Treatment of timber products with gaseous borate esters

Part 2. Process improvement

P. Turner, R. J. Murphy

Abstract This paper forms a continuation of the work on treatment of timber products with gaseous borate esters. Turner and Murphy (1995) in an earlier paper indicated that gas flow rate into the wood substrate was the principle factor limiting the rate of boric acid retention and the depth of penetration into wood products. The current paper considers the impact of this factor on treatment efficacy and considers experimental work designed to evaluate qualitatively, the impact of proposed modifications to the process. Significant improvements in treatment performance were observed.

Introduction

Turner and Murphy (1995) considered some of the basic factors influencing the gas phase treatment of timber products with borate esters. The current paper considers the influence of gas flow rate, one of the fundamental limitations impacting on the efficiency of the treatment process.

The findings of Turner and Murphy (*op.cit*) indicated that gas flow rate into the wood substrate was the principle factor limiting rate of boric acid retention. It was also proposed that slow gas flow rate associated with treatment of low permeability material such as solid wood was the primary reason for reduced penetration (envelope treatments) as moisture contents increased. Gas flow rates were insufficient to prevent "stripping out" of the preservative gas at the wood surface during the rapid hydrolysis reaction (Vinden et al. 1985; Turner, Murphy 1985; Turner et al. 1990; Burton et al. 1990).

It is proposed that if gas flow rate into the wood could be increased substantially for a specific temperature (i.e. Rate constant) then depth of preservative penetration might be increased with the aim of achieving better penetration of solid wood when treated at higher moisture contents than is at present achievable. An additional benefit might lie in more rapid, high retention treatments suitable for flame retardant protection.

Assuming Darcy's law (equation 1) is valid for the situation under discussion (Turner and Murphy *op.cit*) then gas flow rate (V) is directly related to substrate

P. Turner[1] and R. J. Murphy
Department of Biology, Imperial College, London SW7 2BB, UK

[1]*Present address*
CSIR, Pretoria 0001, South Africa

Correspondence to: P. Turner

permeability (K) and pressure differentials (ΔP) across the material during treatment:

$$V = \frac{k}{\eta} \cdot \frac{\Delta P}{l} \tag{1}$$

V = linear rate of flow; 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.

Under the circumstances of treatment in part one of this work (Turner and Murphy *op.cit*) the initial pressure prior to injection of preservative liquid was approximately zero mbar. ΔP was dependent upon the vapour pressure of the gas (P) which in turn is dependent upon the latent heat of vaporization of the preservative (ΔH_{vap}) and the treatment temperature (T) as described earlier (equation 2):

$$P = 10^{a' - \frac{\Delta H_{vap}}{2.303RT}} \tag{2}$$

R = Universal gas constant (0.0820561 atmK^{-1}Mol^{-1})
a' = constant

From the above, initial gas flow rate within material of a specific permeability can be described by substituting equation 2 into equation 1 (equation 3):

$$V = \frac{K}{\eta} \cdot \frac{\left(10^{a' - \frac{\Delta H_{vap}}{2.303RT}}\right)}{l} \tag{3}$$

It follows from this that if improvements in gas flow are to be obtained; ΔP and therefore P needs to be maximised. The simplest approach would be to increase overall treatment temperature. This solution, does provide significant increases in rate of retention (Turner 1991; Turner and Murphy *op.cit*). However, it is not ideal, primarily due to the inconvenience associated with having to heat an entire plant and its contents to uniform temperature. In addition, a substantial increase in wood might exacerbate the problem of stripping of the gas at the wood surface due to rapid reaction. This might result in a net improvement in penetration which is not proportional to the increase in boric acid retention. In addition to the above, the option of treating at elevated temperature in itself does not address one of the fundamental limitations of the process to date.

A factor not considered in part 1 of this study (Turner and Murphy *op.cit*) was the heat required for vaporisation of the total amount of preservative liquid in order to achieve satisfactory boric acid retention levels in the wood. At temperatures between 20 °C and 90 °C, the quantity of an active ingredient in the gas phase would be insufficient to fulfil preservative (or flame retardant) retention requirements of a cylinder full of wood material. In the early stages of treatment, a large proportion of the preservative remains in the liquid phase until a reduction in pressure (due to reaction of the preservative gas within the wood) leads to further vaporisation (Turner 1991). During the initial stages of treatment where very rapid vaporisation occurs, residual liquid cools rapidly, leading to an effective reduction in vapour pressure, gas concentration, ΔP and therefore gas

flow. The result is a reduction in the potential rate of retention and rate of preservative penetration for a specific treatment temperature.

The results of findings to date indicate that boric acid retention requirements of up to 1.0% w/w OD wood are readily attainable at a 20 °C in less than one hour (Turner 1991; Turner and Murphy *op.cit*). However, to obtain boric acid retention levels required for flame retardant protection (8%–13% w/w OD wood), treatment times would have to be lengthened considerably, even at temperatures of 90 °C (Turner 1991). It is proposed that the lengthy period required is largely due to the inefficiencies associated with vaporisation of the trimethyl borate which becomes an increasing problem, as larger boric acid retentions for flame retardant levels are required.

The objective of this investigation was to explore the potential for increasing rates of retention and depth of penetration of active ingredients for a specific moisture content by limiting cooling of the residual liquid. This was done, using two options. The first was to utilise the specific heat capacity of the liquid itself through preheating of the liquid. This way the liquid would act as a heat sink for residual liquid after initial vaporisation. The second was to apply heat via an electrical heating element in the base of the vessel. The temperature of the treatment vessel and wood material was maintained at ambient temperature of 20 °C.

Materials and method

The work was carried out in two phases. The first considered the potential for maximising boric acid retention and was undertaken using a 9 mm, pine based oriented strand board manufactured in the UK (emc 6% at 20 °C and 65% relative humidity). In this case the two heating options (preheated liquid plus an electrical element) were combined. The board samples were cut to dimensions 300 mm (length) × 140 mm (width) × board thickness, then edge sealed as in our previous studies (Turner and Murphy *op.cit*).

The second section of the work concentrated on depth of penetration of solid wood (*Pinus patula*) and the effect of preheating the wood preservative liquid alone was considered. The material selected for treatment included standard construction material (40 mm × 114 mm), flooring board (20 mm × 100 mm), and ceiling board (10 mm × 65 mm). All the wood samples were cut to 400 mm length then end sealed as above. The material was treated at wood moisture contents of 11% at all temperatures, but also at a reduced moisture content of 6% at the highest liquid temperature of 170 °C.

Two sets of treatment equipment were used in the work. Both were similar to that used in Part 1 (Turner and Murphy *op.cit*) but varied in detail, as described below.

For the first part of the work, the apparatus consisted of a stainless steel treatment cylinder (300 mm (length) × 200 mm (diameter)) and a 500 ml pressure vessel to contain the liquid preservative required for treatment (Figure 1). In order to create an environment within the cylinder that was as representative as possible of commercial application of the process, the cylinder was filled to maximum capacity with board samples. 1.5 mm glass fillets were used to separate the samples and the top and sides of the treatment cylinder were squared with blocks cast from an inert, non-porous resin (see Figure 1). A 0.25 KW heating an element attached to the base of the reaction chamber was used to add additional energy for vaporisation of the liquid mixture injected into the base. The apparatus used, did not permit accurate quantification of heat transfer from heating an
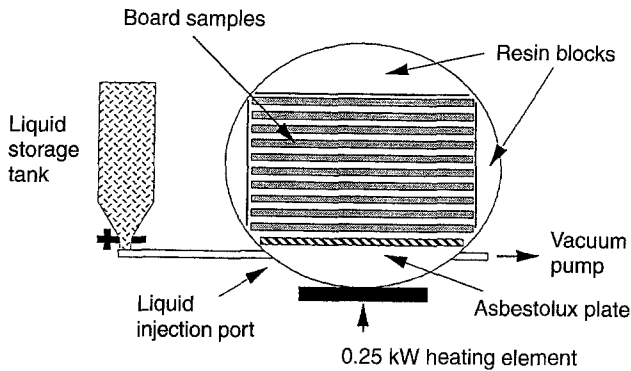
Fig. 1. Treatment plant

element to the liquid. An asbestolux plate was placed under the board stack to assist in even diffusion of the boron gas and to prevent heat transfer from the heating element to the wood material.

In each case fourteen panels were loaded into the treatment vessel. The vessel was then sealed and evacuated to <0.5 mbar over a 20 minute period. After full vacuum had been reached, the heating element under the base of the vessel was turned on to preheat the base. After a further two minutes the vacuum pump was disconnected and the vessel sealed. A preheated cylinder (90 °C) containing sufficient preservative liquid to give up to 16% boric acid retention in the wood material was then connected to the reaction vessel. Under pressure, liquid was forced into the base of the cylinder where a proportion vaporised to initiate treatment. As gas reacted, further liquid was drawn into the vapour phase. The heating element in the base of the cylinder was left on for the duration of the predetermined treatment time to limit cooling of the residual liquid. Treatment times of 10 and 30 minutes were selected. At the end of the treatment period the cylinder was vented to atmospheric pressure and residual liquid drained from the base of the cylinder before removing the samples for assessment.

In the second part of the work, the treatment chamber had squared sides of dimensions (400 mm (length) × 320 mm(height) × 320 mm (width)). A thermocouple was placed in the base of the larger vessel to monitor liquid temperature in the vessel during treatment. As before, an asbestolux plate was placed under the board stack to facilitate even diffusion of the boron gas and to prevent heat transfer to the wood material. The treatment vessel was first filled with one of the selected products, stickered with 10 mm thick fillets, then evacuated to approximately 30 mbar (absolute pressure) over a 20 minute period. During the evacuation period the liquid preservative storage vessel was filled with a quantity of trimethyl borate calculated to give 1% boric acid retention in the wood and conditioned to one of the three preselected temperatures of 20 °C, 100 °C and 170 °C. Once full vacuum was reached, the vacuum chamber was sealed and the heated liquid injected into the base of the reaction vessel. After 30 minutes exposure time, the cylinder was vented to atmospheric pressure and the samples removed. The samples were weighed to determine boric acid retention (Turner 1991) and then cross cut and sprayed with circumin reagent to determine level of penetration. During treatment of the 20 mm flooring material, the temperature of the liquid in the base of the vessel was monitored and recorded at regular intervals (see Figure 2).

Results

Table 1 indicates that, after 10 minutes, 10.2% w/w boric acid retention was obtained. In the second treatment (duration 30 minutes) retention was again significantly greater than in previous treatments at 12.3% w/w boric acid. The mean rate of a retention increase over the full time of the second treatment, however, was substantially lower than in the first (10 minute) treatment. This indicates a "slowing down" of the rate of retention increase in the later parts of the second treatment.

Table 2 gives the results for the penetration of boric acid in solid pine samples at different preservative liquid temperatures. Increased penetration occurred as treatment liquid temperature was raised. In the treatments of solid wood at normal working moisture contents full penetration was not achieved although this was found at the reduced moisture content level (6%).

Figure 2 indicates the rapid drop in temperature of the preservative liquid during vaporisation at all three temperatures. The temperature in the base of the vessel remained higher when preservative was added at 170 °C compared with 100 °C and 20 °C and the upturn in the temperature curve for the cylinder base is more rapid with the liquid at the higher temperature.

Discussion

The objective of the investigation was to determine the effects of maintaining a high preservative vapour pressure during treatment. The results on OSB indicated that rate of boric acid retention can be increased compared with the 0.5% w/w boric acid achieved at 20 °C over the same time period in our earlier work (Turner and Murphy *op.cit*). The reduced rate of retention increase in the latter part of the longer 30 minute treatment, as compared with the 10 minute treatment

Table 1. Boric acid retention levels achieved in OSB after 10 & 30 minutes treatment

Treatment time	Boric Acid Retention	Standard Deviation
10 minutes	10.2%	(0.9%)
30 minutes	12.3%	(1.2%)

Table 2. Variation in preservative penetration with liquid temperature

| Liquid Temperature	Moisture Content	Material Thickness	No. of Samples	Penetration (mm)	
				X	SD
20 °C	11	40 mm	9	10 mm	3.3
20 °C	11	20 mm	24	4.0 mm	1.2
20 °C	11	10 mm	39	2.5 mm	0.8
100 °C	11	40 mm	9	12.5 mm	4.0
100 °C	11	20 mm	24	5.5 mm	1.4
100 °C	11	10 mm	39	3.2 mm	1.1
170 °C	11	40 mm	9	17 mm	5.4
170 °C	11	20 mm	24	6.5 mm	2.0
170 °C	11	10 mm	39	3.8 mm	1.5
170 °C	6	40 mm	9	Full penetration	
170 °C	6	20 mm	24	Full penetration	
170 °C	6	10 mm	39	Full penetration	

Flooring board (20 mm)
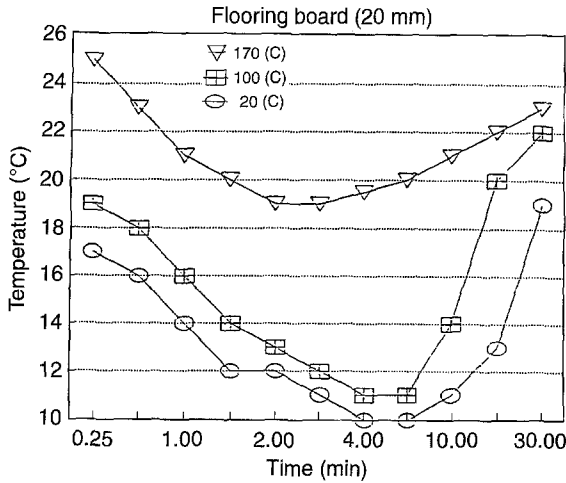
Fig. 2. Liquid temperature in the base of the treatment vessel during treatment

was predicted, since beyond approximately 8% boric acid retention, water present in the wood would have decreased to a point where it becomes a limiting factor in reaction rate (Turner 1991). If retention levels significantly higher than those achieved are required, then higher wood moisture contents would be needed.

In section 2 of this work, the objective of the exercise was to determine whether an incremental addition of heat to the treatment liquid resulted in any significant changes in preservative penetration in the different timber products. In addition, liquid temperature in the base of the vessel was monitored to identify the influence of the increased liquid temperature on the rate of cooling during the vaporisation process.

The results for solid wood treatments demonstrated that increased penetration was achieved as preservative liquid temperatures were elevated. Figure II indicates well, how rapidly the temperature of the liquid drops during vaporisation of the preservative and the addition of extra heat to the preservative liquid to compensate for this is the reason for the improved treatment quality at higher preservative temperatures. The results have clearly indicated that rate of vaporisation during treatment can be substantially increased by preventing the liquid from dropping below ambient temperature.

An interesting finding from the investigation was the improved levels of penetration observed in the thicker wood products. This may be due to the greater surface area of the thinner material resulting in a greater rate of gas reaction on the wood surfaces. This in turn will theoretically lead to more rapid cooling of the preservative liquid and therefore reduced gas pressure, flow rate and depth of penetration. Whilst this is interesting and warrants further study, it should be noted that retentions and penetrations achieved in both the small and larger cross-section samples are considered more than adequate for protection of the timber from microorganisms and insects.

Full penetration of the solid wood was not achieved at working moisture contents, even at preservative liquid temperatures of 170 °C. However, penetration was as high as 17 mm on a 40 mm cross section (2.8 mm on a 10 mm cross section). These levels are considered to provide a very high degree of protection. It is not yet known what the maximum permissible moisture content would be at which full penetration might be achieved using the set of treatment conditions

described, since only two levels (11% and 6%) were tested in this study. Furthermore, with regard to the cooling of preservative illustrated in Figure II, the results suggest that there is still room for significant improvement of the process. Further studies, including some at commercial pilot plant scale, are in progress to optimise such parameters of the vapour boron treatment process.

Conclusions

The results have indicated that the problem of long treatment times required for higher retention treatments at ambient temperatures is not a limiting factor for the vapour boron process.

Increase in trimethyl borate vapour pressure and therefore increased reactant concentration and gas flow throughout the duration of the treatment lead to improvements in both the rate of retention and depth of penetration. Incremental increases in the rate of preservative vaporisation led to incremental increases in depth of preservative penetration.

Whilst some questions remain unresolved, it is clear that the proposed approach to the vapour boron treatment process has resulted in some significant process improvements. Work is ongoing to optimise process conditions in order to determine the full potential of the treatment process both for flame retardant treatment of timber products and preservative treatment of solid timber at normal working moisture contents.

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