling measurements have been made on cellulosic materials by determining the increase in weight of the material after immersion in various liquids and solutions. This, however, gives a measure of the absorbency and depends

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upon the capillary structure of the material, the surface tension of the liquid, and the ability of the liquid to wet the solid, as well as upon the extent of swelling. It would therefore be preferable to make swelling measurements of cellulosic materials on a volume change basis. This, however, is difficult if not impossible to do experimentally because of the internal as well as external dimensional changes. Even in wood where the external dimensional changes are easy to determine, the internal changes in the fiber cavities may be very complicated, thus making possible only approximations of the magnitudes of the changes. A study of these dimensional changes is nevertheless worth while as it may lead to a better understanding of the mechanism of the swelling of fibrous materials.

Swelling and Shrinking of Wood

The swelling and shrinking of wood as manifested by the external dimension changes vary with the species, structure, structural directions, density of the wood, and drying conditions. On drying green wood no shrinkage occurs until the moisture content is reduced below the fiber-saturation point (the moisture content below which the activity of the water becomes less than one). This varies for most species from about 27 to 32 percent of the weight of the dry wood (13). The shrinkage is greatest in the tangential direction (tangent to the annual rings), varying from 5 to 12 percent. In the radial direction (from the center of the tree to the periphery) it varies from 2 to 7 percent, and in the longitudinal direction (parallel to the fibers) it is only a small fraction of 1 percent. The practically negligible longitudinal swelling and shrinking is accounted for on the basis of the swelling taking place only between the threadlike micelles of the cellulose fibers which, in general, are oriented parallel to the length of the fibers. The greater shrinkage in the tangential direction than in the radial is accounted for on the basis of ray cells which have their longitudinal component in the radial direction of the wood, restraining the dimension changes in that direction.

Moisture Content versus Swelling and Shrinking

The external dimensional shrinkage of small specimens of wood, dried under gradual stepwise reduced relative humidity conditions so as to practically eliminate moisture gradients, has been shown by both Mørath (4) and the author (14) to be practically a direct function of the amount of moisture removed from the fiber-saturation point to the oven-dry condition for all the structural directions. Further data on the external dimensional volumetric shrinkage of thin tangential sections of Douglas fir, cut from material with broad annual rings so that varying proportions of spring wood and summer wood of a single ring exist in each section thus giving adjacent sections of quite widely varying density, likewise show this linear relationship (Fig. 1). Even data obtained on considerably larger specimens (8-1/2 by 5-1/2 by 7/8 inch)

in which drying moisture gradients cannot be eliminated deviate but slightly from the linear relationship (8). Part of these data for loblolly pine sapwood are plotted in Figure 2. Appreciable deviations from the linear relationship occur only at the high moisture content values. These deviations result from the outer part of the material falling below the fiber-saturation point and tending to shrink while the average moisture content is still above the fiber-saturation point. This effect of moisture gradients upon the dimensional shrinkage will be considered more at length later.

The linear relationship between shrinkage and moisture content might be expected to hold on a total shrinkage basis over the sorption range if the effect of adsorption compression is small or if it changes in a practically linear manner with changes in moisture content. The fact that it holds for shrinkage manifested externally indicates that the internal shrinkage into the fiber cavities must be either proportional to the external change or practically negligible. The following data will show that drying of small specimens under carefully controlled conditions causes a practically negligible change in the size of the fiber cavities.

Internal Swelling and Shrinking

The internal dimensions of the voids in a hypothetical gel free from stresses would change the same as the dimensions of the bulk of gel that would just fill the voids. Under these conditions swelling and shrinking as transmitted to the external dimensions would be independent of the bulk density or degree of porosity of the gel. This is not the case for wood, which shows an appreciably greater swelling and shrinking for a greater density, indicating that the external swelling is not independent of the volume of the voids. The increase in the volume of the voids on swelling is thus necessarily less than that for the same volume of gel; in fact, the voids may not increase in size at all or may even decrease during the course of swelling. This is perhaps to be expected on the basis of the structure of wood fibers, which are made up of bundles of fibrils approximately parallel to the length of the fiber with outer fibril wrappings at right angles (10). External dimension changes are easily restrained because of the structure, thus necessitating compensating internal changes in order that equilibrium may be attained.

The volumetric shrinkage of small sections of wood dried under minimum stress conditions is approximately proportional to the bulk density of the sections with but slight shifts of the proportionality constant for different species. The proportionality constant is practically equal to the fiber-saturation point. As a first approximation the relationship

$$S_e = \rho_w f_s \quad (1)$$

seems to hold, where S_e is the percentage volumetric shrinkage from the saturated to the oven-dry condition on an external dimension change basis, ρ_w is the bulk density of the wood on a dry weight-green volume basis, and f_s is the fiber-saturation point expressed in terms of the volume of water held per 100 grams of dry wood. The relationship requires that the volume of the grosser capillaries does not change with changes in moisture content and that the total volumetric swelling is approximately equal to the volume of water taken up.

This fiber-saturation point on a volume basis is, in general, 2 to 5 percent less than the generally accepted fiber-saturation point on a weight basis and would indicate that the average compression of the sorbed water is of this order of magnitude. These results are in keeping with the predicted adsorption compression values obtained from measurements of the density of wood substance in water and in a non-swelling medium for which an average compression of the sorbed water for spruce of 2.5 to 3.5 percent has been obtained (15). For example, a small transverse section of Sitka spruce with a density of 0.401 gave an external dimension volumetric shrinkage of 11.3 percent (14). The fiber-saturation point constant f_s is thus equal to 28.2. The normal fiber-saturation point on a weight basis as obtained from electrical conductivity measurements (13) and shrinkage measurements (14) is 29.0. The compression in this case is thus 2.8 percent. The compression for white pine was found in a similar manner to be 4.2 percent. Values for the shrinkage of thin tangential sections of Douglas fir of different density are given in Figure 1 and Table 1. The data show that the constant f_s obtained from the equation is within the experimental error of the fiber-saturation point expressed on a volume basis. The fiber-saturation point on a weight basis was obtained from the zero shrinkage intercept of the moisture content-shrinkage relationship. Dividing this by the average density of the adsorbed water gives the fiber-saturation point on a volume basis.

Schwalbe and Beiser (11) found from an analysis of their data for the swelling of wood that the fiber cavity dimensions are practically unchanged when assuming a fiber-saturation point of their wood of 30 percent.

The author has also obtained data on the permeability of the fiber cavities of wood to air of different relative humidities that indicate that the size of the openings changes only very slightly with swelling and shrinking of the wood. Over a complete cycle of relative humidity changes the maximum permeability variation for the heartwood of western hemlock was 3.5 percent which value is equivalent to a maximum change of the diameter of the fiber cavities of only 0.7 percent, the mean deviation being less than half of this percentage.

Even in the drying of larger specimens of wood the change in the fiber-cavity dimensions may be relatively small. Newlin and Wilson

Table 1.--Volumetric shrinkage-density data for thin transverse sections of Douglas fir

Number	ρ_w Density green volume basis	S_e External volumetric shrinkage	f_s Fiber-saturation constant on volume basis	
			From equation	From point of initial shrinkage $\left(\frac{29.2}{1.035}\right)$
	Gms. per cc.	Percent	Cc. per 100 gms.	Cc. per 100 gms.
1	0.256	7.27	28.4	28.2
2	.273	7.80	28.8	
3	.277	7.78	28.1	
4	.283	8.12	28.7	
5	.362	10.11	28.0	
6	.372	10.41	28.0	
7	.382	10.77	28.2	
8	.385	10.75	27.9	
9	.401	11.36	28.3	
10	.444	12.35	27.8	
11	.511	14.16	27.7	
12	.538	14.99	27.9	
		Average.....	28.15	

(6) give the relationship between the external volumetric shrinkage from the green to the oven-dry condition and the density of the wood on a green volume basis for the average of several thousand tests on 121 different species. The shrinkage for the average increases linearly with an increase in density giving an average value of f_s of 28. The average fiber-saturation point for all of these species is perhaps about 30 percent on a weight basis. This value corresponds to about 29 cc. per 100 grams of wood on a volume basis. There is thus an indication of the shrinkage being slightly less than that required by the foregoing equation which means that a slight increase in fiber-lumen dimensions may accompany shrinkage. The data of Peck (8), which are plotted in Figure 2 and the corresponding calculations given in Table 2, illustrate this point still further. If these larger specimens could have been dried under conditions giving negligible moisture gradients and negligible resulting stresses the moisture content intercept of the extended straight line to zero shrinkage would be a measure of the normal fiber-saturation point on a weight basis. The premature shrinkage caused by the presence of moisture gradients shifts the linear part of the shrinkage curve to lower moisture content values. The fiber-saturation point, instead of being 27 to 28 percent, is in reality perhaps nearer to 29 percent or on a volume basis 28 cc. per 100 grams of wood. The values of f_s calculated from the densities are given in Table 2. In all cases they are less than 28. The deviation for the average of all the specimens is 4.2 cc. per 100 grams of wood. In order for equilibrium to be attained this difference in volume must be accounted for by an internal shrinkage that will cause an increase in the fiber-cavity dimensions. The percentage increase in the cross section of the fiber cavity is given in the last column of Table 2. It was obtained by dividing the difference between the theoretical volumetric shrinkage, on an external dimension basis using 28.0 for the value of f_s , and the actual value by the void cross section of the wood. The void cross section of the wood is equal to 1 minus the ratio of the bulk density of the wood to the density of the wood substance (approximately 1.5). If the wood had shrunk as an ideal gel free from internal as well as drying stresses, the fiber-cavity cross section would have decreased rather than increased in size by approximately 42 percent.

The internal dimension change will be a function of the drying conditions and the resulting stresses. When a specimen of appreciable size dries, the surface falls below the fiber-saturation point before the inner part of the wood reaches this stage, thus causing stresses to be set up that may result in surface checking. If the surface can withstand this stress, it sets in tension and when the center finally dries and tries to shrink it, too, is put under tension because of the reduced external dimensional shrinkage of the exterior. Unless the stresses in the center of the specimen are relieved by failure, resulting in honeycombing, the external dimensional shrinkage of the interior is also reduced (16). In order for shrinkage equilibrium to be established the shrinkage that was unable to manifest itself externally must occur internally. Tiemann (17) has carried out an

Table 2.--Volumetric shrinkage-density data for loblolly pine sapwood boards

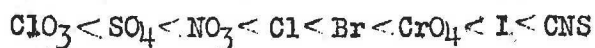
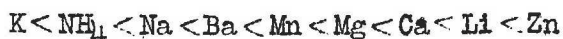
	:	:	:	f_s	:
	:	:	:	Fiber-saturation	:
	:	:	:	constant	:
	:	:	:	volume basis	:
	:	P_w	S_e	-----	Average
Nature of specimen	:	Density	:	External	increase in
	:	green	:	volumetric	fiber
	:	volume	:	shrinkage	From
	:	basis	:	equation	initial
	:		:	shrinkage	cross section
	:		:	$\left(\frac{29.0}{1.035}\right)$	
	:		:		
	:	<u>Gms. per</u>	<u>Percent</u>	<u>Cc. per</u>	<u>Cc. per</u>
	:	<u>cc.</u>	:	<u>100 gms.</u>	<u>100 gms.</u>
	:		:		
Average, 50 specimens..	:	0.471	:	11.2	:
	:		:	23.8	:
Densest specimen.....	:	.629	:	15.8	:
	:		:	25.1	:
Least dense specimen..	:	.358	:	8.9	:
	:		:	24.8	:
Least deviation.....	:	.538	:	13.9	:
	:		:	25.8	:
Greatest deviation....	:	.409	:	7.7	:
	:		:	18.8	:
	:		:		:
	:		:		:

interesting experiment that illustrates the shift from external to internal swelling under externally restrained conditions. A block of wood is clamped in a mechanical device so that its external dimensions cannot change. It is then placed in saturated air or water and allowed to reach saturation. When removed from the clamp and dried, the external dimensional shrinkage is practically the same as if the block had previously swollen normally. The block is again placed in a clamp and the process repeated. After ten such cycles the volume of the block is reduced to about two thirds of its original volume.

The shrinkage of wood under conditions that practically eliminate drying stresses is thus shown to take place almost entirely by changes of the external dimensions. When stresses are set up during the course of the shrinkage, part of the shrinkage is internal and results in an increase in the dimensions of the fiber cavities. The extent of the internal change depends on the magnitude of the stresses.

Swelling in Aqueous Solutions

Wood in concentrated aqueous solutions of salts will swell beyond its normal water-swollen dimensions. Series of saturated salt solutions of chlorides and potassium salts gave the following order of increasing volumetric swelling as transmitted to the external dimensions (14):



The order of increasing swelling is practically the same as the order of increasing solubility of the salts, increasing fractional volume of salt in solution, increasing surface tension of the salt solutions, and decreasing relative vapor pressure over the salt solutions. The pH of the solution has a practically negligible effect upon the swelling, although wood swells in alkalies and not in mineral acids (14). The fact that the swelling increases with a decrease in relative vapor pressure over the salt solution indicates that salt enters the fine structures within which swelling takes place, for if it merely entered the fiber cavities the desiccation action would allow the least swelling in the case of the salt solution of lowest vapor pressure. Adsorption measurements and measurements of the shrinkage to the oven-dry condition of salt solution treated sections indicate that the salt virtually attains the same concentration in the swelling structures as in the bulk solution (14). The retardation of shrinkage is equal to the volume of the salt deposited in the swelling structure from a solution the concentration of which is the same inside as outside the swelling structure. The swelling of wood beyond the normal water-swollen dimensions in salt solutions is, however, in all cases less than the partial specific volume of salt in the volume of liquid originally

held in the swelling structure. Water is thus replaced from the swelling structure when salt is taken up. The amount replaced is, however, less than the volume of salt taken up; hence the swelling. Evidently a solution pressure-structural resistance equilibrium is set up. The attraction of the wood for the water and the water for the salt tends to cause the wood to swell beyond the normal water-swollen dimensions. Work, however, has to be done in order to separate farther the solid structural units of the swelling material. This resistance exceeds the force with which the last few increments of sorbed water are held but it does not exceed the force with which the last few increments of salt are held by water to form a saturated solution; hence, water is removed from the swelling structure as salt enters. In slightly soluble salts the work required to cause swelling beyond the normal water-swollen dimensions is greater than that expended to remove the bulk of water equal to the partial molal volume of the salt; hence, no swelling occurs. In the more soluble salts more water would have to be removed to make room for the salt taken up. More work has to be done to remove the water considerably below the fiber-saturation point than is required to separate the solid structural units; hence, swelling occurs.

This explanation for the swelling in solutions beyond the normal swelling in the solvents is also applicable to nondissociated solutes and solvents. It may explain the swelling of cellulose in aqueous solutions of highly soluble organic compounds described by Katz (1). Whether this explanation is preferable to the polar adsorption explanation given by Katz will depend upon the demonstration of the extent of adsorption of the organic solutes.

Although Pauli's (7) hydrated ion theory for explaining swelling might be applied to the foregoing swelling beyond the normal water-swollen dimensions in the salt solutions, the other two generally accepted explanations of swelling do not apply. The electrical repulsion theory of Tolman and Stearn (18) is eliminated on the basis of the disappearance of a ζ potential in concentrated electrolyte solutions. The Donnan equilibrium theory (9) is inapplicable because of the high salt concentration and the extremely low ionization constant predicted for cellulosic materials (5).

Nonaqueous Swelling Media

The swelling of cellulosic materials in dry organic liquids is, in general, less than in water, decreasing with a decrease in the polarity of the liquid. A series of measurements by R. C. Rounds and the author on the external dimensional volumetric swelling of oven-dry wood in dry organic solvents showed that formamide and formic acid caused greater swelling than did water. A series of normal alcohols from methyl to butyl alcohol gave a decrease in swelling with an increase in molecular weight. These values are shown in Figure 3 together

with the swelling in water. The sorption at saturation pressure on a volume adsorbed basis is also plotted for the same series of alcohols and water sorbed by cotton linters as obtained from the data of Sheppard and Newsome (12). The two curves not only have similar shapes but differ by only an approximately constant multiple factor as is shown by the values given in the figure. This factor involves conversion of the external swelling to a volume increase basis per unit of weight, taking into account the adsorption compression, and the difference in adsorptive power of the two materials. The adsorption compression is the only factor that would be expected to vary with the different adsorbed materials, decreasing as the swelling power decreases. This would require a slight increase in the multiple factor with an increase in swelling as is the case.

A series of fatty acids gave a similar decrease in swelling with an increase in the molecular weight except that the decrease per CH_2 group added was less than for the alcohols. A series of benzene derivatives gave an increase in swelling in the order:



This order of swelling is practically the same as the increasing order of ζ potentials of these liquids against cellulose (3). Further benzene causes a negligible swelling and also gives a zero ζ potential. This indicates that the swelling of wood in various liquids can be explained on the basis of the electrical repulsion theory of Tolman and Stearn (13). Oriented adsorption of the liquid on the solid surface, which will be the greatest for the greatest ζ potential, will cause a mutual repulsion of adjacent adsorbed polar groups. If this repulsion exceeds the structural resistance of the solid, capillaries will be opened, thus exposing more surface for adsorption and making possible further repulsion of the structural units. This mechanism can account for swelling by large molecules without postulating pre-existing capillary spaces for them to enter. The theory in fact seems to be generally applicable for explaining all swelling phenomena with the exception of the swelling in concentrated solutions of electrolytes described in the previous section. Further correlation of ζ potentials and swelling would thus be desirable.

Replacement of Swelling Media

Although nonpolar liquids will not swell wood they can replace the swelling liquids in the swollen structure to a large extent by using a series of replacement steps in which the liquid to be removed is completely miscible with the one replacing it. The general replacement principle has been developed by Kistler (2) who applied it to silica gel, gelatin, and cellophane. R.C. Rounds and the author were able to replace a large part of the sorbed water in wood by toluene in the following manner. Small water-swollen sections of wood were kept

immersed in alcohol in a continuous extraction apparatus. The alcohol overflow returned to a distillation flask containing calcium oxide to remove the water. The dried alcohol was returned to the extractor by distillation where it again took up water before returning to the still. In this way all but about 1.4 percent of water on the basis of the weight of the dry wood was removed with a resulting volumetric shrinkage of only 0.4 percent. The alcohol was, in turn, removed by acetone by the same extraction process with a total shrinkage from the original dimensions of 0.7 percent. Removal of the last traces of water in boiling toluene resulted in a total shrinkage of 1.2 percent as compared with 10.1 percent for the direct removal of water by toluene distillation. Accordingly, 88 percent of the total sorbed water was replaced by toluene without shrinkage taking place. Water was removed by replacement with cellosolve by merely boiling the water-swollen sections in cellosolve under reduced pressure. Cellosolve causes the swelling of green wood beyond the normal water-swollen dimensions. Although some shrinkage occurs on the removal of water, the dimensions remain greater than the normal water-swollen dimensions.

When swollen sections of wood in which the water has been replaced by different organic liquids are dried, the normal shrinkage occurs. This is true even in the case of benzene which causes a negligible swelling of wood. The benzene must thus be held almost entirely by capillary forces and the shrinkage must result from overcoming these capillary forces.

Summary

The characteristics of all swelling systems and the differences in the swelling phenomena for elastic gels such as gelatin and cellulosic materials are pointed out. Volume changes accompanying the swelling of wood are estimated from external dimension changes measured under conditions where the internal changes are shown to be practically negligible. The external volumetric shrinkage of small specimens of wood dried under as nearly stress-free conditions as possible is approximately equal to the bulk density times a constant that is equal to the fiber-saturation point expressed on a volume basis. This relationship requires that the internal volume change be negligible and that the total volume change be nearly equal to the volume of water taken up, indicating that adsorption compression must be small. Data for the swelling of wood in aqueous saturated solutions of electrolytes and in dry organic liquids are presented and considered from the standpoint of swelling theories. Data on the replacement of water in swollen wood by other materials are presented.

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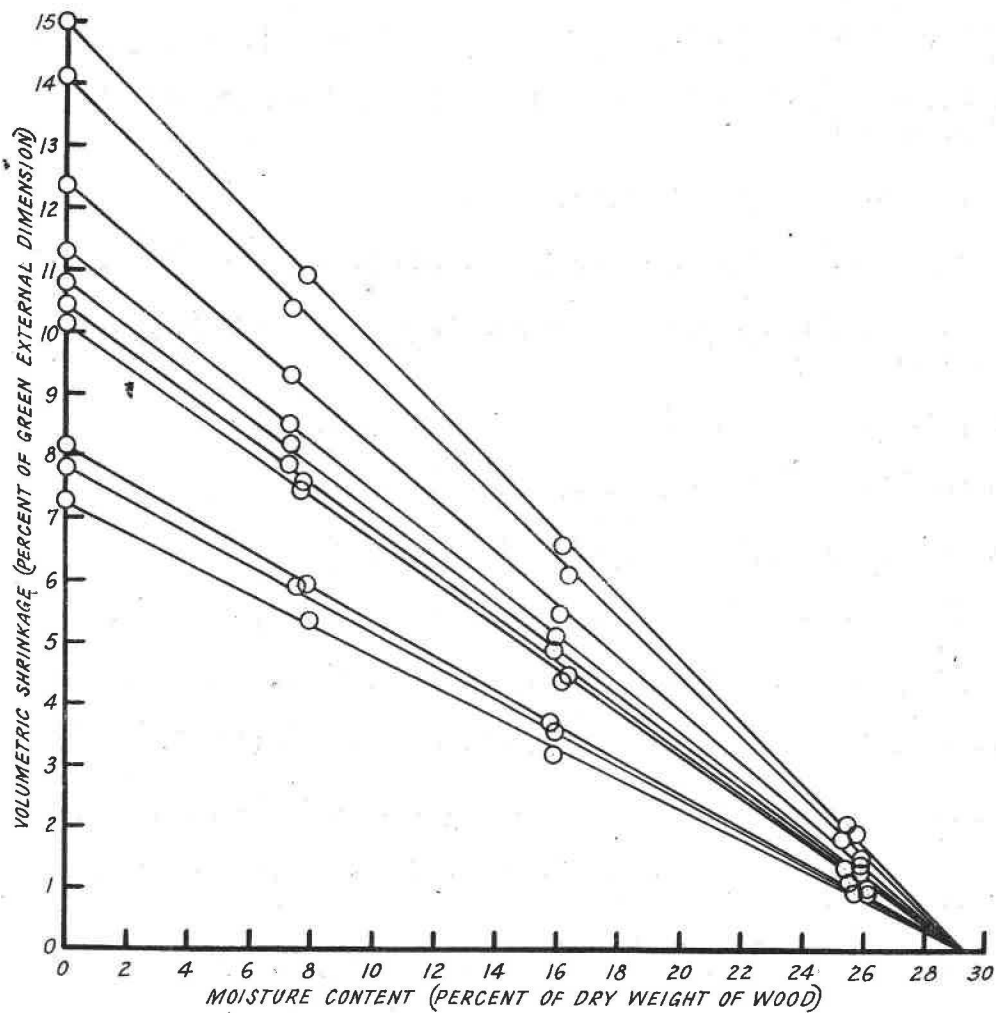


Figure 1.

Volumetric shrinkage of thin tangential sections
of Douglas fir heartwood of different density

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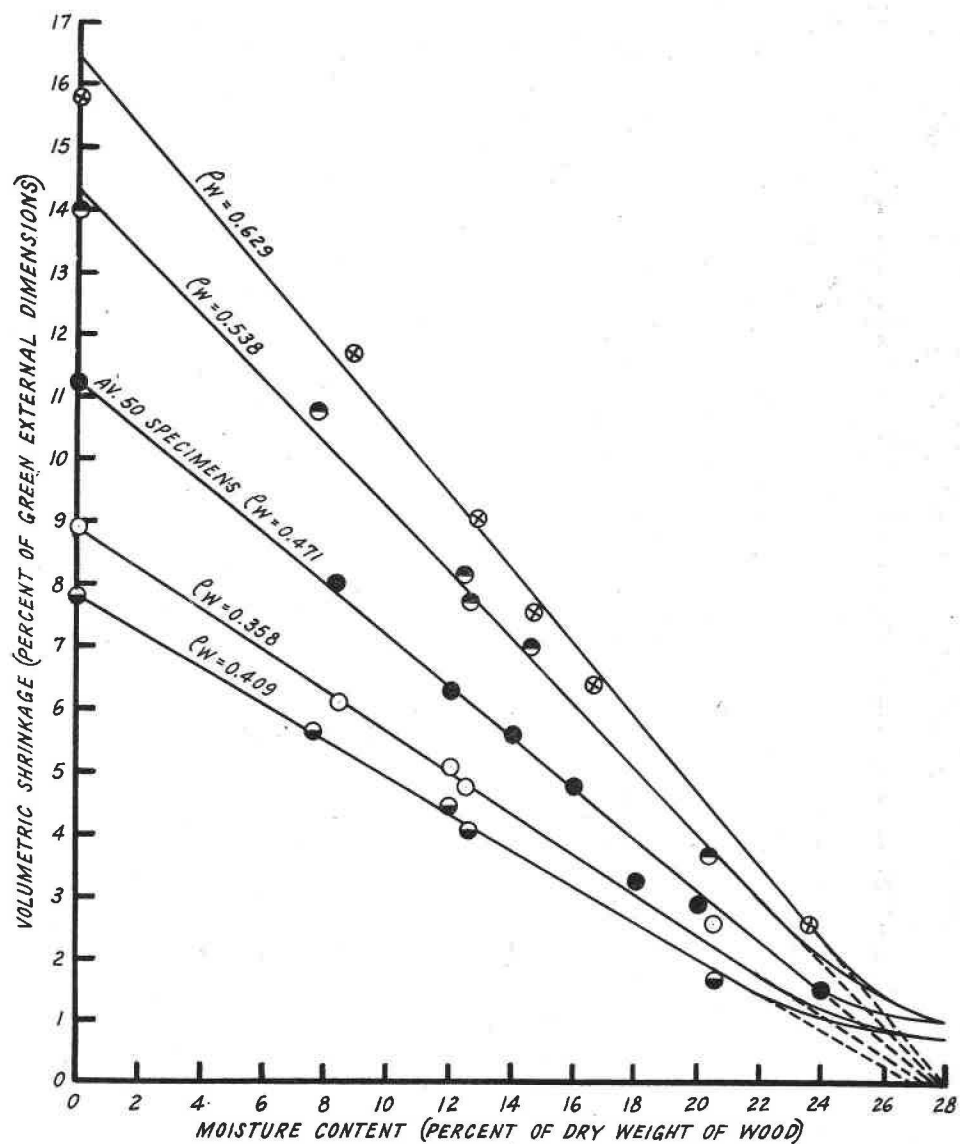


Figure 2.
Volumetric shrinkage of
loblolly pine sapwood boards of different density
M24098F

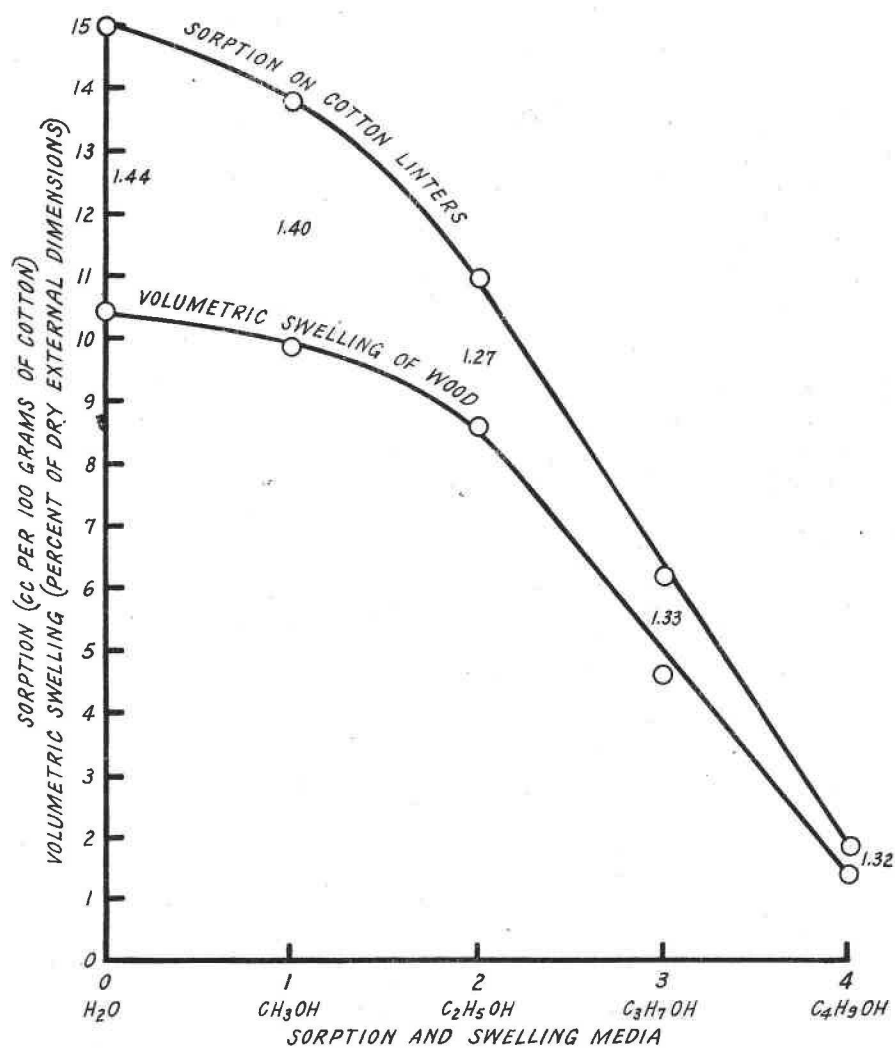


Figure 3.
Sorption and swelling -
Homologous series of normal alcohols
ZM24095F