

# THE WOOD-WATER-FORMALDEHYDE SYSTEM<sup>1</sup>

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## ABSTRACT

The physical interactions of the wood-water-formaldehyde system are reviewed.

Swelling data at 20 and 40 C (68 and 104 F) are presented which show that Douglas-fir and red alder wood shrink relative to pure water in low concentration water-formaldehyde solutions, and swell in higher concentration solutions ultimately to 18% by volume for a 24% (weight) solution of formaldehyde at 40 C (104 F).

The composite sorption isotherms of the wood-water-formaldehyde system are complex. There is seen, however, an initial relative increase in water concentration of the sorbed phase, followed by a general decrease of water concentration for most of the other concentrations studied. The reasons for this are not known.

*Keywords:* Swelling, water, formaldehyde, shrinking, composite sorption isotherm, Douglas-fir, red alder.

## INTRODUCTION

Concern for the effects of formaldehyde on the health and well-being of those exposed is a topic of continuing concern. Formaldehyde enters our lives by our contact with many types of materials, including fabrics used for clothing, upholstery and rugs, many plastics and other polymeric materials, and certain glued wood products. Many efforts are currently being directed at developing a better understanding of the ultimate source of formaldehyde in our environment and of the part wood panel products play in contributing to the detectable formaldehyde.

While we know that the ultimate source for most of the formaldehyde released from panel products is the resin, we are also aware that wood makes up the predominant material in the panel and that wood must somehow be involved in the system. It is the intention of this paper to review the physical aspects of the interactions of wood and formaldehyde in the presence of water, as well as to provide new experimental data regarding this system.

Prior to an assessment of the wood-water-formaldehyde system, a review of the water-formaldehyde system would be of value.

Formaldehyde exists in water in three states—as  $\text{CH}_2\text{O}$ , the hydrated monomer

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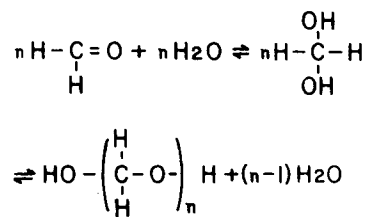


FIG. 1. Dynamic equilibrium between formaldehyde–methylene glycol–polyoxymethylene glycol.

of formaldehyde, namely, methylene glycol, and as its polymeric forms of polyoxymethylene glycol as shown in Fig. 1.

Regardless of the initial form of formaldehyde, i.e., either gaseous or paraformaldehyde, aqueous solutions demonstrate an equilibrium between methylene glycol and its polymeric forms with a degree of polymerization (DP) ranging up to several hundred. Table 1 shows that the proportion of polymeric methylene glycol can be quite high; for instance, at 50% formaldehyde by weight, there is less monomeric material than material with a DP of 6 or more (Walker 1964). Also of interest is the observation that the proportion of monomer to polymer is relatively unaffected by temperature. For instance, at 0 C (32 F) a 25% formaldehyde solution has 36% of its total solids as methylene glycol, while at 35 C (95 F) the value is 41%, and at 100 C (212 F) only 43% (Walker 1964). The ability of aqueous formaldehyde to demonstrate a distribution of molecular weights is a fundamental difference between formaldehyde and most other compounds that might be used to treat wood in aqueous solution.

Information regarding the interaction of wood with the water-formaldehyde system is surprisingly sparse. Stamm (1964) reports that Sitka spruce wood swells more in water-formaldehyde solutions than in water alone for all concentrations of formaldehyde up to approximately 37% by weight. These data are consistent with other data for the aqueous solutions of phenol, resorcinol, furfuryl alcohol, urea, cellosolve, and acetone as also reported by Stamm (1964) and the water-dioxane system reported by Oberg and Hossfeld (1960), where the swelling of wood was at a maximum at a mole fraction of 0.8 water. The work of Franks (1968) demonstrated that the structure of water is effectively disrupted at the same 0.8 mole fraction concentration for the water-dioxane system, implying that the effective swelling component of water may be its monomeric form.

The comparable information about the effects of formaldehyde on the structure of water has not been found. However, alcohols, e.g. methylene glycol, can have

TABLE 1. Distribution of formaldehyde molecular weights (Walker 1964).

CH <sub>2</sub> O wt %	Monomer	Degree of polymerization		
		2	4	≥6
5	82.2	14.3	0.5	0.02
25	40.1	23.3	9.4	5.9
50	19.0	15.5	12.7	27.8

an effect on the structure of water, and this in turn results in similar swelling responses of wood in the anticipated manner. Thus, the report by Stamm (1964) that wood swells more in water-formaldehyde solutions than in water alone is not all surprising. Only one other direct report of the effects of water-formaldehyde solutions on the swelling of wood was found. Walker (1964), in a discussion of the storage containers for formaldehyde solutions, advises against the use of wood since, "Wood shrinks on exposure to formaldehyde and for this reason is not entirely suitable for use in bulk storage . . . ."

With this apparently conflicting background, an attempt was made to explore the basic wood-water-formaldehyde interactions to provide a baseline of understanding of the system for future work in the area of formaldehyde release from panel products.

The specific objectives of this study are to determine the swelling and composite absorption isotherms for Douglas-fir and red alder in water-formaldehyde solutions.

#### MATERIALS AND METHODS

Clear, straight-grained Douglas-fir and red alder boards were obtained and cut into nominal  $1 \times 1 \times \frac{1}{8}$  inch ( $25.4 \times 25.4 \times 3.2$  mm) square wafers. Pieces were selected at random and milled in a Wiley mill fitted with a coarse screen (3 mm). The total fraction was used. Both wafers and milled material were extracted in boiling distilled water for 1 h and then rinsed with room-temperature distilled water twice before oven-drying and storage prior to use.

#### *Formaldehyde*

Paraformaldehyde (Baker—reagent grade) was refluxed with sufficient distilled water to yield a nominal 30% concentration solution. This solution was then allowed to age at room conditions for 3 weeks prior to use.

Solutions of 1, 2.5, 5, 10, 15, 20, 25, and 30 weight percent were prepared by dilution; exact concentration was determined by the sulfite method (Walker 1964). These were allowed to age at room conditions for a period of at least one week prior to use.

#### *Swelling*

Wood wafers of both species were selected for straight-grain and freedom from all defects, numbered, placed in wide-mouth bottles, and oven-dried at 105 C. The bottles were sealed upon removal from the oven and allowed to cool. As quickly as possible, the tangential, radial and longitudinal dimensions of each wafer were measured to the nearest 0.0001 inch (0.0025 mm). The wafers were returned to the bottles, and the formaldehyde solutions were poured over them. Three wafers per bottle and two bottles per solution were used. A stainless steel wire mesh held the wafers below the level of the solution. Swelling was determined for wafers in all solutions listed above plus distilled water at two temperatures, 20 and 40 C, after 14 days—a time period which, based on the personal experience of the authors, was adequate to insure wood-solution equilibrium. The solutions were maintained at the appropriate temperature for at least 20 h prior to contact with wood. Temperature cabinets for the exposure were regulated to  $\pm 0.5$  C for the exposure period.

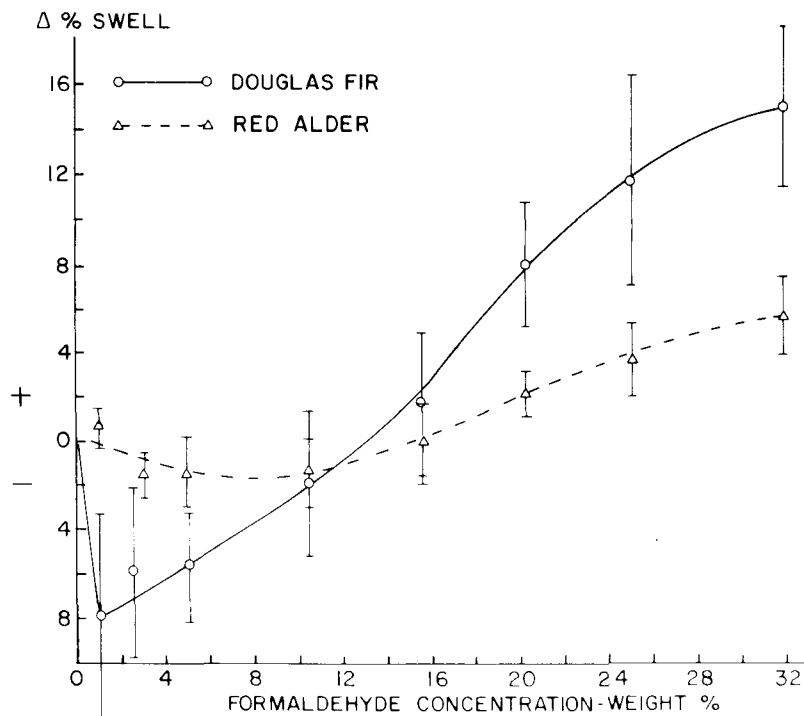


FIG. 2. Douglas-fir and red alder swell at 20 C.

Anticipating a process of competitive sorption between water and formaldehyde onto the wood, a volume of solution judged to be in substantial excess of what was actually needed was used for each bottle to minimize the effect of changes in solution concentration.

Data as reported in Figs. 2 and 3 show error brackets calculated as  $\pm$  the standard error of the mean,  $s_{\bar{x}}$ , for the 6 swelling specimen per concentration relative to the swelling in water.

#### *Composite isotherms*

Composite isotherms are a measure of the change of concentration of a solution above a sorbate as a function of the amount of solution and the amount of sorbate. Composite isotherms were determined for the milled wood samples, as well as for cotton (Parke-Davis, absorbent grade). Cotton was chosen because it contains cellulose but not lignin. Composite isotherms were determined at 20 and 40 C.

Two-ounce (55-ml) prescription bottles fitted with teflon cap liners were used; wood or cotton was placed in the clean, pre-weighed bottles and oven-dried, the weight of the substrate was determined, and then either water or a formaldehyde solution was pipetted into the bottle. The bottles were then sealed and reweighed. All solutions were maintained at the exposure temperature for at least 24 h prior to contact with wood. As with swelling, the exposure period was 14 days.

The bottles were shaken periodically during the exposure period to insure com-

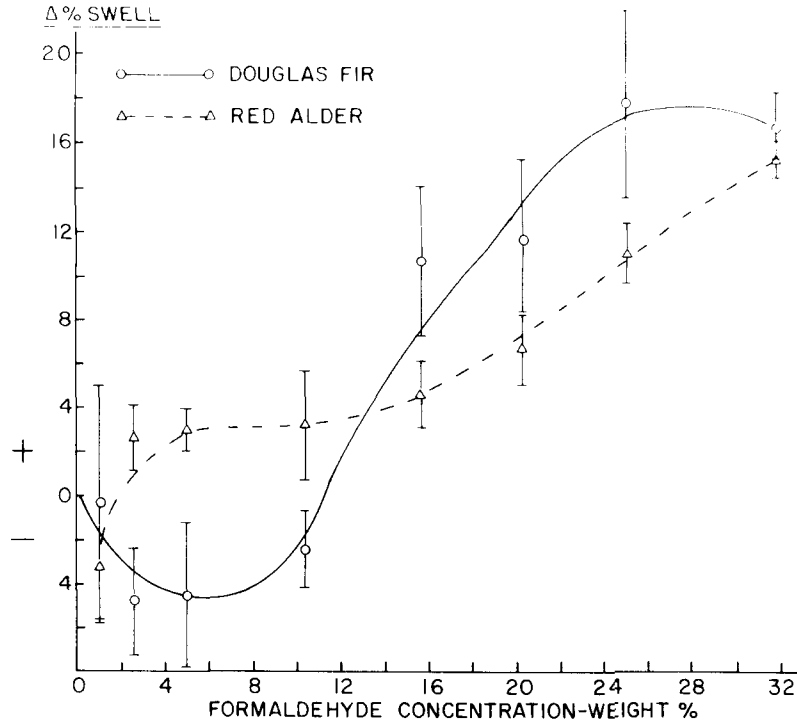


FIG. 3. Douglas-fir and red alder swell at 40 C.

plete and uniform formaldehyde-water contact with all wood particles. After 14 days the concentration of the formaldehyde above the milled wood or cotton was determined using the sulfite method. The composite isotherm was calculated and plotted  $w\Delta c/m$  against the initial concentration of the formaldehyde solution, where  $w$  is the initial weight of liquid brought into contact with  $m$  grams of wood or cotton, and  $\Delta c$  is the change in weight percent of the formaldehyde solution. This calculation technique is reported by Kipling (1965).

Data as reported in Figs. 4 and 5 are the mean of the 2 points. Error brackets identify the range of the two readings. For several points the error brackets are smaller than the point locating the mean value.

#### RESULTS AND DISCUSSION

Swelling results at 20 and 40 C are presented in Figs. 2 and 3, respectively. While all dimensions showed an increase, the dimensional change in the longitudinal direction was so small that statistically it was not significantly different from zero change. Thus, swelling reported here is radial times tangential swelling relative to that for pure water. What is seen is an initial shrinkage followed by swelling up to the values reported by Stamm (1964). Stamm reports an increase in volume for all concentrations of formaldehyde.

The swelling reported for Douglas-fir and red alder in this paper was measured in uninhibited or essentially methanol-free formaldehyde-water solutions. No

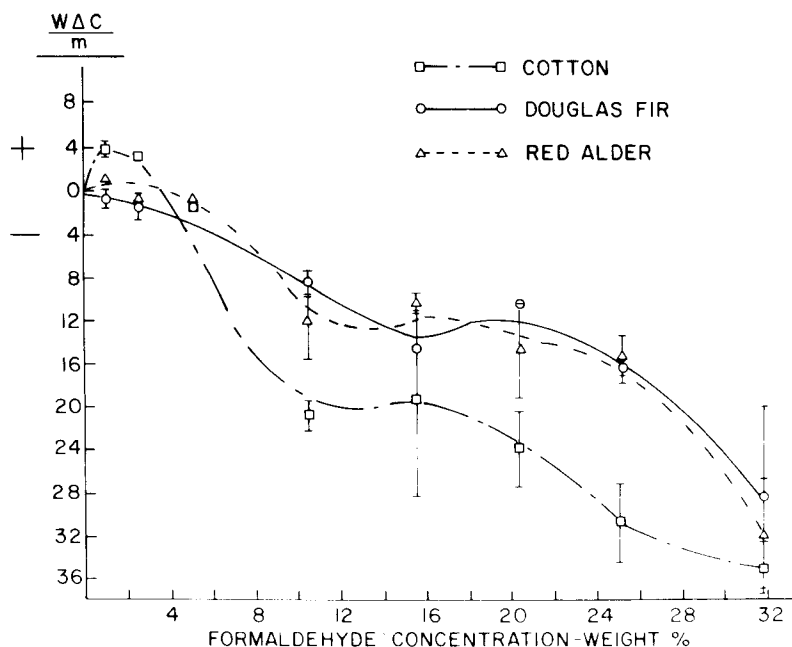


FIG. 4. Composite sorption isotherm at 20 C.

mention was made by Stamm (1964) of the type of formaldehyde solution used in his work; thus there is a distinct possibility that he used inhibited formaldehyde. Since alcohol also tends to swell wood, the differences reported here are not necessarily in conflict with earlier work. While the amount of methanol in a dilute solution of inhibited formaldehyde is quite small (0.25–0.4%), the possibility of a synergistic action between formaldehyde and methanol to yield the swelling reported by Stamm (1969) in an aqueous environment cannot be ruled out. This, however, does not explain why the wood shrinks relative to water when placed into dilute solutions of formaldehyde. Based on the limited scope of this particular effort, the question cannot be answered; however, a model can be suggested.

At the dilute concentrations where the shrinking takes place, most of the formaldehyde is in monomeric form and is hydrated to form methylene glycol. It can be suggested that absorption of both water and formaldehyde takes place so that enough water is present to provide sufficient plasticization of wood, permitting the bifunctional hydroxyls of the methylene glycol to draw adjacent sections of cellulose chains together, bridging the gap with a methylene glycol molecule.

The concentration at which shrinking is greatest is approximately 0.031 mole fraction formaldehyde. The enhanced swelling of wood in various solutions with water seems to occur in the range of 0.2 mole fraction solute. Thus the effects of the structural disruption of water (Franks 1968) may not yet have the opportunity to come into play.

Maximum wood swelling in the water-formaldehyde system is reported here as being at 0.26 mole fraction formaldehyde. This might suggest that since the maximum swelling occurs in the approximate range of maximum disruption of, or

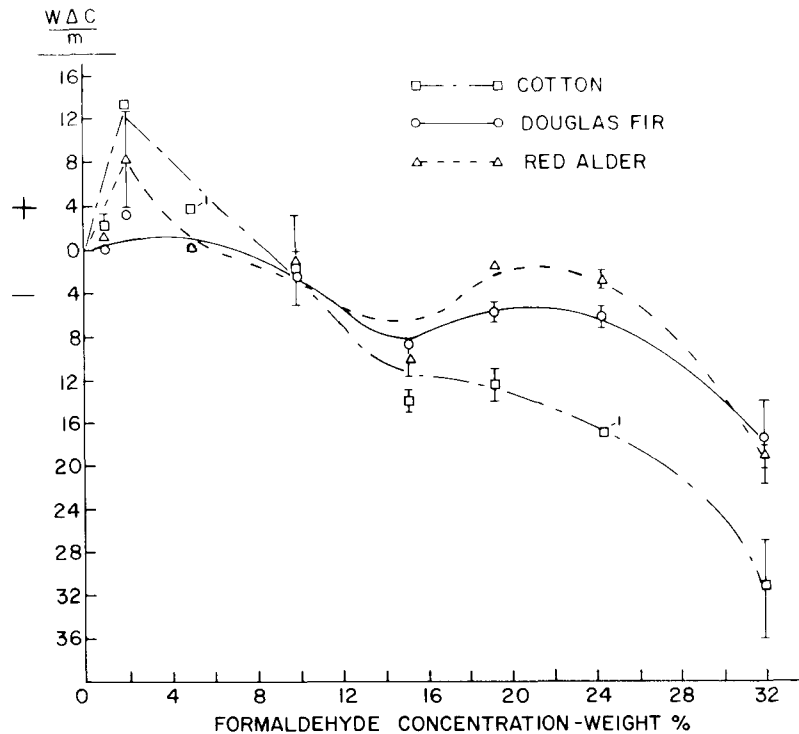


FIG. 5. Composite sorption isotherm at 40 C.

interaction with, water by solutes that swelling greater than that of water alone may fit the model reported earlier for the water-dioxane system. The work of Franks and Ives (1966), in reviewing the effects of organic solutes on the behavior of water, notes that, "A second hydroxyl group in the solute molecule (glycols) shifts the balance of competing influences in favor of 'aqueous behavior' and the anomalies become less marked." Thus, while both this paper and the earlier work by Stamm (1964) point out a swelling maximum, the current existing models may not fit, again pointing to the complexity of the wood-water-formaldehyde system.

Maximum swelling for wood was reported as occurring in the highest concentration formaldehyde solution used for the experiment. This concentration was selected as being the highest practical level of stability at the 20 C exposure condition. Higher concentrations may lead to precipitation of paraformaldehyde. Perhaps future work at higher temperatures will show whether this concentration yields the highest swelling for wood.

The error brackets in Figs. 2 and 3 show an interesting phenomenon, in that the standard error of the mean for the Douglas-fir specimen is significantly larger than for the red alder. An effort was made to secure uniform straight grain wood for both species, but the Douglas-fir obtained was of a particularly uniform, even-grained, slow-growth nature. The differences in the standard error of the mean for Douglas-fir and red alder seem to suggest that perhaps there may be a species effect in wood-water-formaldehyde interactions.

The composite sorption isotherms are shown in Figs. 4 and 5 for 20 C and 40 C respectively. In general the curves correspond well to the general form of such data as reported by Kipling (1965) in that both positive and negative values of  $w\Delta c/m$  are present. It must be realized that even though  $w\Delta c/m$  may show both positive and negative values corresponding to relative increases and decreases in one component when compared to another, that this does not mean that either component is sorbed exclusively. Positive or negative values of  $w\Delta c/m$  indicate relative proportions of one component to another. As shown at 20 C, the isotherm for cotton shows a slight initial increase in the formaldehyde concentration of the liquid phase and then a decrease. Isotherms for both wood species show essentially no change initially and then a decrease in concentration of formaldehyde in the solution.

The 40 C composite isotherm shows more of the same pattern. In this case the wood as well as the cotton shows a relatively greater increase in the concentration of formaldehyde in the low-formaldehyde section of the curve and then a decrease for all three sorbates with increasing formaldehyde concentration. Wood shrinkage is shown to occur over that range of concentrations that show an increase in the concentration of formaldehyde in solution: i.e., the wood sorbs more water relative to formaldehyde. This seems inconsistent with what is known about wood-water interactions, and will probably remain a puzzle until such time as it is possible to determine quantitatively the composition of the sorbed phase.

Another interesting feature of the composite isotherms is that the curves themselves are not smooth although curves of this type usually are. Even considering the complexity of the molecular weight distributions of the water-formaldehyde system itself, it is suspected that the presence of wood provides a further confounding factor. This is suggested by the undulating nature of the isotherm curves.

The data developed for the composite isotherms seem to suggest that the active component in the reactions of wood with formaldehyde is most likely the cellulose and not the lignin. This is consistent with the observations of Roff (1959), who studied the reactions of the water-formaldehyde-methanol system with cotton. In Roff's study, composite sorption isotherms plotted from data (his table 8) show a uniform decrease in formaldehyde concentration with increasing concentration of formaldehyde in the immersing liquid. This parallels the uniformly increasing swelling for Sitka spruce as reported by Stamm (1964). Our work shows that those areas of the composite sorption isotherm that show a decrease in formaldehyde concentration correspond to the areas of increasing swelling similar to the work of Roff and Stamm. Thus, initial increase in the formaldehyde concentration reported in our work which parallels the shrinkage of wood relative to water may very well be related to the absence of methanol.

Of interest in Roff's work was the observation that it was possible to quantitatively remove all the formaldehyde sorbed onto the cotton after a variety of exposure conditions. This seems to be inconsistent with the observations of Stamm and others who reported the permanent stabilization of wood with formaldehyde. As reported, formaldehyde is most effective in stabilizing wood only in the presence of an acid; typically, the stronger the acid, the more efficient the stabilization. Work in the chemical bonding of wood (Willey and Ruthman 1950) has shown that oxidative coupling of wood is possible in the presence of strong



acids alone, and that the stronger the treatment the greater the stability, but the more brittle the wood after treatment. Since these observations are consistent with those for acid-formaldehyde stabilization of wood, it seems reasonable that the acid and not the formaldehyde is the more important of the reactants in the stabilizing process.

#### CONCLUSIONS

The following conclusions can be drawn from this study:

1. Wood shrinks in low concentration formaldehyde-water solutions when compared to water alone.
2. Wood swells more in higher concentration solutions of formaldehyde-water than in water alone. Maximum swelling occurred at the highest concentration of formaldehyde used in the experiment, 31.9% by weight. Swelling increases with increasing temperature in the formaldehyde-water system.
3. At low concentrations of formaldehyde in water, the concentration of formaldehyde in the liquid phase of the wood-water-formaldehyde system increases followed by a decrease at higher concentrations. The magnitude of concentration change increases with increasing temperature.

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