

Treatment of timber products with gaseous borate esters

Part 1. Factors influencing the treatment process

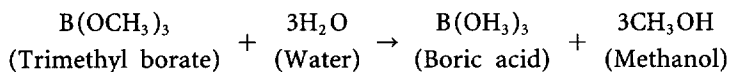
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Summary Several factors which influence the treatment of timber products with vapour phase preservatives such as borate esters are considered. Gas flow rate through the substrate was found to be a significant factor limiting both preservative penetration and its rate of deposition. A theoretical model of the treatment process was developed and tested experimentally to determine the influence of several factors on the retention and distribution of boric acid. Gas flow into the timber product was influenced by permeability, pressure gradient and substrate moisture content. The implications of the findings are considered with regard to the treatment of wood and wood products with gaseous reagents.

Introduction

In earlier reports on the gas-phase preservative treatment of panel products using a volatile borated ester, tri-methyl borate, (Murphy and Turner, 1989; Turner et al, 1990) successful treatment of several different products was demonstrated at both elevated and ambient temperatures (50 and 20 °C). The process involved placing the timber material in a vacuum cylinder which was then sealed and evacuated. Once a predetermined vacuum level was reached liquid preservative was admitted which vapourised to produce a saturated gas mixture. The rapid initial increase in pressure within the cylinder created a pressure differential between the gas atmosphere and the core of the material being treated. This induced flow of gas into the wood material where it reacted with the moisture present in the wood to form the preservative end product, boric acid, in the following reaction:



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As gas reacts with the wood to deposit boric acid (solid), the pressure decreases in the cylinder and further trimethyl borate is drawn from liquid into gas phase to maintain gaseous equilibrium (Turner, 1991). The reaction will continue until either a required retention of boric acid or a saturation retention is obtained, or all active ingredient has been consumed. Treatment is terminated by withdrawing any remaining gas and methanol by-product under vacuum, the treatment vessel is then vented to atmospheric pressure and the treated material removed, ready for immediate use. Depending on the retention deposited, protection against microbial and insect attack or protection against flame spread can be achieved.

One of the most notable findings of our earlier work was the observation that boric acid deposition in oriented strandboard (OSB) increased in proportion with the square root of time for which the material was in contact with the preservative gas. The relationship was observed at treatment temperatures of 20 and 50 °C and is illustrated in Figs. 1 and 2. The points plotted in Fig. 2 are the squares of the mean values from

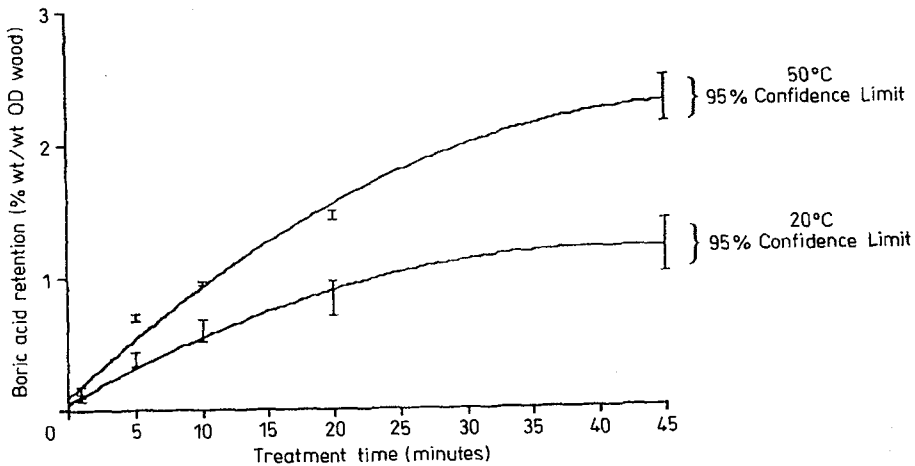


Fig. 1. Comparison of treatments on OSB at 20 °C and 50 °C (Turner 1991)

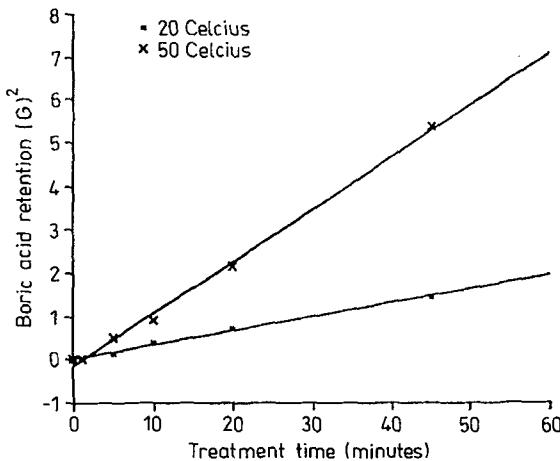


Fig. 2. The relationship between the square of boric acid retention and treatment time for OSB (Turner 1991)

Fig. 1, illustrating the relationship:

$$\text{Retention} \propto \sqrt{\text{time}}$$

It is clear from the results shown in Figs. 1 and 2 that treatment time and temperature have a fundamental influence upon boric acid retention, with retention being greater at the higher temperature and increasing as treatment time progresses. In order to better understand the process of treatment of such wood products with the reactive gas trimethyl borate, the theories governing reaction rates and gas flow in porous media were utilised to build a model describing the influence of the main factors affecting the process. The following section considers the development of this model.

Model for gas phase treatment

When treating wood products with a reactive gas such as trimethyl borate (TMB), it is proposed that rate of reaction (R') can be described by the following relationship (Turner 1991):

$$R' = K [TMB_{(g)}] [H_2O_{(l)}] \quad (1)$$

Where: K = The rate constant: a measure of rate of reaction independent of concentration. Square parentheses indicate concentration of the reactants. Steinberg and Hunter (1955) have shown experimentally that the reaction rate is directly proportional to the concentration of the two reactants. The reaction system is heterogeneous involving reactants in both the gas (g) and liquid (l) phases.

The theoretical influence of temperature upon the rate constant and reactant concentrations is considered below.

Influence of temperature on rate constant and reactant concentration

Influence of temperature on rate constant

It is known that the rate constant of a reaction increases rapidly with increasing temperature. Arrhenius (1989) identified a linear relationship between the rate constant and temperature described in Eq. 2 below:

$$\frac{d \log K}{d \left(\frac{1}{T} \right)} = - \frac{\Delta E}{2.303 R} \quad (2)$$

Where: T = Temperature (Kelvin); R = Universal Gas Constant ($0.0820561 \text{ atm K}^{-1} \text{ Mol}^{-1}$);
 E = Activation energy

Rewriting Eq. 2 in the form of a linear equation ($y = a + bx$)

Then:

$$\text{Log } K = a - \frac{E}{2.303 R} \times \frac{1}{T} \quad (3)$$

$$y = a + bx$$

or

$$K = 10^a \times 10^{-\frac{E}{2.303 RT}} \quad (4)$$

or

$$K = 10^{a - \frac{E}{2.303 RT}} \quad (5)$$

Influence of temperature on reactant concentrations

Temperature also exerts a significant effect on gas concentration. For many gases their concentration can be estimated using the ideal gas equation:

$$PV = nRT \quad (6)$$

Where: P = Pressure (in atmospheres); V = Volume (liters); n = Number of moles of gas; R = Universal gas constant; T = Temperature (Kelvin);

TMB concentration

Under the conditions described earlier for the treatment of wood products with TMB and assuming ideal behaviour, gas concentration should be dependent on the relationship between temperature and equilibrium vapour pressure of the TMB liquid in the treatment apparatus, minus the initial vacuum drawn at the start of the treatment. If the initial vacuum is taken as effectively Zero mbar (<1 mbar) then treatment pressure (and therefore preservative gas concentration) in the treatment vessel is effectively determined by the relationship between vapour pressure and temperature of the gas.

As for the rate constant, vapour pressure increases rapidly with increasing temperature. The relationship for TMB is shown in Fig. 3.

A general equation describing the change in equilibrium pressure with temperature was developed by Clapeyron and Clausius (Rowlinson, 1969):

$$\frac{d \log P}{d \left(\frac{1}{T} \right)} = - \frac{\Delta H_{\text{vap}}}{2.303 R} \quad (7)$$

The equation is directly analogous with that of Arrhenius for the rate constant, with Log P being directly proportional with the reciprocal of absolute temperature as illustrated in Fig. 4. Equation 7 can be rewritten in linear form as done with Eq. 2:

$$\text{Log } P = a' - \frac{\Delta H_{\text{vap}}}{2.303 R} \times \frac{1}{T} \quad (8)$$

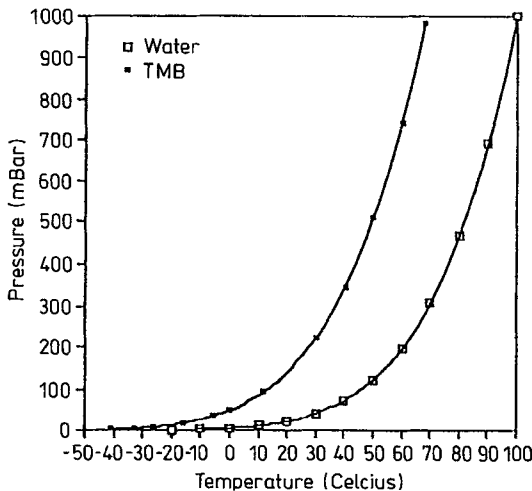


Fig. 3. Vapour pressure/temperature relationship for trimethyl borate and water (Turner 1991)

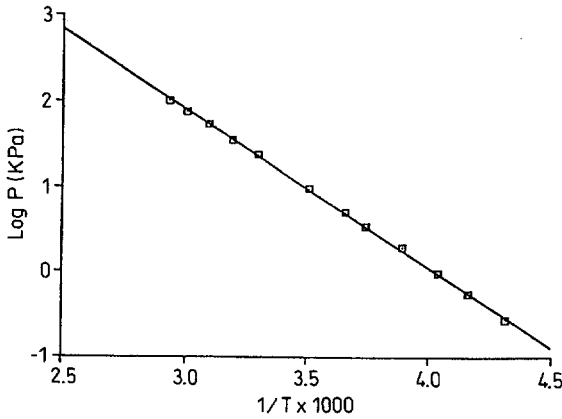


Fig. 4. Log P versus 1/T for trimethyl borate (Turner 1991)

therefore

$$P = 10^{a'} \times 10^{-\frac{\Delta H_{\text{vap}}}{2.303 RT}} \quad (9)$$

or

$$P = 10^{a' - \frac{\Delta H_{\text{vap}}}{2.303 RT}} \quad (10)$$

Assuming that TMB is behaving as an ideal gas, relationships between gas concentration and temperature can be determined by rearranging the general gas equation:

$$P = \frac{nRT}{v} \quad (11)$$

and combining it with Eq. 10

$$\text{Log} \frac{nRT}{v} = a' - \frac{\Delta H_{\text{vap}}}{2.303 RT} \quad (12)$$

if

$$\frac{\text{Log} nRT}{v} = \text{Log} \frac{n}{v} + \text{Log} RT \quad (13)$$

then

$$\text{Log} \frac{n}{v} = a' - \frac{\Delta H_{\text{vap}}}{2.303 R} - \text{Log} RT \quad (14)$$

or

$$\frac{n}{v} = \frac{1}{RT} \times 10^{a' - \frac{\Delta H_{\text{vap}}}{2.303 RT}} \quad (15)$$

H₂O concentration

The above illustrates the relationship between temperature and the concentration of one principal reactant of the system, TMB. However, the hydrolysis reaction is heterogeneous with water present in the liquid phase. During treatment of wood products with TMB gas, water concentration will be dependent upon moisture accessibility which is governed by substrate moisture content and gas flow rate into the material. Clearly, gas

flow is an important treatment parameter since it influences the bringing together of the two principal reactants.

The most generally cited empirical law governing laminar flow of fluids through porous media is that of Darcy in 1956 (Kollman et al. 1975; Banks 1975). From Darcy's law, the rate of flow of a fluid through a porous medium can be expressed as:

$$V = \frac{k}{\eta} \cdot \frac{\Delta P}{l} \quad (16)$$

Where: V = linear rate of flow (cm/second); l = length of porous medium through which flow occurs; ΔP = pressure drop over l ; k = permeability constant of the medium; η = viscosity of the fluid.

From Darcy's law, flow rate is directly related to substrate permeability and pressure gradient. In the present study, where air was first evacuated from the wood product and treatment vessel, the initial pressure in the system prior to injection of the preservative was less than 1 mbar. Under these circumstances, ΔP and therefore initial gas flow rate into the wood product will be dependent upon the latent heat of vapourisation of the TMB and the treatment temperature as described in equation 10. In practice, ΔP will be a function of ΔH_{vap} rather than an absolute value due to the potential for a reduction in the level of vacuum within the wood after the initial stages of treatment. However, since reaction is very rapid (Steinberg and Hunter, 1955) the assumption that $P_{TMB} = \Delta P$ is considered valid.

Substituting Eq. 10 into Eq. 16

$$V = \frac{K}{\eta} \cdot \frac{\left(10^{a' - \frac{\Delta H_{vap}}{2.303 RT}}\right)}{l} \quad (17)$$

$$\therefore [H_2O] = \left(\frac{k}{\eta} \frac{\left(10^{a' - \frac{\Delta H_{vap}}{2.303 RT}}\right)}{l}\right) \times C \quad (18)$$

Where: C = a constant: dependent upon substrate moisture content.

The equations for rate constant (5) and reactant concentrations (15 and 18) can now be substituted into Eq. 1 to derive a relationship between rate of reaction and temperature:

$$R' = \left[10^{a - \frac{E}{2.303 RT}}\right] \times \left[\frac{1}{RT} \cdot 10^{a' - \frac{\Delta H_{vap}}{2.303 RT}}\right] \times \left[\left(\frac{k}{\eta} \frac{\left(10^{a' - \frac{\Delta H_{vap}}{2.303 RT}}\right)}{l}\right) \times C\right] \quad (19)$$

$$R' = K \times [TMB] \times [H_2O]$$

simplified

$$R' = \frac{KC}{RT\eta l} \times 10^{a+a' - \frac{E+2\Delta H_{vap}}{2.303 RT}} \quad (20)$$

The relationship described by Eqs. 19 and 20 illustrates the overall effect that an increase in temperature has upon rate of reaction. An increase in temperature should increase TMB concentration, the rate constant and H_2O concentration (from increased gas flow rate into the wood material) giving a rapid increase in the rate of reaction. Figure 1 indicates that there is indeed an increase in the deposition of boric acid

(retention) at the higher treatment temperature although the data are inadequate to fully define the relationship; this is considered later in the paper.

Influence of gas flow rate on boric acid deposition (retention)

Both the rate constant and TMB concentration, as defined by Eq. 5 and 15 respectively, are theoretically independent of treatment time if temperature remains constant. However, the effective H₂O concentration, as defined in Eq. 18, is dependent upon the rate of gas flow through the wood substrate.

Taking the rate of gas penetration (dl/dt) to be equal to linear flow (V) of preservative, and substituting Eq. 10 into Eq. 16 as in Eq. 17:

$$\frac{dl}{dt} \cdot \frac{k}{\eta} \cdot \frac{\left(10^{a'} \cdot \frac{\Delta H_{vap}}{2.303RT}\right)}{1} \tag{21}$$

$$\int l \cdot dl = \frac{k}{\eta} \left(10^{a'} \cdot \frac{\Delta H_{vap}}{2.303RT}\right) \int dt \tag{22}$$

$$\therefore \frac{l^2}{2} = \frac{k}{\eta} \cdot \left(10^{a'} \cdot \frac{\Delta H_{vap}}{2.303RT}\right) \cdot t \tag{23}$$

or

$$l = \sqrt{t} \cdot \sqrt{\frac{2k \left(10^{a'} \cdot \frac{\Delta H_{vap}}{2.303RT}\right)}{\eta}} \tag{24}$$

For any one set of treatment conditions, k, P and η will be constant.

$$\therefore l = \sqrt{t} \cdot \text{Constant} \tag{25}$$

The curves in Figs. 1 and 2 for boric acid deposition (retention) and treatment time follow behaviour predicted by Darcy’s law suggesting that the flow rate of TMB gas to sites where it can react with H₂O within the wood is the rate limiting step for preservative deposition. Since permeability (k) and viscosity of gas (η) are constants for a particular substrate and treatment temperature, it would appear that the rate of boric acid deposition is principally dependent upon the vapour pressure of TMB under the treatment conditions (Eq. 24).

Vapour pressure can be increased via an increase in temperature. However, this also leads to an increase in rate constant. Since high rates of reaction can limit the depth of penetration of the active ingredient in low permeability and/or high moisture content material (Vinden et al. 1985; Turner and Murphy, 1987; Burton et al, 1990), it is important for efficient treatment, to maximise vapour pressure for any given temperature and rate constant.

Having developed the theoretical model to describe the effect of temperature on the treatment of wood products with TMB an experimental study to define the effect of temperature on retention of boric acid was conducted. This is described in the following section.

Experimental study - temperature influence on gas phase treatment

An experimental investigation was made of the influence of treatment temperature on boric acid retention in oriented strandboard (OSB). The objective was to determine whether an increase in treatment temperature would lead to the substantial increases in the retention of boric acid predicted by the theoretical model.

Materials and methods

Board material

A PF bonded 18 mm Oriented Strandboard manufactured from Scots pine was used (emc 6% at 20 °C, 65%RH). Boards samples were cut to dimension 100 × 100 mm × board thickness and edge sealed with ABS polymer before treatment to restrict penetration of gas to the board faces, and simulate the treatment of a large panel. Eight replicate samples were used for each treatment.

Boron ester

A proprietary mixture containing the active ingredient, Trimethyl borate (TMB) was used for all treatments.

Treatment equipment and operation

A 300 mm × 200 mm (diameter) stainless steel vacuum cylinder and a smaller vessel to contain the liquid preservative were used for treatment. The two vessels were connected via a stainless steel pipe into which a manually operated valve was inserted. The apparatus was contained within a temperature controlled environment chamber capable of operation over a wide temperature range. The equipment is illustrated in Fig. 5.

Prior to treatment, the environment chamber was set to a pre-determined temperature (between 10 and 90 °C) and run for two hours to condition the apparatus and TMB in the reservoir to the required treatment temperature. The treatment cylinder, containing the eight replicate board samples, was then evacuated to approx. 1 mbar over approx. 20 minutes. After evacuation the valve to the TMB reservoir was opened resulting in vaporisation of the preservative which passed into the treatment vessel and board samples where it reacted to deposit boric acid.

The gas contact time was 45 minutes for all temperatures. After treatment the valve to the TMB reservoir was closed, the treatment vessel returned to atmospheric pressure and purged and the board samples removed for assessment of penetration and boric acid retention.

Assessment of boric acid distribution and retention

The distribution of boric acid was assessed qualitatively by spraying a centrally cross cut face of each sample with a curcumin reagent in accordance with BS: 5666 Part 2 (1980). A red colouration indicates the presence of boric acid at retentions above approximately 0.2% w/w boric acid in oven dry wood. Quantitative analysis of boric acid retention across the full cross-section of all replicates was made using the colorimetric method of Williams (1968, 1970) on 2 g samples taken from face to face across the

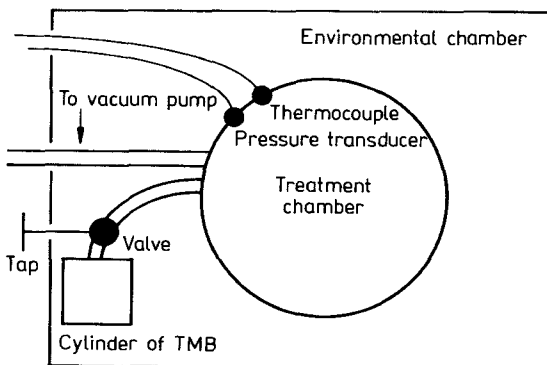


Fig. 5. Diagram of treatment apparatus (Turner 1991)

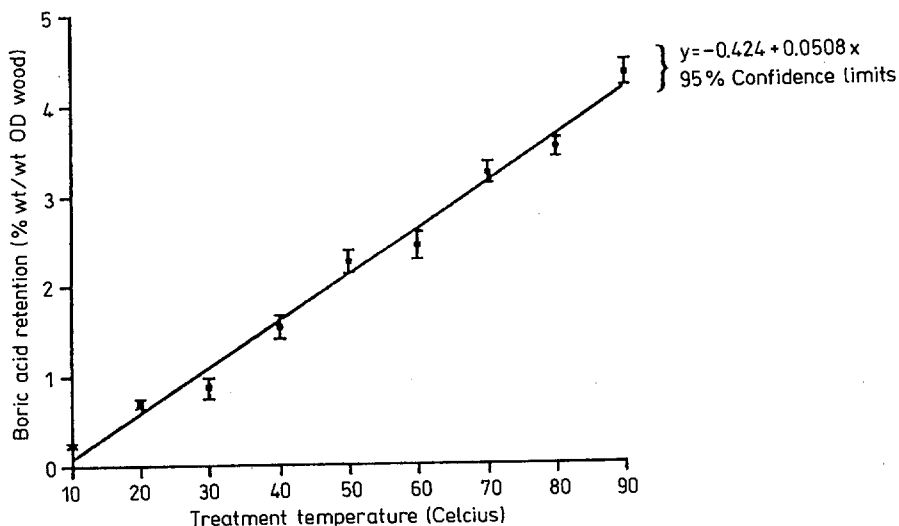


Fig. 6. Relationship between boric acid retention and treatment temperature for OSB (Treatment time 45 minutes)

central part of the board sample using the non-curcumin sprayed half. The method is described in full in Turner (1991).

Results

Full cross-section penetration of the boric acid preservative through the board was found in the qualitative assessment for all treatment temperatures. Mean boric acid retention for each set of replicates at the various treatment temperatures is shown in Fig. 6.

Discussion

The linear increase in boric acid retention with increasing treatment temperature is not in agreement with the theoretical model. In developing the model it was proposed that the rate of boric acid deposition would be largely dependent upon laminar flow (the basis of Darcy's law) of TMB gas into the wood material. Flow rate, as predicted by Darcy's law (Eq. 16), would be directly proportional to the pressure differential ($V \propto \Delta P$). Since ΔP is largely determined by the vapour pressure of the preservative gas (see Eq. 17) the rate of retention increase was predicted to closely follow the observed relationship between vapour pressure and temperature given in Fig. 3.

The reason for divergence of the experimental values from the theoretical predictions is not yet certain although a possible explanation may lie in a change from "laminar flow" to "turbulent flow" at higher gas rates. It has been shown by Reynolds (1833), that as the rate of fluid flow in a tube is increased, a point is reached where flow ceases to be laminar; at this point the streamlines become disturbed and eddies form. This type of flow is referred to as turbulent. Under these circumstances, the principal forces resisting transport are inertial rather than shearing (Banks, 1975). Turbulent flow is complex and cannot be defined in the same manner as Darcy's treatment for laminar flow. However, experimental work by Reynolds (1833) has shown that turbulent flow through tubes is characterised by the relationship:

$$V \propto (\Delta P)^{1/2}$$

(26)

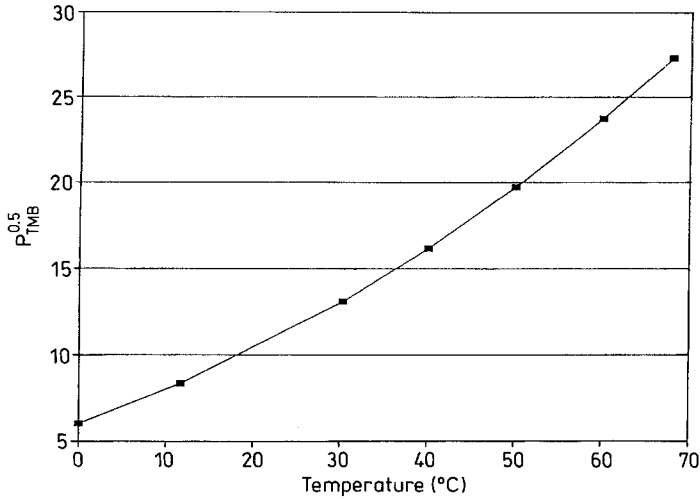


Fig. 7. The effect of temperature on $P^{0.5}$ TMB: simulating turbulent flow conditions

Using the vapour pressure/temperature relationship given in Fig. 3 and the relationship in Eq. 26 the effect of temperature on $P^{0.5}$ TMB (proportional to gas flow rate) under turbulent flow conditions can be predicted. The result of this analysis is shown in Fig. 7. The resulting curve, although not completely linear, more closely matches the relationship between temperature and boric acid retention determined by experiment.

Banks (1975) has observed turbulent flow in solid wood using liquids over a pressure of range from 0,04 to 0,7 bar. The vapour pressure of TMB over the temperature range of 10 to 90 °C is considerably in excess of this range, being from approximately 0,1 to <2,0 bar (Turner, 1991).

Clearly timber and timber products are far more complex than the simple tube models to which Darcy's law and Reynold's work apply. However, if the vapour pressure of TMB is the driving force for pressure differentials (ΔP) across the material being treated, as in suggested in the present study, then a turbulent flow model rather than one based on laminar flow appears to be the most appropriate to account for the experimental observations with this system.

A complete explanation for the experimental observations requires further study. However, a potential benefit of the linear relationships determined between boric acid retention and treatment temperature and between the square of boric acid retention and treatment time is that these should permit empirical prediction of the treatment conditions needed to achieve specific results for a variety of board treatments.

The findings of this study suggest that gas flow rate as defined in Eqs. 17 and 18 is the principal factor controlling the rate of boric acid deposition in OSB. If the rate constant (Eq. 5) or TMB concentration (Eq. 15) were the main determinants, the increase in retention with temperature would have been significantly greater than that found by experiment. The implications of these observations in exploring the potential for increasing gas flow rates and subsequent rates of boric acid deposition by gas phase treatment with TMB are considered in a following paper.

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