PENETRATION OF TWO ORGANIC LIQUIDS INTO HARDWOODS[1]

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ABSTRACT

A theory previously described for determining the nonpressure or natural penetration of water into hardwoods was also shown to be valid for two organic liquids. The theory was verified by data from a swelling cell, which continuously and simultaneously measured the uptake of t-amylol and n-propanol with time in wood samples as well as the resultant swelling. The initial stages of bound liquid and free liquid penetration were shown to be linear when plotted against the square root of time. The maximum swelling in n-propanol was lower in red oak and black walnut than in yellow-poplar and ranged from 24 to 60% of the maximum swelling for the same species in water.

Additional keywords: *Liriodendron tulipifera*, *Quercus shumardii*, *Juglans nigra*, swelling, fiber saturation point, bound liquid, free liquid, alcohols.

INTRODUCTION

New treatments involve the combination of wood with fluids other than water: acetone as a solvent for drying wood; methyl methacrylate for producing wood plastic composites; and acetic anhydride for wood dimensional stabilization. Considerable information is available regarding the penetration and movement of water and water vapor in wood; however, knowledge of how other liquids penetrate into the fiber structures and voids of wood can give insight into new treatment techniques. The purpose of this paper is to extend the application of the theory and mathematical relationships previously used to describe the penetration of water into hardwoods without application of vacuum or pressure (Rosen 1974a) to the penetration of organic liquids into hardwoods.

In Rosen (1974a), the author discussed the longitudinal penetration of water into hardwoods using the following model: As liquid is brought into contact with one surface of a wood specimen that has been dried below the fiber saturation point, the liquid penetrates into the wood moving towards the opposite surface of the wood. The author also developed mathematical equations relating volumetric swelling, bound moisture uptake, free moisture uptake, and time of penetration during the initial stages of penetration. The bound moisture uptake, M_B, was shown to be linearly related to S, the swelling relative to an initial moisture content, M_o.

$$M_B = \frac{S(1 + 0.01\ K\ M_o)}{K}\ , \qquad (1)$$

where K is the coefficient of volumetric swelling. The constant K was evaluated from several physical parameters of the wood.

$$K = \frac{S_m'}{M_{fsp} - M_i(1 + 0.01\ S_m')} \qquad (2)$$

where S_m' is the maximum swelling of the wood relative to moisture content, M_o, and M_{fsp} is the fiber saturation point of the wood. The total water penetrating into the wood, M_T, was divided into bound moisture uptake and free moisture uptake, M_F, such that:

$$M_T = M_B + M_F\ . \qquad (3)$$

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[1] Excerpts from this manuscript were included in a paper presented at the 27th Annual Meeting of the Forest Products Research Society at Anaheim, California, on June 26, 1973.

For very permeable hardwoods such as red oak, an initial surge of water fills some of the vessel elements of the wood during penetration. The free water was divided into the vessel water, M_v, and the remaining free water, M_F' (Rosen 1974b), such that:

$$M_T = M_B + M_F' + M_V \quad . \tag{3a}$$

The value of M_v was determined by observing the M_F intercept of the plot of M_F against $\sqrt{t}$.

The bound moisture penetration constant, P_B, and free moisture penetration constant, P_F, were evaluated from the following:

$$P_B = \pi \left[\frac{L}{2(M_{fsp} - M_o)}\right]^2 \frac{M_B^2}{t} \tag{4}$$

$$P_F = \pi \left[\frac{L}{2(M_m - M_{fsp})}\right]^2 \frac{M_F'^2}{t} \quad , \tag{5}$$

where M_{fsp} is the fiber saturation point, M_m is the maximum moisture content, t is time, and L is the length of the sample. P_B and P_F are related to the rate of movement through the wood of the bound water front and the free water front. Equations 4 and 5 assume that the bound water front moves much faster through the wood than does the free moisture front, which is necessary to satisfy the boundary conditions of the differential equations used to obtain Eqs. 4 and 5. Equations 4 and 5 are applicable up to two-thirds the maximum value of M_B or M_F', respectively.

The mathematical assumptions are now applied to the penetration of other liquids into hardwoods. Therefore the definitions in Eqs. 1 to 5 must be extended to include liquids in general; e.g. M is "liquid content" rather than the moisture content; M_T refers to the "total liquid content" rather than the total moisture content; and fiber saturation point refers to the "liquid content" at which the cell wall is fully saturated but the cell cavity is empty of the "liquid." Swelling and moisture contents are expressed in percentages. Two organic solvents are used to demonstrate the applicability of the theory for two general types of penetration: (1) when only free liquid movement is involved (t-amylol); and (2) when bound and free liquid movement occur simultaneously (n-propanol).

EXPERIMENTAL AND ANALYTICAL PROCEDURES

The experimental equipment and procedure used were detailed in Rosen (1974a); therefore, only the more pertinent factors need repetition here.

Three species were used in this study: yellow-poplar (*Liriodendron tulipifera*), red oak (*Quercus shumardii*), and black walnut (*Juglans nigra*). Straight-grained and defect-free sections 5 by 5 by 40 cm were cut from the bolts of trees found locally in southern Illinois and were kiln-dried to 8% moisture content.

These square sections were then turned on a lathe along the grain to make cylinders 3.6 cm in diameter and 10 cm or 5 cm in length of yellow-poplar heartwood (YPH) and sapwood (YPS), red oak heartwood (ROH), and black walnut heartwood (BWH). These cylinders were stored until needed for a swelling cell run in an environmental chamber controlled for 8% equilibrium moisture content. This value was chosen because it is accepted as reasonable for commercially dried hardwood.

A swelling cell apparatus (Rosen 1973) was used to simultaneously and continuously measure liquid uptake and the resultant swelling in wood samples using two solvents: tertiary amyl alcohol (t-amylol) and normal propanol (n-propanol). The top face of the wood cylinder was subject to a head of liquid of approximately 4 cm. The rubber gasket encircling the lateral surface of the wood prevented transverse penetration.

Amylol does not swell wood and is nearly immiscible in water; n-propanol swells wood about half as much as water does (Stamm 1964) and is completely miscible in water. Amylol boils at 102 C and has a density at 20 C of 0.806 g/cc; n-propanol boils at 97 C and has a density at 20 C of 0.804 g/cc.

At least three swelling cell runs were made for each of the four types of wood at 8% moisture content using 10 cm-long samples for t-amylol and 5 cm-long samples for n-propanol. The runs were conducted in a room controlled at 22 ± 1 C.

Unfortunately, n-propanol interacted with the moisture in the wood samples at 8% moisture content by removing part of the bound water from the cell walls. This removal was reflected by Karl Fischer titration tests: the n-propanol that remained in the top of the swelling cell gained 2.0 to 3.8% water by the end of the run. The evaluations of P_B and P_F for n-propanol from the samples at 8% initial moisture content were confounded by this water and n-propanol interaction. Consequently, three 10 cm-long samples of each wood were dried over phosphorous pentoxide to make additional n-propanol runs with dry wood; i.e. $M_o = 0$.

On the other hand, Karl Fischer titration tests revealed that an insignificant amount of water in the t-amylol was left in the top of the swelling cell; thus t-amylol did not remove the water in the wood.

Maximum swelling (amount of swelling attained after which no further change occurs with additional n-propanol uptake) was reached at the top of the cylinder near the liquid-wood interface soon after initiation of a swelling cell run. Assuming a negligible longitudinal swelling, the change in cross-sectional area of a sample is proportional to the swelling of a sample. To compute maximum swelling values, radial and tangential measurements were taken at the top of the cylindrical samples before and after penetration for calculation of the change in cross-sectional area at that point.

TABLE 1. *Penetration constants for t-amylol*[a]

Run	M_m %	M_v %	P_F $cm^2/sec \times 10^7$
	Yellow-poplar sapwood[b] (G = 0.51)[c]		
1	109	7	82.4
2	113	26	35.1
Average			58.8
	Yellow-poplar heartwood (G = 0.45)		
3	139	0	0.50
4	127	0	0.60
5	132	0	0.98
6	125	0	1.65
Average			0.94
	Black walnut heartwood (G = 0.57)		
7	90	0	2.08
8	97	0	1.70
9	90	0	1.60
Average			1.79
	Red oak heartwood (G = 0.77)		
10	52	2	6.36
11	55	0	1.26
12	52	0	6.19
Average			4.60

[a]Samples 10 cm long at 8% initial moisture content run at 22 C.

[b]Only two runs recorded because of equipment trouble during one run.

[c]Specific gravity, G, is relative to oven-dry conditions.

RESULTS AND DISCUSSION

When t-amylol was added to the samples, measurable swelling was not observed; thus, no bound liquid uptake occurred. The t-amylol that penetrated the wood was entirely free liquid; therefore $P_B = 0$. The penetration of t-amylol is similar to the penetration of water in wood that is above the fiber saturation point relative to water. P_B is also 0 in this case, because no more bound water can be absorbed by the cell walls.

Free t-amylol penetration constants were evaluated for each of the four wood types by obtaining linear least squares statistical fits for M_F' against the square root of t (Table 1). Rearranging Eq. 5, the value of P_F was determined from the slope of the least-squares line and pertinent physical data. The regressions were significant at the 5% level, and the percent of data accounted for by the variation in the regression line was above 83% in all cases. Over 20 data points were used to determine each slope.

Because t-amylol is only slightly miscible in water and does not adhere to the cell walls, little bound water was expected to

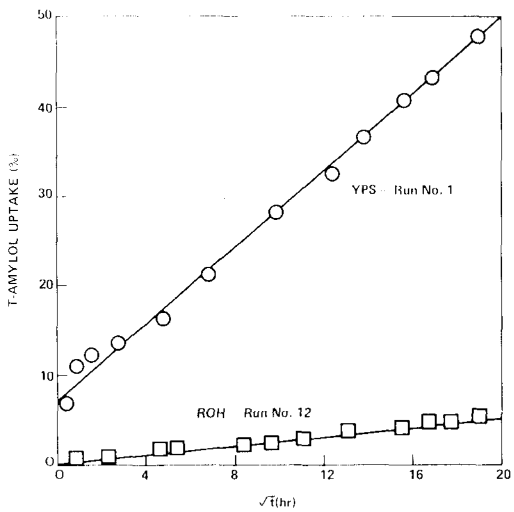

FIG. 1. Penetration of t-amylol into yellow-poplar sapwood and red oak heartwood at 22 C.

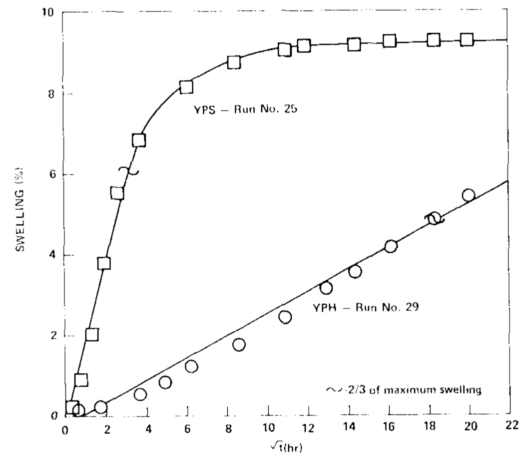

FIG. 2. Swelling of dry wood in n-propanol at 22 C.

be removed from the 8% moisture content samples by the t-amylol. However, the rate of t-amylol movement could possibly have been affected by the magnitude of the initial moisture content. Consequently, the values of P_F reported are valid only for 8% initial moisture content.

The uptake of t-amylol varied considerably within wood types as well as between wood types as shown by the variation in

TABLE 2. *Penetration constants for n-propanol in dry hardwood at 22 C*

Run		Coefficient of volumetric swelling, K	M_m %	M_v %	P_B $cm^2/sec \times 10^5$	P_F $cm^2/sec \times 10^7$
			Yellow-poplar sapwood (G = 0.50)[a]			
25		0.500	121	32	110	41.0
26		0.543	123	39	178	30.6
27		0.543	126	35	147	33.0
	Average				145	34.9
			Yellow-poplar heartwood (G = 0.42)			
28		0.320	147	0	3.41	0.55
29		0.355	150	0	3.56	1.25
30		0.360	153	0	3.04	0.69
	Average				3.34	0.83
			Black walnut heartwood (G = 0.59)			
31		0.535	87	0	2.66	6.50
32		0.527	94	0	1.51	2.16
33		0.550	94	0	1.63	6.11
	Average				1.93	4.92
			Red oak heartwood (G = 0.69)			
34		0.480	71	3	3.29	12.6
35		0.480	69	2	2.78	12.8
36		0.488	69	5	3.24	8.6
	Average				3.10	11.5

[a]Specific gravity, G, is relative to oven-dry conditions.

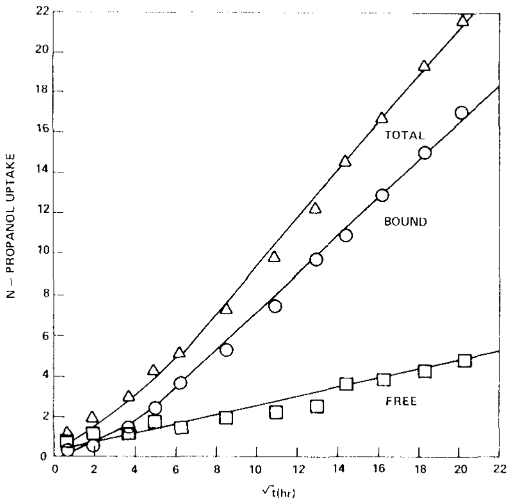

FIG. 3. Penetration of n-propanol into dry yellow-poplar heartwood at 22 C.—Run No. 29.

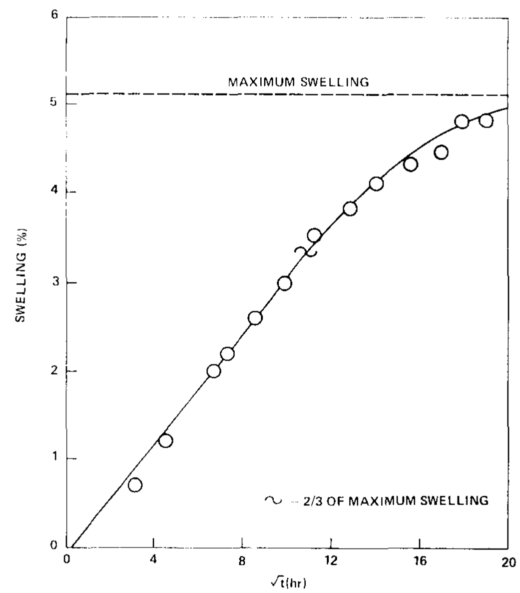

FIG. 4. Swelling of yellow-poplar heartwood at 8% initial moisture content in n-propanol at 22 C.

P_F in Table 1. Except for YPS, the uptake of t-amylol was very small even after 400 h. In Run No. 12, the t-amylol uptake in ROH was only 5% after 380 h (Fig. 1).

An initial surge of t-amylol was observed in YPS (7% as seen in Run No. 1 in Fig. 1) and, to a slight extent, in ROH (less than 2%) but was not detectable in the other wood types (M_v, Table 1). This surge, also found with penetration of water in these woods (Rosen 1974a), was thought to be the rapid flow of liquid through the large unobstructed vessels of YPS and ROH.

Before using Eqs. 4 and 5 to determine bound and free liquid penetration constants for n-propanol in the dry wood, values of fiber saturation point must be determined and the linearity between swelling and bound n-propanol uptake must be established. Rosen and VanEtten (1974) have shown that the relationship between n-propanol content and swelling from ovendry condition to fiber saturation point can be approximated by a straight line for BWH and YPS. Linearity is assumed to be valid for the wood types of this study. Rosen and VanEtten (1974) also evaluated the fiber saturation point in n-propanol for BWH (12.9%) and YPS (18.4%) using a linear extrapolation of swelling versus

TABLE 3. *Maximum swelling (in percent) of hardwoods in n-propanol at 22 C*

Species	Ovendry specific gravity	Dry wood[a]			8% Moisture wood
		N-prop.	Water[b]	N-prop/water	N-prop.
Yellow-poplar heartwood	0.44	7.3	12.2	0.60	5.2
Yellow-poplar sapwood	0.50	9.7	16.0	0.60	6.6
Black walnut heartwood	0.58	6.8	18.5	0.37	4.2
Red oak heartwood	0.75	6.5	26.7	0.24	4.2

[a]Swelling values corrected for specific gravity.

[b]Rosen (1974a).

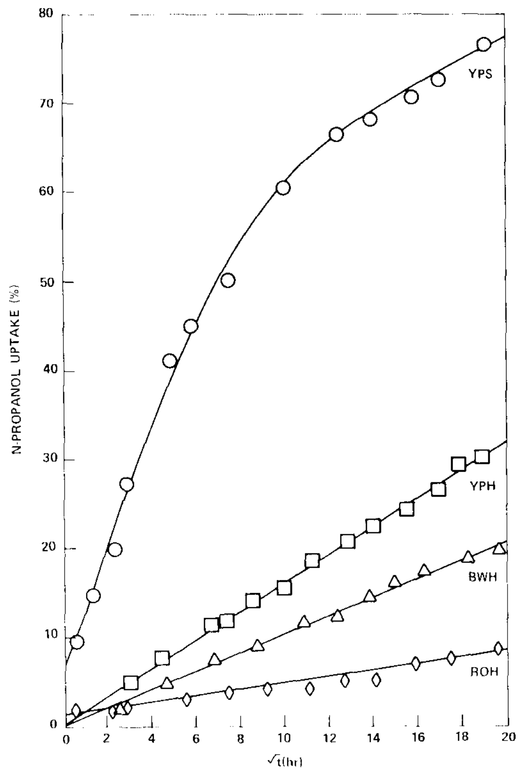

FIG. 5. Total n-propanol uptake in 8% initial moisture content wood at 22 C.

liquid content to maximum swelling. Applying the technique described in the above article, the fiber saturation points in n-propanol for ROH and YPH were evaluated as 12.3 and 20.3%, respectively.

Plots of swelling against the square root of the time during the penetration of n-propanol show a linear relationship up to two-thirds of maximum swelling (Fig. 2). Similar results were observed for each run. The time necessary to reach two-thirds maximum swelling in n-propanol can vary considerably between wood types.

Bound and free n-propanol penetration constants were evaluated in a similar manner as with t-amylol (Table 2). The regressions of bound n-propanol uptake and free n-propanol uptake against the square root of time were all significant at the 5% level. The percent of data accounted for by the regression line was generally above 90%.

The lower curve in Fig. 2 demonstrates the approach to maximum swelling by a sample of YPH (Run No. 29) as it is penetrated by n-propanol. Equation 1 was used to obtain M_B from S and Eq. 3 or 3a to obtain M_F for a plot of M_B, M_F, and M_T for the same sample (Fig. 3).

The greatest penetration of n-propanol among the wood types was observed in the YPS samples as reflected by the large values of P_B and P_F compared to other woods. An initial surge of n-propanol was observed in YPS and ROH (M_V in Table 2) but not in the other wood types.

Maximum swelling values listed in Table 3 are an average of the values obtained for each wood type in Table 2, after being corrected to the specific gravity as listed in the table. Because the degree of maximum swelling varies considerably with

TABLE 4. *Comparison of average bound and free liquid penetration constants for water, t-amylol, and n-propanol*[a]

Species	P_F, cm²/sec x 10⁷			P_B, cm²/sec x 10⁵	
	Water[b]	N-propanol	T-amylol	Water[b]	N-propanol
Yellow-poplar sapwood	97.0	34.9	59.0	57.0	145.0
Red oak heartwood	25.0	11.5	4.6	6.2	3.1
Black walnut heartwood	8.8	4.9	1.8	2.2	1.9
Yellow-poplar heartwood	1.9	0.8	0.9	1.0	3.3

[a]Water and t-amylol in wood at 8% moisture content, n-propanol for dry wood.

[b]Rosen (1974a).

wood type, a relative comparison of swelling of wood in an organic liquid to the swelling of the same wood in water gives an insight into how the organic solvent enters the cell walls of the wood. The difference in the n-propanol fiber saturation points listed previously in this paper indicates that the cell walls of BWH and ROH are less accessible to n-propanol than YPS and YPH. This difference in accessibility does not exist for water because the fiber saturation points relative to water are nearly the same for each wood (31 to 34%, Rosen 1974a). The lower amount of bound n-propanol in the cell walls of BWH and ROH compared to YPS and YPH appears to account for the difference in swelling relative to water.

In an analysis described by Skaar (1972), a constant was evaluated to indicate whether the cell cavity shrinks or swells during adsorption of water. The analysis is extended for the adsorption of any polar liquid:

$$\bar{R} = \frac{K\, G_L}{G_0} \qquad (6)$$

if $\bar{R} > 1$, the cell cavity swells
$\bar{R} = 1$, the cell cavity remains constant
$\bar{R} < 1$, the cell cavity shrinks

G_L is the specific gravity of the penetrating liquid and G_0 is the oven-dry specific gravity of the wood. The values of $\bar{R}$ for each run with n-propanol in Table 2 averaged for each wood type are:

YPS	0.83
BWH	0.71
YPH	0.63
ROH	0.56

The lumens of the cells appear to shrink upon n-propanol addition to dry wood.

Although Eqs. 1 to 5 are not applicable for n-propanol using wood with 8% initial moisture content, qualitative observations can be made from the data. The swelling for each of the wood types was linear up to two-thirds of the maximum swelling (Fig. 4). Total n-propanol uptake was shown to occur most rapidly in YPS (Fig. 5). The initial surges of liquid in YPS and ROH were not as great in the 8% initial moisture content wood as in the dry wood. The rate of n-propanol uptake was greater in the more permeable YPS and ROH in the dry wood than in the wood at 8% moisture content, but the rate was slower in the less permeable YPH and BWH for the dry wood than the 8% moisture content wood (compare total uptake of n-propanol in YPH—Fig. 3 and 5). Maximum swelling values were consistently about 35% less than for the dry wood. This difference is reasonable because the 8% wood has already partially swelled; thus, its potential would be less than that of dry wood.

The interaction of cell wall, n-propanol, and water is not very well understood. Ellwood et al. (1960) found that wood did not change dimensionally when n-propanol was replaced in green wood having a residual water content of 7.4% or more. Such dimensional changes depend on the way n-propanol enters the cell wall, rather than the amount of n-propanol in the cell wall.

A comparison of penetration constants for water (Rosen 1974a), t-amylol, and n-propanol shows some general trends (Table 4). Free and bound liquids penetrate most readily in YPS for the three liquids compared. The bound and free liquid penetration tends to be slowest in the nonpermeable wood types (BWH and YPH) and fastest in the permeable wood types (ROH and YPS).

Communication between cells in the ultrastructure of the wood is important for the movement of bound and free liquid in the wood. Many of the vessels of ROH are larger than YPS (tyloses were not observed in either wood type), yet the accessibility to the interior of the wood is greater for YPS as indicated by higher values of M_v in Tables 1 and 2 and P_F in Table 4. Although there is 30% greater void space in YPH than in ROH, the movement of free liquids is considerably lower in YPH, as seen by comparing the values of P_F in Table 4. Although the uptake of free n-propanol in ROH is moderately rapid compared to YPH, the uptake rate for bound n-propanol is the same for the two woods probably because of variations in internal structure of the two species.

If Eq. 4 and 5 are rearranged and substituted into Eq. 3a, the general relationship between M_T and t is:

$$M_T = C_1 + C_2 \sqrt{t} \tag{7}$$

where C_1 and C_2 are constants related to physical parameters of the wood.

$$C_1 = M_v$$

$$C_2 = (M_{fsp} - M_i)\left(\frac{4P_B}{\pi L^2}\right)^{\frac{1}{2}} + (M_m - M_{fsp})\left(\frac{4P_F}{\pi L^2}\right)^{\frac{1}{2}}$$

The general form of Eq. 7 also has been verified by Stamm and Petering (1940) and Morgan and Purslow (1973) based upon accepted relationships governing surface tension forces in the small capillaries of the wood. In the latter case Morgan and Purslow defined C_1 as the initial surface absorption and C_2 as related to the viscosity, surface tension, and density of the penetrating liquid, as well as the capillary dimensions of the wood. Until more data are available showing the effects on penetration of the variations of physical properties of wood and liquids, the choice of which mechanism best describes the penetration of liquid into wood will remain a hypothetical question.

SUMMARY

The general theory and mathematical relationships for penetration of liquids are adequate to describe the longitudinal penetration of n-propanol, and t-amylol, as well as water in hardwoods. Bound and free liquid uptake is shown to be linear when plotted against the square root of time up to two-thirds of the maximum uptake. The maximum swelling of yellow-poplar, red oak, and black walnut in n-propanol ranges from 24 to 60% of the maximum swelling of the same species in water.

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