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# TREATMENT OF WOOD WITH AQUEOUS SOLUTIONS: Effect of Wetting Agents

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UNITED STATES DEPARTMENT OF AGRICULTURE  
FOREST SERVICE

In Cooperation with the University of Wisconsin

## TREATMENT OF WOOD WITH AQUEOUS SOLUTIONS:

### Effect of Wetting Agents<sup>1</sup>

By

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U.S. Department of Agriculture

The pulping of wood chips and the treatment of dry or partially dry wood with aqueous preservatives, fire retardants, and antishrink chemicals all involve the taking up of the solution within the cell-wall structure. It is of considerable commercial importance to know the factors involved in this take-up of solutions by wood and the possibilities of increasing the rate by the addition of aqueous wetting agents. These factors have therefore been analyzed, and the effect of wetting agents has been determined for the simple case of soaking dry wood in aqueous solutions.

### Theoretical Considerations

Three steps are involved in the process of taking up of a solution by wood: (a) Wetting of the wood surfaces by the solution, (b) capillary rise of the solution in the coarse capillary structure of the wood, and (c) diffusion of the solution into the cell walls of the wood.

Although wood has a great affinity for water, water does not wet the surface of dry wood readily. This is due to the fact that water has a high surface tension, which makes it hard to displace surface-adsorbed air, and the fact that it is not a solvent for a large part of the extractive content of wood, which films the capillary surfaces (1). The addition of a wetting agent which greatly reduces the surface tension of water should materially increase the ease of wetting. The use of an alcohol should be effective both in reducing the surface tension and in dissolving the surface resinous films. That this is the case can be readily demonstrated by placing drops of water, water containing a wetting agent, and water containing alcohol on the surface of a dry piece of wood. The water drop will not spread on the surface, whereas

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<sup>2</sup>Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

the solutions will spread almost instantly. When dry wood is placed on the surface of water, only the immersed surface is wet by the water. When dry wood is placed on the surface of an aqueous solution of a wetting agent, a film of the solution spreads rapidly over all the surfaces of the wood.

The rate of capillary rise of a liquid in a porous material was shown by Lucas (3) to depend upon the following relation:

$$\frac{h^2}{t} = \frac{r\sigma}{2\eta} \quad (1)$$

where  $h$  = height of capillary rise in time  $t$

$r$  = effective capillary radius

$\sigma, \eta$  = surface tension and viscosity of liquid, respectively

For a material with a uniformly distributed porosity, the volume of liquid  $v$  that has risen in the material in time  $t$  may be substituted for  $h$ . According to this relation, the capillary rise in wood should be a function of  $\sigma/\eta$ . Wetting agents should thus decrease the rate of capillary rise because of the appreciable decrease in the surface tension and the slight increase in the viscosity.

Free capillary rise will occur when only part of the external surface of the wood is wet, such as is the case when dry wood is allowed to float on water. When dry wood is immersed in a liquid or is allowed to float on a liquid that immediately wets all of the surfaces, the capillary rise has to take place against a continually increasing resistance caused by compression of the air in the capillary structure of the wood.

The entrance of a solution into the cell walls of wood is a diffusion phenomenon. The solution may be considered as going into solid solution in the cell walls or going into capillary structure which is created by the solution itself. Swelling thus accompanies diffusion into the cell walls. The extent of this diffusion will depend upon the swelling pressure of the components of the solution for wood. It should also be a function of the heat of swelling of wood in the various solutions or of the adhesion tension of wood for the solution. In case the affinity of the wood for the solvent greatly exceeds that for the solute, it is possible that the solvent may first enter the cell walls alone, due to swelling forces, followed by a diffusion of the solute into the solvent (5,7). There is evidence to indicate that this often occurs with aqueous solutions (6,7). In such a case, the size of the solute molecule will play a large part in determining the rate of diffusion into the cell-wall structure. The rate of diffusion will, according to Einstein's equation, vary inversely as the cube of the molecular radius. The quantity of solution diffusing into the cell walls or the quantity of solvent diffusion into the cell walls, followed by diffusion of the solute into the solvent, should vary parabolically with time in a similar manner to free capillary rise.

When dry wood is allowed to float on or is immersed in water or an aqueous solution, all three steps are effective in determining the take-up of water or of solution in the cell-wall structure. The slowest of these three steps will naturally be the one to control the rate. If the rate measurements are made by determining the increase in weight of the wood with time, the diffusion factor is eliminated from the possibility of being the controlling factor, since diffusion into the cell wall is, practically speaking, incidental to the weight increase. If, on the other hand, the rate of take-up of the liquid is determined by measuring the rate of swelling, the rate of diffusion into the cell walls may be the controlling factor, since swelling is a manifestation of the diffusion into the cell walls. For this reason both rate of weight increase and rate of swelling measurements were made.

### Experimental Procedure

Most of the measurements were made on western white pine (Pinus monticola) heartwood sections (dry-volume specific gravity, 0.40) cut from a single flat-sawn board. They were 11.2 centimeters in the tangential direction, 2.0 centimeters radially, and 0.6 centimeter in the fiber direction. The tangential direction was chosen for the long direction in which the swelling measurements were made because of the fact that swelling is greatest in this direction. The fiber direction of the wood was chosen as the short dimension to hasten the rate of swelling and also because the specimens could in this case be matched to the best advantage for constancy of physical properties. In order to show the effect of the direction in which the wood is cut, additional specimens were used consisting of 1/16- and 1/8-inch (1.6- and 3.2-millimeter) sugar pine (Pinus lambertiana) veneer, measuring 15 centimeters in the tangential direction and 10 centimeters in the fiber direction. These were side matched from a single sheet of veneer. All specimens were dried for 2 days at 100° C.

The procedure used in the rate of swelling measurements was simple. Each wood specimen was held rigidly in an upright position inside a large test tube by means of a stainless steel support. Each support had a flat base with a sharp needlelike prong in the center. The specimens were pushed down on these prongs until the ends of the specimens were flush with the bases of the supports. The test tubes containing the specimens were rigidly supported in a water bath maintained at  $25^{\circ} \pm 0.05^{\circ}$  C. Ames gages reading to 0.001 inch (0.025 millimeter) were fastened above the specimens on the same mounting as the specimen tubes. The gages were adjusted to give zero reading when resting on the top of the dry specimens. The solution at 25° C. was then rapidly poured into the tube and the time recorded. The time between the removal of the dry specimen from the desiccator and the starting time of the measurements was approximately 2 minutes in all cases. Ames gage readings were then taken at definite intervals.



The swelling measurements on the veneer were made in small metal tanks. The specimens were held in a specimen and gage support between two pairs of small brass rods between which the veneer, when completely swollen, could just be slipped. This device adequately minimized warping and bending of the thin sections during the swelling tests.

Measurements of the rate of increase in weight were made by either floating the specimens on the surface of the liquid in a crystallizing dish or completely immersing the specimens by weighting them down. Specimens were removed at various intervals, rapidly wiped on a towel to remove surface liquid, and weighed. Separate specimens were used for each weighing, so as to avoid errors due to the redistribution of the liquid in the wood which might occur during the time they were out of the liquid.

### Rate of Absorption

Figure 1A shows the increase in liquid content of the white pine sections with time when floating on water, on aqueous solutions of the wetting agents Aerosol OT (the dioctyl ester of sodium sulfosuccinate) and Aerosol OS (the sodium salt of an alkyl naphthalene sulfonic acid), and on a concentrated aqueous solution of sodium chloride. The Aerosol OT, which depresses the surface tension of water to 26.3 dynes per centimeter, and the Aerosol OS, which depresses the surface tension of water to 33.2 dynes per centimeter, both increase the rate of absorption in the early stages of the process. After soaking for 30 minutes the rate of absorption from the wetting agent solutions is inappreciably more than from water alone. Evidently the rate of wetting of the wood surfaces is the controlling factor at the start, since increasing the wetting power increases the rate of absorption. After the initial wetting, the capillary rise must become the controlling factor, as the absorption of water tends to catch up with the absorption of the aqueous wetting agents. The water and the Aerosol OT curves are identical after the first few hours and the Aerosol OS curve is but slightly lower. This would be expected because of the greater surface tension of pure water (equation 1).

The point of chief practical interest is that the wetting agents do not help in attaining appreciable absorption. The small sections were not quite waterlogged in 96 hours in either water or Aerosol OT. Offhand, this result may seem diametrically opposed to the recent startling findings regarding wetting agents (2), but this is not the case. Such materials as filter paper, skeins of cotton, or duck's feathers have a far greater readily available surface per unit mass than that of wood. Even in the case of the thin cross section specimens of wood used in these measurements, the open-fiber cavity capillaries are considerably smaller than the inter-fiber capillaries of these other materials. The smaller effective capillary size in the wood results in a slower capillary rise (equation 1). Evidently this capillary rise is so slow that increasing the rate of wetting cannot

increase the combined rate. In the case of filter paper or a skein of cotton, the capillary rise between the fibers is so rapid, owing to the large effective capillary size, that wetting controls the rate of the combined wetting and capillary rise processes.

Figure 1B shows the increase in liquid content of the 1/16-inch sugar pine veneer with time when floating on water and on an aqueous solution of Aerosol OT. With the veneer, the wetting factor apparently controls the rate of absorption for a shorter time than it does for the cross sections of white pine (fig. 1A). This can be explained on the basis of the effective capillary radius of the wood capillaries being smaller in the tangential direction than in the fiber direction, since so many more very small pit-membrane pores have to be traversed per unit height of capillary rise (7). Because of the smaller effective capillary radii, the capillary rise should be slower in the tangential than in the fiber direction (equation 1). This can be shown to be the case if the data of figures 1A and B are put on a unit surface rather than a unit mass basis, the absorption being about 1.7 times as great per unit time for the cross sections as for the veneer. The slower capillary rise in the veneer thus diminishes the chance of the wetting being the slower controlling factor. After the first 10 minutes of soaking, the absorption per unit of time for water exceeds that for the aqueous wetting agent solution, undoubtedly, because of the larger  $\sigma/\eta$  value.

Another factor which might affect the relative rates of absorption of water and of wetting agents in these experiments in which the wood is floating on the surface of the liquid is the fact that the wetting agents spread over the entire surface of the wood in a few seconds, whereas the water did not wet all of the faces until capillary rise occurred over the total thickness of the specimen. Several days were required for this condition to be attained. More faces were available for capillary rise in the case of the specimens that were wet by the wetting agent, but the capillary rise was restricted as a result of compression of the air in the specimens. When the specimens were completely immersed (fig. 1C) instead of floating on the water (fig. 1A), the rate of absorption of water and of aqueous salt solutions was decreased owing to the fact that in this case capillary rise is opposed by the compression of air within the specimens. When wetting agents were added, the spreading of a film of water over all of the faces of the floating specimens made them more like immersed specimens. The increased rate of absorption caused by the use of wetting agents in the early stages of absorption when the wood is floating on the surface may have been due in large part to the fact that absorption occurred from more faces of the wood than when water alone was used.

Wood absorbs a concentrated sodium chloride solution considerably more slowly than it does water (figs. 1A and C). The surface tension of the solution is 1.17 times that of water and the viscosity is 2.2 times that of water, so that the ratio  $\sigma/\eta$  is 0.53 of the value for water and  $\sqrt{\sigma/\eta}$  is 0.73 of the value for water. If the capillary rise is the controlling factor, the rate of absorption of the salt solution should be this latter fraction of the value for water. This can be shown to be the case, after the first 25 minutes of absorption, from the curves of figure 2 in which the absorption is plotted against the square root of time. The linear relation after the first 25 minutes indicates that the absorption is in accordance with equation 1. Further, the ratio of the slope of the linear part of the salt curve to that of the water curve for the data of figure 1A is 0.715 and for the data of figure 1C is 0.705. These values are in excellent agreement with the square root of the surface tension-viscosity quotient. The data thus show that capillary rise is the controlling factor after the first few minutes and that the wetting factor cannot control the rate of absorption after the first few minutes, even in the case of a solution like the concentrated sodium chloride, in spite of the fact that the sodium chloride solution does not wet the wood as well as water.

#### Rate of Swelling

The rate of water take-up by wood, in the cases so far considered, can be controlled only by the wetting or by the capillary rise factors. For the following data on rate of swelling, the rate of diffusion into the cell walls also becomes a possible controlling factor.

Figure 3 gives the data for the tangential swelling versus time for water, aqueous solutions of the wetting agents Aerosol OT, Aerosol OS, and sorbitol laurate, aqueous solution of sodium chloride, and sodium chloride plus a wetting agent. The water and Aerosol give identical rate-of-swelling curves over the entire test time. The sorbitol laurate gives a slightly slower rate for the first few minutes, but the difference between this and the water curve has no practical significance. The rate of swelling in sodium chloride solutions decreases with an increase in the concentration of the salt. The addition of a wetting agent to the salt solution has no real effect upon the rate of swelling.

It would be of interest to analyze the swelling data of figure 3 in a manner similar to the analysis of the absorption data on figures 1A and C by plotting the swelling against the square root of time. This analysis should be possible since the linear swelling is proportional to the volumetric swelling (5), and this, in turn, is proportional to the volume increase of the cell walls (5,7). No difficulty should be encountered by substituting swelling for absorption. Diffusion, as well as capillary rise, should give a linear relation when plotted against the

square root of time. In the case of diffusion, however, the relation will no longer hold after some moisture reaches the center of the cell walls. After this point is reached, there should be a continual decrease in rate of diffusion because of the diminishing moisture gradient per unit cell-wall thickness. When plotted against the square root of time, the data of figure 3 give a linear relation only for the first few minutes, as would be expected if diffusion were the controlling factor. The same is true for the swelling of wood in ethylene glycol and glycerol solutions.

Figure 4 shows the effect of aqueous solutions of methanol, ethanol, and n-propanol upon the rate of swelling of wood. None of the alcohols nor, in fact, any of the other solutes tested increases the rate of swelling in the early stages of swelling. With some solutes, notably ethanol and propanol, the rate of swelling during the early stages of swelling decreases markedly as the concentration of the solute increases. This is not true for methanol. The apparent explanation is that methanol has a great affinity for cellulosic materials which ethanol and n-propanol do not, according to the heat of swelling data of Morrison, Campbell, and Maass (4). This affinity, together with the fact that the methanol molecule is relatively small, accounts for its ready diffusion into the cell walls in all concentrations.

In the later stages of swelling, a number of aqueous solutions cause greater swelling than that which results from water alone because of the fact that some solutes increase the equilibrium swelling (6). This increased swelling increases with an increase in concentration of the solute followed, as pure solute is approached, by a decrease in swelling (fig. 4). This behavior can be explained on the basis of the sorption-solution pressure structural resistance equilibrium theory previously described (5,7).

Data were also obtained for the rate of swelling of the white pine sections in aqueous solutions of several other solutes--butanol, sorbitol, phenol, urea, and a commercial phenol-formaldehyde-catalyst resin-forming mix (Bakelite resinoid 5995) used in the antishrink treatment of wood (8). Because of the limited solubility of butanol, it was possible to make measurements only up to 8 percent concentration by volume. The butanol caused greater swelling beyond the water-swollen dimensions than did the other alcohols in like concentrations. The phenol, urea, and resin-forming mix all caused a large swelling beyond water-swollen dimensions, but they too caused a decrease in the rate of swelling in the early stages of swelling.

The rate of swelling of 1/8-inch sugar pine veneer was also studied. Water, aqueous solutions of wetting agents, and a 25 percent aqueous solution of methanol gave almost identical curves. The direction in which the wood is cut and the size of the specimen will materially affect the rate of swelling and can cause a variation to some extent in



the relative effectiveness of the various factors controlling the phenomenon. Among the few test made with thin veneer specimens of other species of wood, there were cases in which the wetting agents caused an increase in swelling over that in water for the first few minutes. In no case, however, did this increase in rate continue to the time necessary to approach swelling equilibrium.

#### Conclusion

Wetting agents have no practical value in increasing either the rate of absorption or the rate of swelling of wood in water or aqueous solutions under ordinary soaking conditions. After the first few minutes, capillary rise is the controlling factor in determining the rate of water absorption, and diffusion into the cell walls is the controlling factor in determining the rate of swelling.

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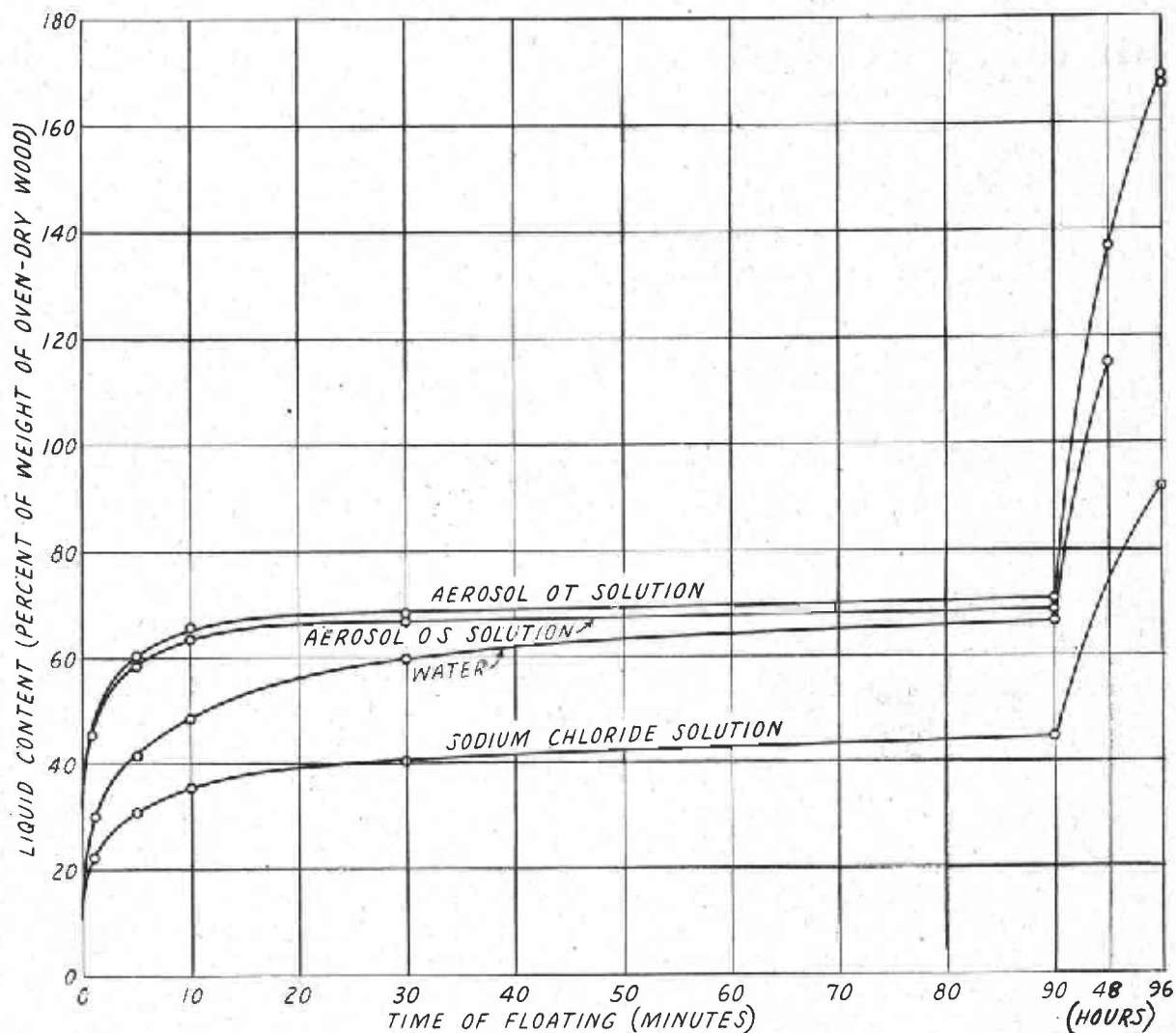


Figure 1.--Absorption versus time curves for cross-section specimens of white pine when floating on water and aqueous solutions of Aerosol OT (1.5 grams per 100 cc.), Aerosol OS (2.0 grams per 100 cc.), and sodium chloride (35.0 grams per 100 cc. of water).

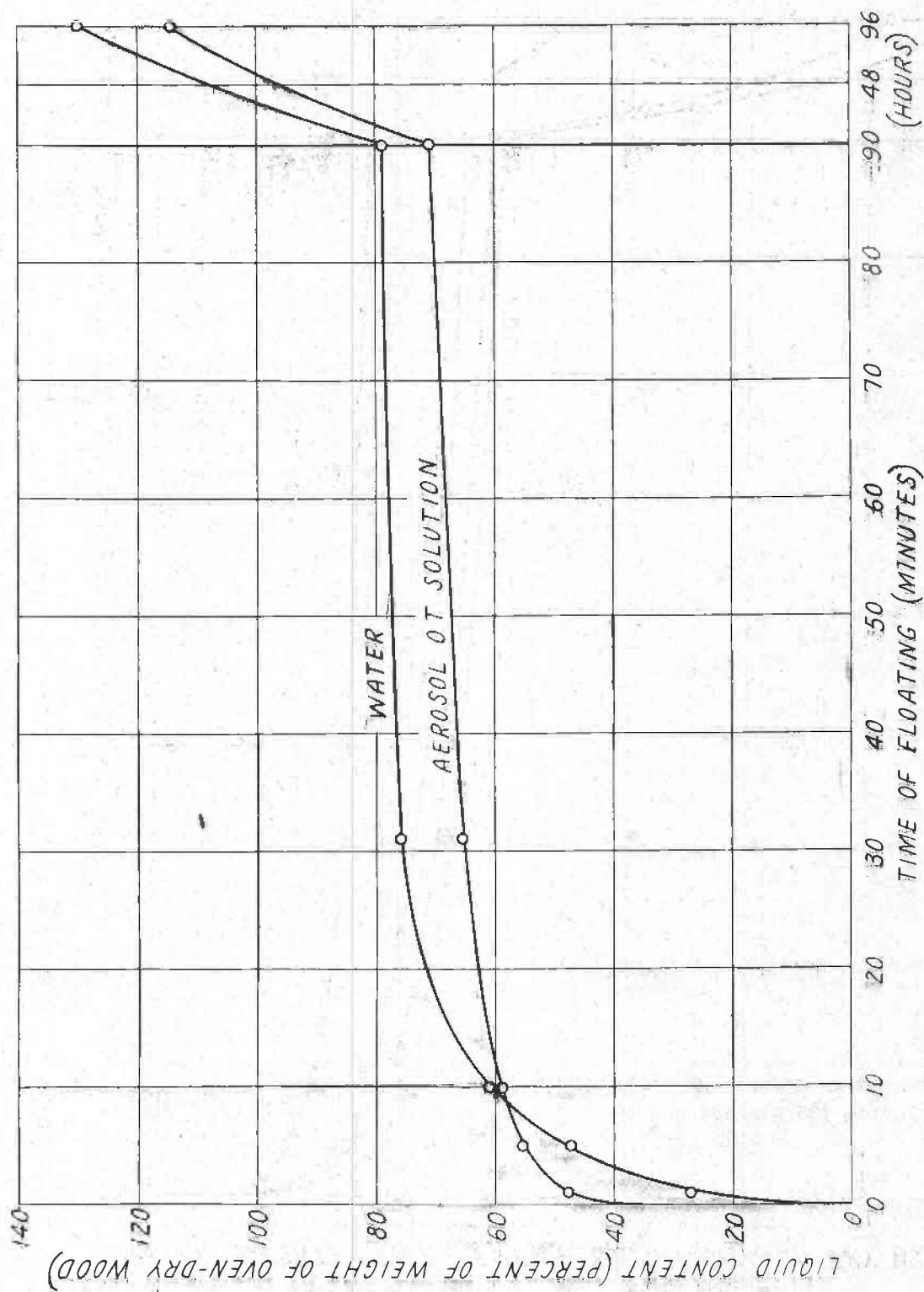


Figure 2.--Absorption versus time curves for sections of 1/16-inch sugar pine veneer when floating on water and on aqueous solution of Aerosol OT (1.5 grams per 100 cc.).



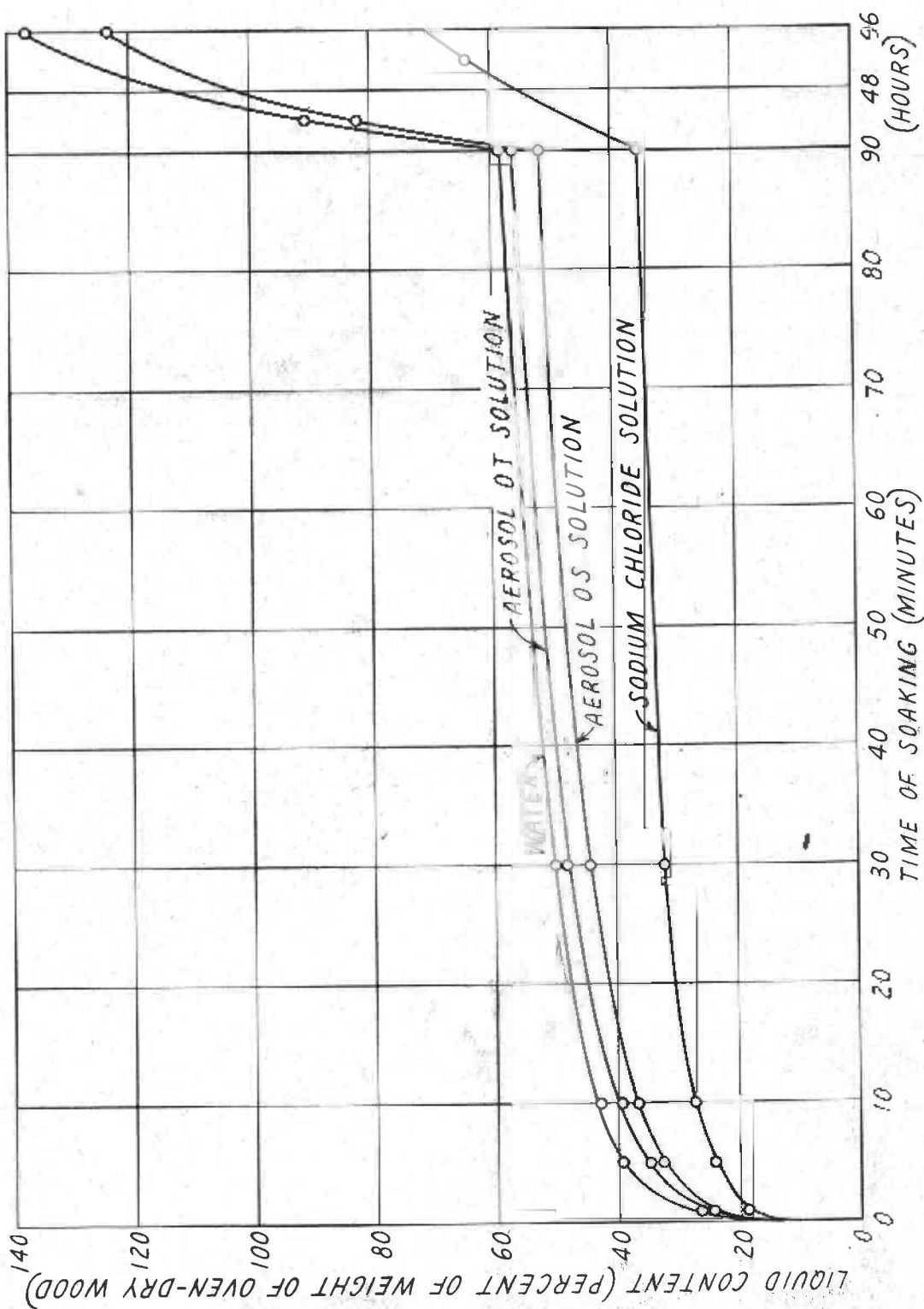


Figure 3.--Absorption versus time curves for cross-section specimens of white pine when immersed in water and in aqueous solutions of Aerosol OT (1.5 grams per 100 cc.), Aerosol OS (2.0 grams per 100 cc.), and sodium chloride (35.0 grams per 100 cc. of water).

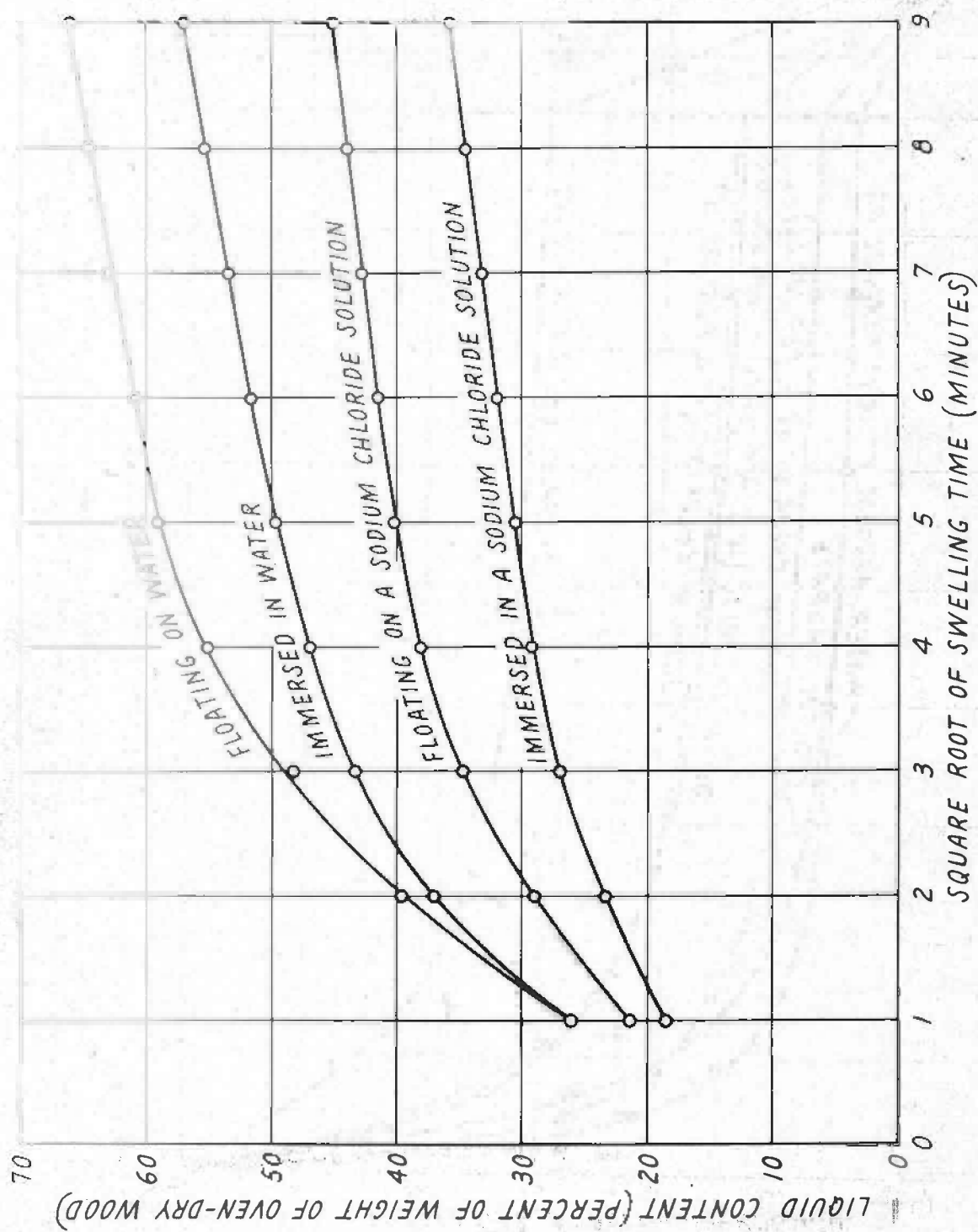


Figure 4.--Absorption versus the square root of time curves for cross-section specimens of white pine, both when floating on and when immersed in water and in aqueous solutions of sodium chloride (35.0 grams per 100 cc. of water).

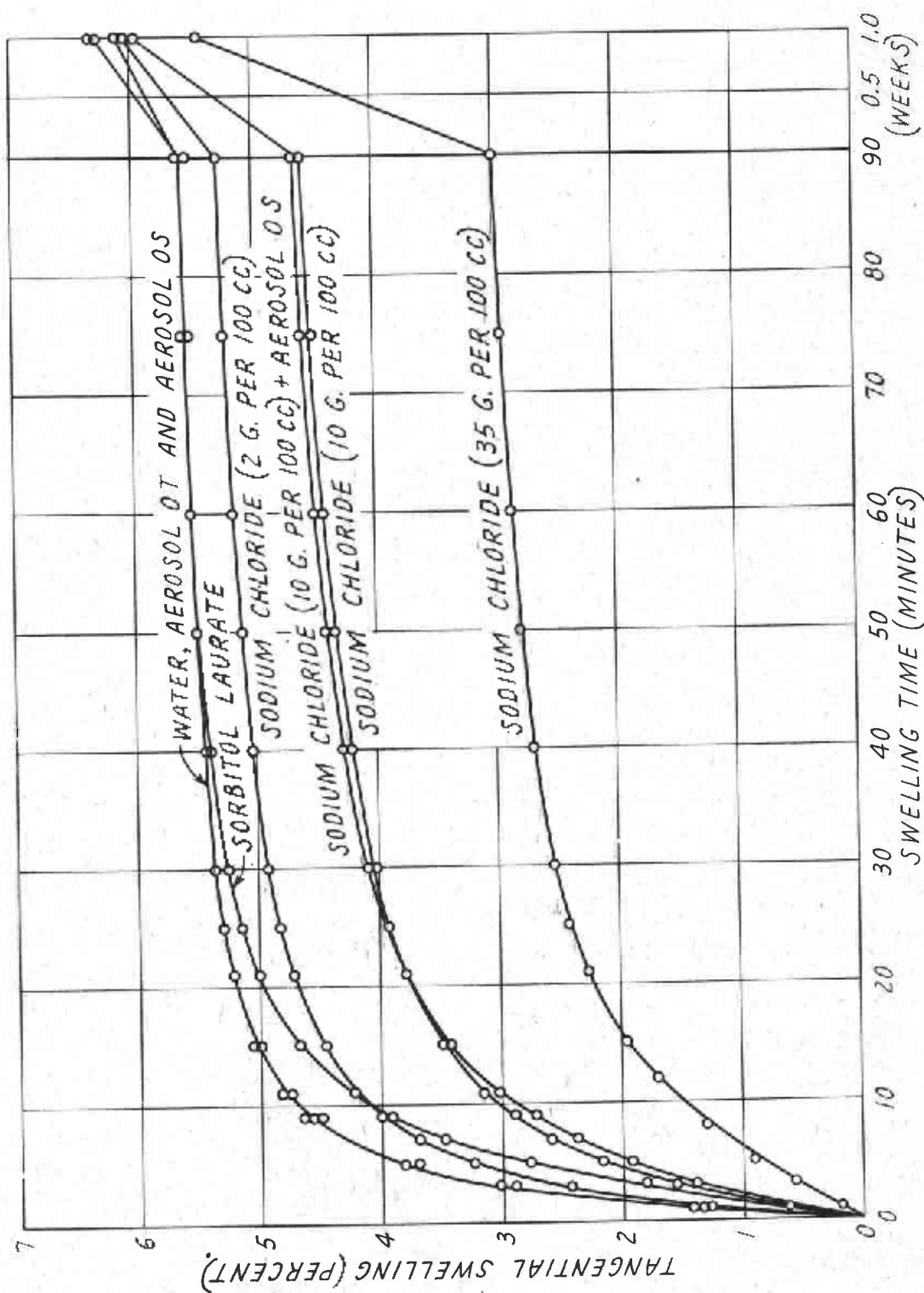


Figure 5.--Tangential swelling versus time curves for cross sections of white pine in water and in aqueous solutions of Aerosol OT (1.5 grams per 100 cc.), Aerosol OS (1.5 grams per 100 cc.), sorbitol laurate (0.25 gram per 100 cc.), sodium chloride solutions of different concentrations, and sodium chloride (10 grams per 100 cc. of water), plus Aerosol OS (0.5 gram per 100 cc.).

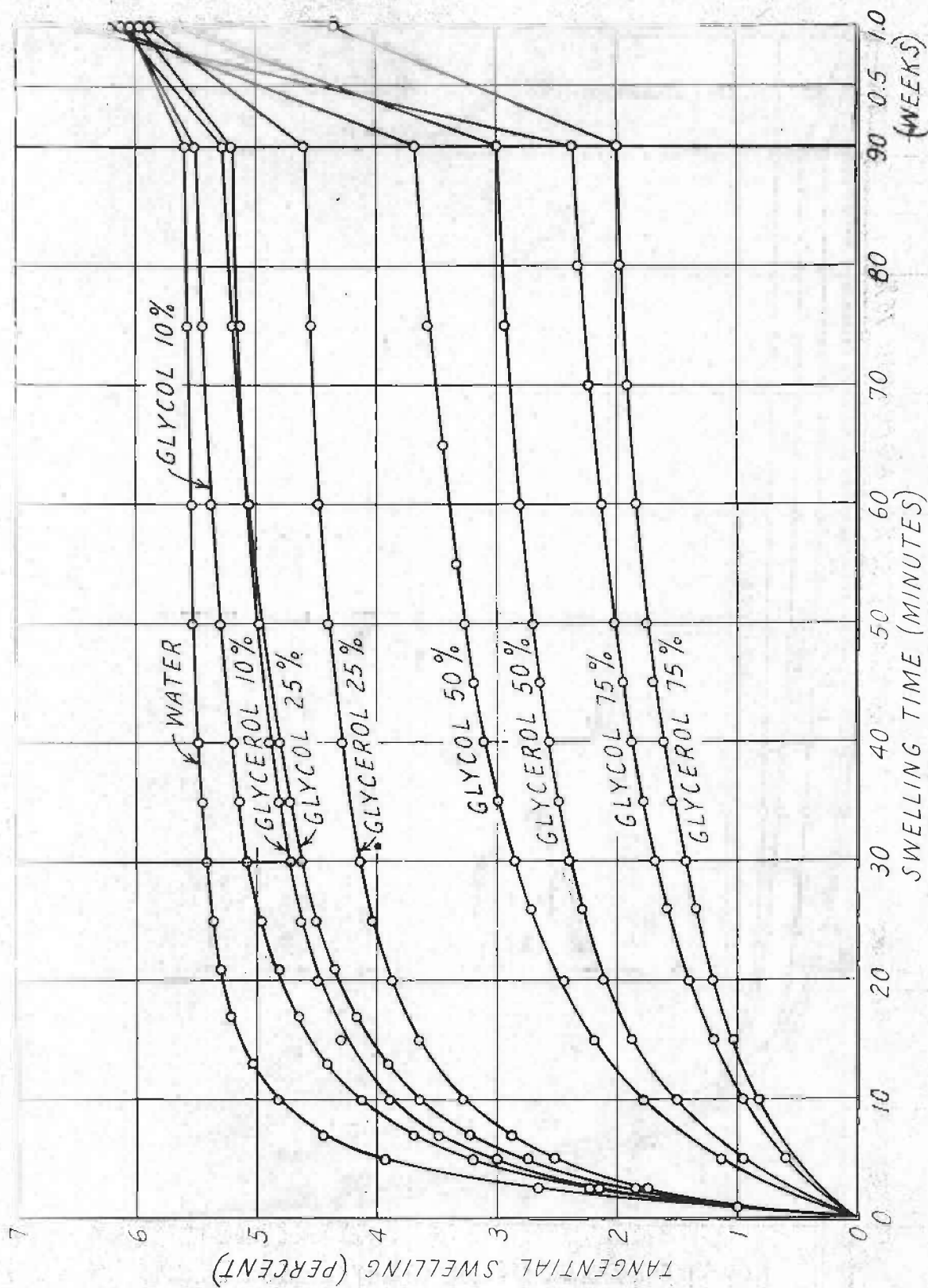


Figure 6.--Tangential swelling versus time curves for cross sections of white pine in water and in aqueous solutions of ethylene glycol and glycerol (expressed in weight percent).



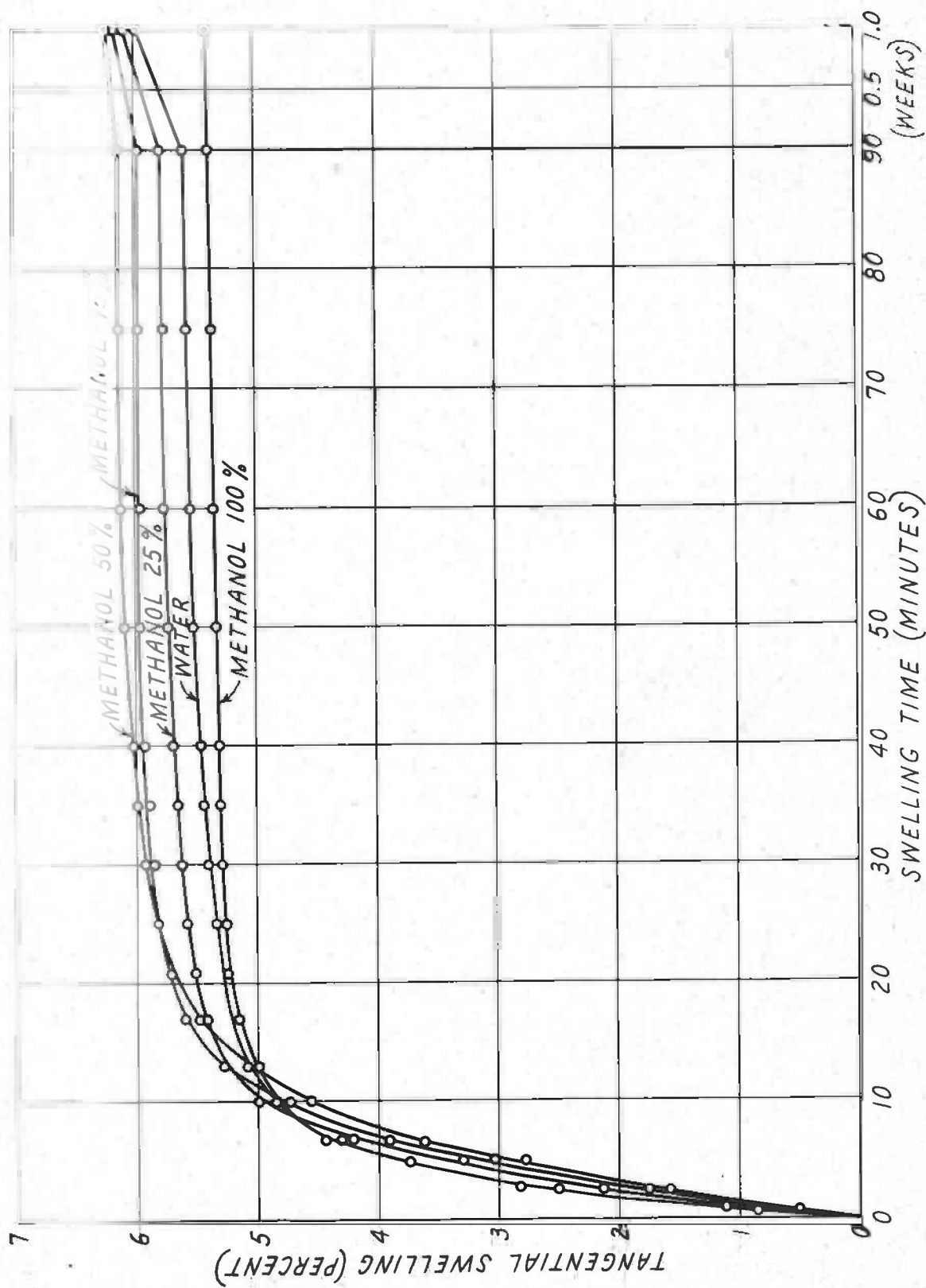


Figure 7.--Tangential swelling versus time curves for cross sections of white pine in water and in aqueous solutions of methanol (expressed in volume percent).

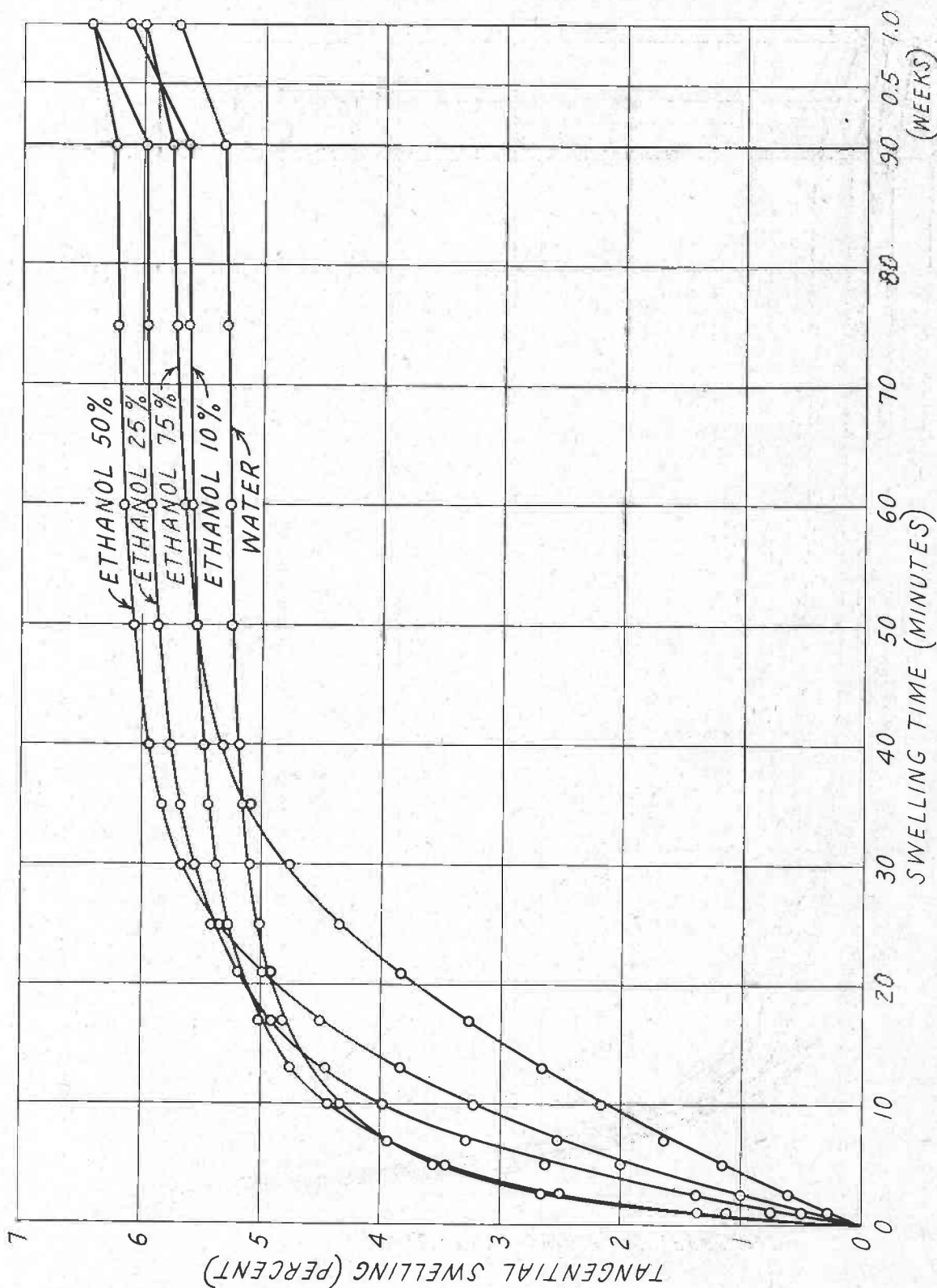


Figure 8.--Tangential swelling time curves for cross sections of white pine in water and in aqueous solutions of ethanol (expressed in volume percent).

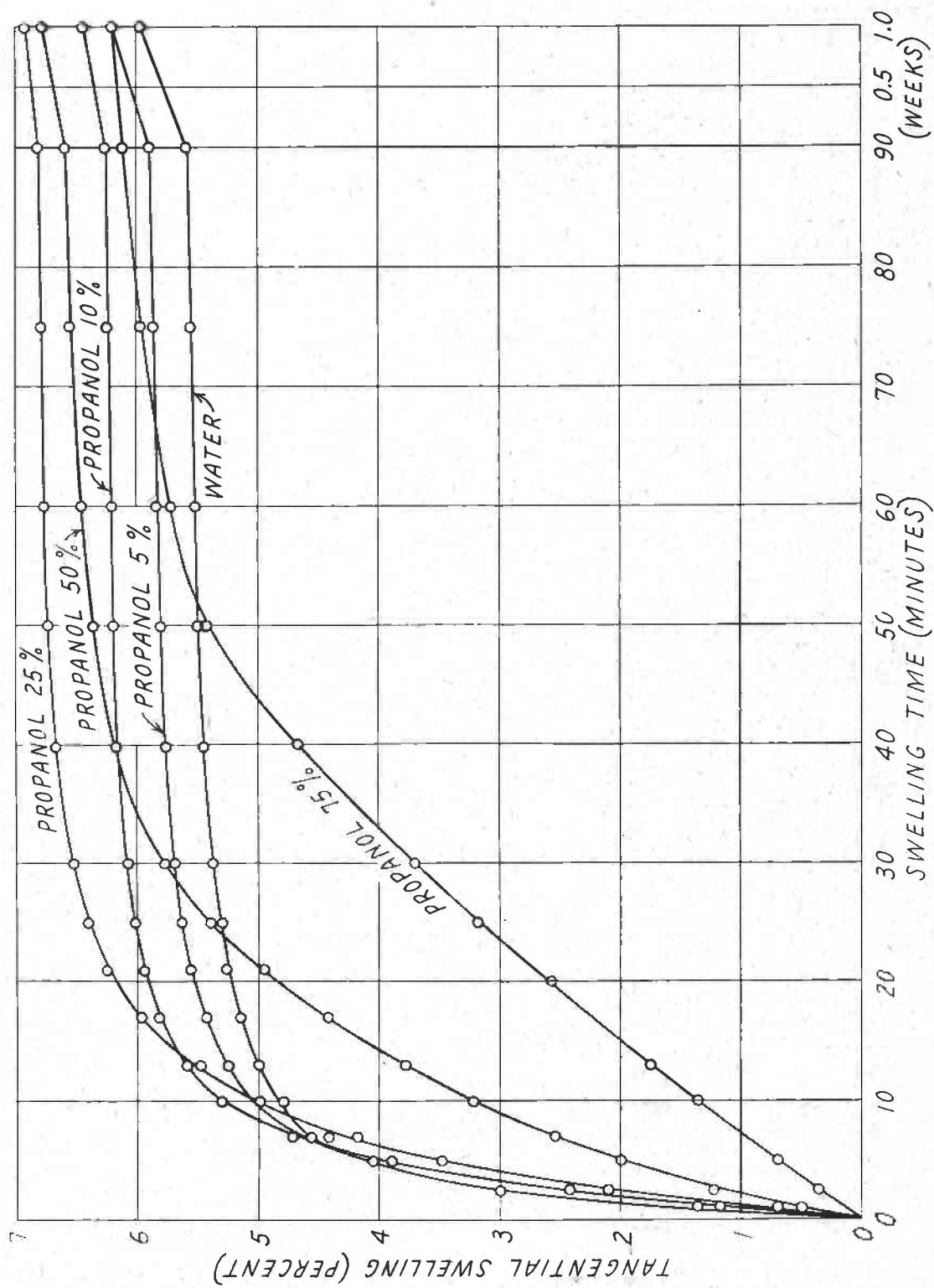


Figure 9.--Tangential swelling versus time curves for cross sections of white pine in water and in aqueous solutions of n-propanol (expressed in volume percent).

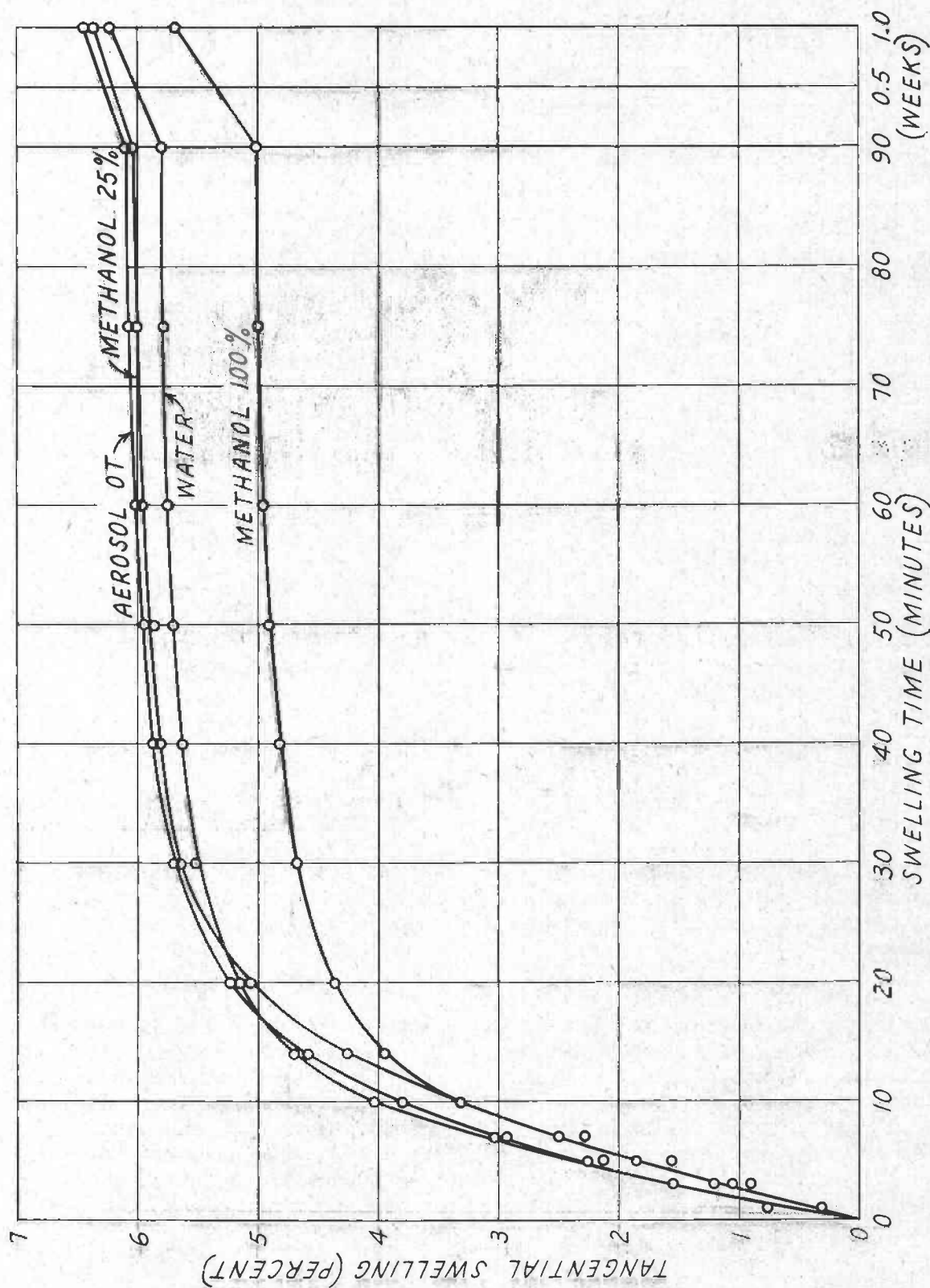


Figure 10.--Tangential swelling versus time curves for sections of sugar pine veneer in water and in aqueous solutions of Aerosol OT (0.5 gram per 100 cc.) and methanol (25 percent and 100 percent by volume).



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