

THE GAS-PHASE TREATMENT OF RUBBERWOOD

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ABSTRACT

Rubberwood (*Hevea brasiliensis*) was treated with gaseous trimethyl borate [(MeO₃)B] and with gaseous trimethyl borate-methanol azeotrope [(MeO)₃B-MeOH] for reasons of greater ease of penetration, relative homogeneity, and high transport rate. The trimethyl borate-methanol azeotrope gave better impregnation and relatively higher boric acid concentration. The concentration of boric acid is greater at the periphery of the wood and decreases rapidly towards the centre. The use of the trimethyl borate-methanol azeotrope might be commercially feasible as it uses cheap starting materials and gives good impregnation.

INTRODUCTION

The use of gaseous trimethyl borate for the treatment of cellulosic materials has been developed to a limited extent (Madacsi and Kneopler, 1980). Treatment of newsprint with gaseous methyl borate leads to the deposition of boric acid in the fibers and this imparts smoulder-resistance (Madacsi *et al.*, 1977; Anderson and Freischel, 1978).

One advantage claimed for the use of gaseous methyl borate is that less boric acid is required for successful treatment than with other systems. Gas-phase treatment of timber, which has been dried at > 100°C, with trimethyl borate is rapid and can be achieved within 1 - 2 h (Vinden *et al.*, 1985)

Treatment of wood-based composite materials with gaseous trimethyl borate at 65°C and 50mm Hg, provides such materials with excellent protection against decay by fungi such as *Coniophora puteana* and *Coriolus versicolor* (Turner and Murphy, 1987).

This study was carried out to investigate the treatment of rubberwood with boron compound in the gas phase and to study the distribution of boron in rubberwood

MATERIALS AND METHODS

Wood samples

Air-dried rubberwood was cut into square-section blocks (35mm x 150mm) and the surfaces were sanded until smooth and clean. The blocks were oven-dried at 105°C to constant weight, end-coated with a wood filler, and then allowed to equilibrate either with the water-vapour present in the ambient air of the laboratory at 20°C, or with air saturated with water-vapour at 20°C inside a closed container.

Trimethyl borate and the azeotrope

The trimethyl borate (bp 65°C) was used because it is cheap and easily handled. The trimethyl-borate-methanol azeotrope was prepared by reacting boric oxide (70g) with methanol (150ml) according to the method of Schlesinger *et al.* (1953)



Gas-phase treatment

Gas-phase impregnation of rubberwood was undertaken for reasons of easy penetration, homogeneity and fast rate of transport (Schuerch, 1968).

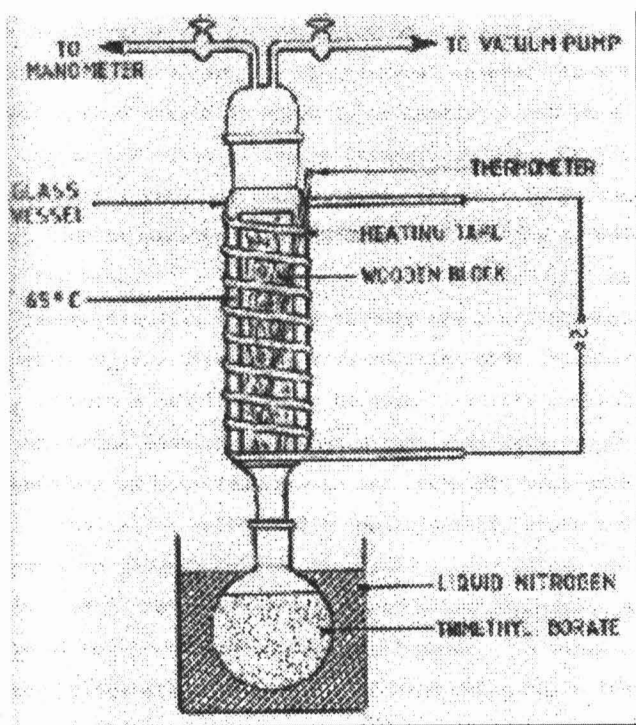


Figure 1: Apparatus for the gas-phase treatment of rubberwood

The rubberwood block was placed inside a glass vessel as shown in Figure 1. The upper section was heated by means of an electrical heating tape until temperature inside reached 65°C, i.e the boiling point of trimethyl borate. The trimethyl borate in the lower flask was cooled by liquid nitrogen to -196°C and the system was then evacuated using an oil pump to 0.1 mm Hg to ensure removal of virtually all the air from the wood. After 10 minutes tap A was closed and the frozen trimethyl borate was melted using hot water or steam. Heating was continued until the vapour pressure of the liquid had reached 760mm Hg (absolute pressure) as shown by the manometer. The gaseous trimethyl borate was kept in contact with the wood block for 20 minutes

to ensure complete impregnation, after which it was recondensed and frozen using liquid nitrogen. Air was allowed into the apparatus through tap A and the wood block was removed and weighed. After being allowed to stand in the fume cupboard overnight (~ 16h), the wood block was finally oven-dried at 105°C until all volatile materials had been removed and there was no further change in weight.

A similar sequence of operations was also performed using the trimethyl borate-methanol azeotrope.

Boron analysis

The wood sample was prepared for analysis for boron (Figure 2). The desired woodmeal (40 mesh) was analysed by a standard analytical method developed for use with wood samples (William, 1970).

The absorbance (optical density) of the resulting solution (intense red colour) was measured relative to a blank solution on a Perkin-Elmer model 402 uv/vis spectrophotometer. The intense red colour of the solution was attributed to the formation of a boric acid - curcumin complex exhibits an absorption maximum at 555nm. From the absorbance value at this wavelength and the specimen calibration curve, the boric acid concentration could be measured. The concentration of boric acid in the original wood meal is given by

$$\%H_3BO_3 = \frac{\text{Conc. of } H_3BO_3(\mu\text{g}/100\text{ml}) \times \text{dilution factor}}{\text{Weight of oven-dried wood meal (g)}} \times 100$$

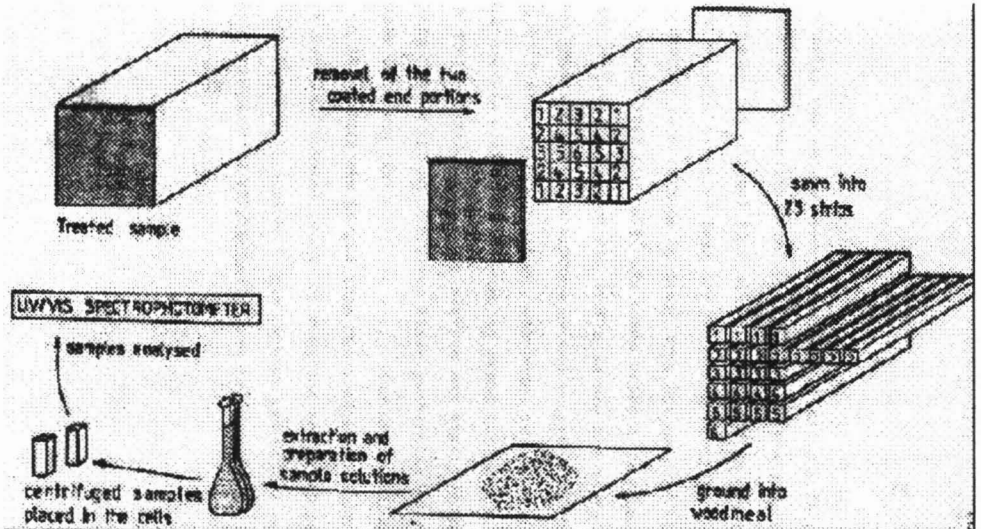


Figure 2: Sample preparation for boron analysis

RESULTS AND DISCUSSION

The analytical data obtained after treating rubberwood (a) with gaseous trimethyl borate and (b) with gaseous trimethyl borate-methanol azeotrope are shown in Tables 1 and 2 respectively. For ease of comparison, the boron in the wood is assumed to be present as boric acid. The concentration of boric acid is noticeably greater (by a factor of $\sim 1.7 - 2.6$) in the wood samples SA1 and SA2 which had been previously equilibrated with air saturated with water vapour at 20°C than in the wood samples LA1 and LA2 which had been equilibrated with laboratory air at 20°C. This would be expected as the more water present, the greater the amount of trimethyl borate which is hydrolysed to boric acid and methanol.

The results of the trimethyl borate-methanol azeotrope treatment are interesting (Table 2). Here there is a somewhat increased concentration of boric acid in the outer layer of the laboratory -air equilibrated samples LA1 and LA2 [2.69% and 2.58% for the azeotrope, 1.96% and 1.85% for trimethyl borate]. The concentrations of boric acid in the outer layer of the SA wood samples are somewhat closer [4.88% and 4.13% for trimethyl borate, 5.50% and 4.54% for the azeotrope]. There is a marked increase in the boric acid content of the inner samples (4, 5 and 6) in each case. Thus suggest that the azeotrope penetrates more efficiently into the wood than does pure methyl borate. Presumably the methanol present reverses to some extent by hydrolysis of the methyl borate to boric acid.

This view is supported by the observation that sawdust treated with a methanolic solution of boric acid gives a product, which after being air-dried at 20°C, shows a net decrease in weight. Hence boric acid in methanol must be very easily esterified to methyl borate which, being very volatile, is easily lost.

In all cases the treated wood showed a gain in weight. This gain may conceivably be due to the formation of either boric acid (by hydrolysis) or a borate ester resulting from reaction of the boric acid with the hydroxy groups some of the components of the wood.

Table 1: Analytical data for the treatment of rubberwood with gaseous trimethyl borate

| Wood sample * | Moisture Content (%) | Oven-dried wt. before treatment (g) | Oven-dried wt. after treatment (g) | Change in wt. (dried at 105°C) (g) | Portion of wood block (as in Fig. 2) | Boric acid (%) |
|------------------|----------------------|-------------------------------------|------------------------------------|------------------------------------|--------------------------------------|----------------|
| SA1 (102.67g) | 13.76 | 90.25 | 90.58 | 0.33 | 1 | 4.88 |
| | | | | | 2 | 4.35 |
| | | | | | 3 | 4.18 |
| | | | | | 4 | 0.19 |
| | | | | | 5 | 0.12 |
| | | | | | 6 | 0.03 |
| SA2 (108.23g) | 9.06 | 100.06 | 100.44 | 0.38 | 1 | 4.13 |
| | | | | | 2 | 2.65 |
| | | | | | 3 | 2.47 |
| | | | | | 4 | 0.16 |
| | | | | | 5 | 0.03 |
| | | | | | 6 | 0.02 |
| LA1 (105.95g) | 5.86 | 100.46 | 100.69 | 0.23 | 1 | 1.96 |
| | | | | | 2 | 1.69 |
| | | | | | 3 | 1.58 |
| | | | | | 4 | 0.20 |
| | | | | | 5 | 0.19 |
| | | | | | 6 | 0.03 |
| LA2 (99.11g) | 5.91 | 94.01 | 94.31 | 0.31 | 1 | 1.85 |
| | | | | | 2 | 1.77 |
| | | | | | 3 | 1.71 |
| | | | | | 4 | 0.89 |
| | | | | | 5 | 0.61 |
| | | | | | 6 | 0.30 |

Note:

* SA – wood sample equilibrated with air saturated with water vapour at 20 C

LA – wood sample equilibrated with laboratory air at 20 C

() – Figures in brackets refer to weight after equilibration before treatment with trimethyl borate

Table 2: Analytical data for the treatment of rubberwood with gaseous trimethyl borate –methanol azeotrope

| Wood sample * | Moisture Content (%) | Oven-dried wt. before treatment (g) | Oven-dried wt. after treatment (g) | Change in wt. (dried at 105°C) (g) | Portion of wood block (as in Fig. 2) | Boric acid (%) |
|---------------|----------------------|-------------------------------------|------------------------------------|------------------------------------|--------------------------------------|--|
| SA1 (105.95g) | 15.73 | 92.55 | 93.40 | 0.85 | 1 2 3 4 5 6 | 5.50 4.34 4.27 1.28 0.91 0.34 |
| SA2 (106.32g) | 15.93 | 92.08 | 93.11 | 1.03 | 1 2 3 4 5 6 | 4.54 3.89 3.69 1.49 1.13 0.21 |
| LA1 (96.71g) | 4.34 | 92.97 | 93.62 | 0.65 | 1 2 3 4 5 6 | 2.58 2.53 2.40 1.20 1.01 0.89 |
| LA2 (99.71g) | 4.85 | 95.41 | 96.73 | 1.32 | 1 2 3 4 5 6 | 2.69 2.49 2.41 1.33 1.28 1.09 |

Note:

* SA – wood sample equilibrated with air saturated with water vapour at 20 C

LA – wood sample equilibrated with laboratory air at 20 C

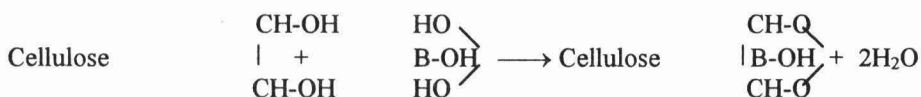
() – Figures in brackets refer to weight after equilibration before treatment with trimethyl borate

Since cellulose is one of the principal components of wood, it was therefore appropriate to examine its reaction with gaseous trimethyl borate. Thus when pure cellulose (100g) in the form of filter paper [(Whatman No. 3), air-dried at 20°C, moisture content 4.38% measured by drying at 105°C] was treated with the gaseous trimethyl borate-methanol azeotrope, there was a net increase in weight (1.07g) after drying at 105°C. This increase can be explained by considering the two possible reaction sequences involving (a) only the moisture present and (b) both the moisture and the hydroxy groups of the cellulose. For (a) the equation is as below:



The amount of water removed in the reaction is 54g, while the gain in weight due to boric acid formation is 61.8g. With the original moisture content of 4.34g in the filter paper, 4.97g of boric acid would be formed giving a net gain in weight of 0.63g.

For (b) the boric acid thus formed would react further with hydroxy groups of the cellulose in the following manner:



and drying would lead to a further loss of water. 61.8g of boric acid would produce 36g of water. In case there would be a net lost in weight of 2.26g (i.e. 2.89g – 0.63g) as a result of the postulated reactions. The net gain in weight (1.07g) observed for the treated cellulose corresponds reasonably closely to that expected (0.64g) from the amount of water present. It seems unlikely therefore that the hydroxy groups of the pure cellulose are involved in the reaction with the gaseous trimethyl borate. The cellulose present in wood is of course in a very different environment and can well react in a different manner.

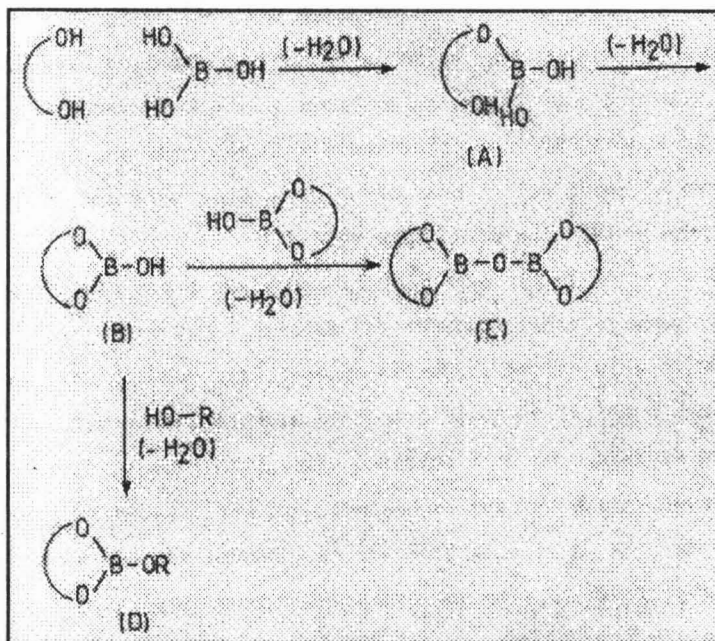
The nature of the boric acid in the treated wood

Treatment of wood containing moisture with trimethyl borate (or its azeotrope with methanol) would be expected to result in hydrolysis of the ester with the formation of boric acid. The weight of boric acid, produced in a wood block can be calculated from the analytical data contained in the preceding Tables. The calculation for the wood sample SA1 (Table1), which had been treated with gaseous trimethyl borate, is as follows. The weight of the block after treatment was 90.58g. Since the block was divided into 25 strips for analysis, the weight of each strip was 3.62g. The weight of boric acid in the various portions of the wood block is then:

$$[(\text{no. of strips in each portion}) \times (\text{wt. of each strip}) \times (\% \text{ boric acid found})] \div 100$$

Example, for portion No.1 the weight of boric acid = [4 x 3.62 x 4.88] ÷ 100 = 0.707g
 For the other portions, the weight of boric acid calculated is as follows – No.2, 1.261g; No.3, 0.60g; No. 4, 0.028g; No. 5, 0.017g; No. 6, 0.004g. The total for the whole block is then 2.623g. Since the observed increase in weight of the block after treatment is only 0.328g, it follows that there has been a loss in weight of 2.295g, presumably in the form of water, produced by condensation reactions during the drying process. A similar “loss” in weight occurred in all the other cases listed in the Tables. This behavior can be explained if it is assumed that the boric acid does react with components of the wood to give borate esters of various types.

The sequence of reactions of boric acid with hydroxy groups present in cellulose, lignin, tannins, etc., can be summarised as follows:



Esters of type A have not yet been isolated but simple esters of types B, C and D, are well known (Steinberg, 1964). The net increases in weight would result, per mole of added boric acid (i.e. 61.8g), in the formation of such esters are as follows:

| Type of borate ester | A | B | C | D |
|--------------------------|------|------|------|-----|
| Net increase in weight/g | 43.8 | 25.8 | 16.8 | 7.8 |

The wood sample SA1 already discussed contained 2.623g of "boric acid" and showed a gain in weight of 0.328g. For 61.8g of boric acid the weight gain would be 7.728g. This indicates that all the "boric acid" in this particular block is present essentially as a trialkyl borate of type D. Similar calculations show that the comparable block SA2 (Table 1) contains 1.944g of boric acid. The observed gain in weight was 0.379g. For 61.8g of boric acid the weight gain would be 12.048g corresponding to a mixture of borate esters of types C and D. Samples LA1 and LA2 (Table 1) which had also been treated with gaseous trimethyl borate give calculated weight increases per mole of "boric acid" of 12.108g and 14.494g respectively, again corresponding to a mixture of esters of types C and D. The blocks treated with gaseous trimethyl borate-methanol azeotrope (Table 2) show higher calculated weight increases per mole of "boric acid". Samples SA1 (17.141g), SA2 (22.850g), and LA1 (21.570g) clearly contain mixtures of borate esters of types B and C. Sample LA2 however gives a value (40.512g) well above these figures, suggesting that an ester of type B was present together with some free boric acid. Clearly the presence of the methanol in the azeotrope not only facilitates the movement of the methyl borate into the wood but also affects the nature of the resulting boron compounds.

CONCLUSION

Gaseous trimethyl borate gives rise to boric acid (in the form of esters) in rubberwood. The amount of boric acid formed appears to depend on the water content of the wood to some extent, contact between the trimethyl borate and the present in the wood is somewhat inefficient. The concentration of the boric acid is greater at the periphery of the wood in all cases and decreases rapidly towards the centre. When the trimethyl borate-methanol azeotrope is used, the methanol appears to facilitate the movement of boric acid into the inner region of the wood. The relatively high concentration near the surface of the wood found after drying is presumably due to the methanol moving out from the interior and carrying with it some of the boric acid. The use of the trimethyl borate-methanol azeotrope might be commercially feasible as it uses cheap starting materials and gives good impregnation. It would be limited to the treatment of timber for use in dry conditions.

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