

REDISTRIBUTION OF SOLVENT AND SOLUTE DURING DRYING OF RUBBERWOOD IMPREGNATED WITH NON-AQUEOUS OR AQUEOUS LIQUIDS

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MUHAMMED S, MUSGRAVE OC & PETTY JA. 2011. Redistribution of solvent and solute during drying of rubberwood impregnated with non-aqueous or aqueous liquids. End-sealed rubberwood blocks were impregnated with a 1:1 v/v mixture of 1-bromopropane and cyclohexane via their radial and tangential surfaces and allowed to dry slowly at 20 °C. X-radiography through the transverse surface showed that the concentrations of 1-bromopropane were consistently higher in the centre than in the periphery of the block. A similar impregnation using cyclohexane alone resulted in the concentration at the centre of the block being initially somewhat lower than that at the periphery. However, after part of the solvent had evaporated, the concentration at the centre was relatively much higher. Two rubberwood blocks were impregnated via their radial and tangential, and transverse surfaces with a solution of copper naphthenate in cyclohexane. The blocks were then covered so that evaporation of the solvent from one block took place only via the radial and tangential surfaces and from the other only via the transverse surfaces. Radiography of the former showed that copper concentration was high at the periphery and low at the centre of the block. Radiography of the latter block showed uniform copper distribution across the transverse section. The substitution of an aqueous solution of copper sulphate resulted in a similar behaviour. These observations support the view that rubberwood offers little resistance to impregnation by liquids. Drying of the treated wood is accompanied by considerable movement of the liquid to the periphery where evaporation takes place. Any involatile solute present is deposited at or near the surface.

Keywords: 1-bromopropane, copper naphthenate, copper sulphate, cyclohexane, X-radiography

MUHAMMED S, MUSGRAVE OC & PETTY JA. 2011. Taburan semula pelarut dan bahan larut semasa pengeringan kayu getah yang diawet dengan cecair bukan akueus atau cecair akueus. Blok kayu getah yang tertutup pada hujung diawet dengan campuran larutan 1-bromopropana dan sikloheksana (nisbah isipadu 1:1) melalui permukaan jejari dan tangen kayu dan dibiarkan mengering secara perlahan-lahan pada suhu 20 °C. Radiografi sinar-X pada permukaan lintang kayu menunjukkan bahawa kandungan 1-bromopropana pada bahagian tengah kayu sentiasa lebih tinggi berbanding dengan bahagian pinggir kayu. Kaedah awetan yang serupa menggunakan hanya larutan sikloheksana sahaja mengakibatkan kepekatan pada peringkat awalnya lebih rendah di bahagian tengah kayu berbanding dengan bahagian pinggir. Namun, setelah sebahagian larutan tersejat, kepekatan pada bahagian tengah kayu menjadi jauh lebih tinggi. Dua blok kayu getah diawet dengan kuprum naftenat yang larut dalam sikloheksana pada permukaan jejari dan tangen serta permukaan lintang. Blok kayu kemudiannya ditutup supaya sejatan berlaku melalui permukaan jejari dan tangen serta permukaan lintang. Radiografi sinar-X pada blok kayu pertama menunjukkan bahawa terdapat kepekatan kuprum yang tinggi pada bahagian pinggir kayu dan kepekatan rendah pada bahagian tengah kayu. Radiografi sinar-X pada blok kayu kedua pula menunjukkan taburan kepekatan kuprum yang seragam pada permukaan lintang kayu. Blok kayu yang diawet dengan larutan akueus kuprum sulfat menunjukkan keputusan yang sama. Penelitian ini menyokong pandangan bahawa kayu getah memberi rintangan yang sedikit terhadap pengawetan dengan cecair. Pengeringan kayu yang diawet disusuli dengan pergerakan cecair dari bahagian tengah ke bahagian pinggir kayu. Di sinilah berlakunya sejatan dan sebarang bahan larut yang tak meruap akan tertinggal hampir atau di permukaan kayu.

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INTRODUCTION

The protection of most hardwood timbers against insect attack requires adequate concentrations of suitable preservatives throughout the wood. However, the treatment of such timbers with preservative solutions frequently leads to the biocidal components being concentrated mainly in the peripheral region of the wood (Muhammed et al. 2009). This has led to the commonly held belief that only partial penetration of the timber has been achieved, with little preservative solution reaching the innermost parts of the wood. While such an explanation may have some validity for timbers having low permeabilities, with their vessels being obstructed by tyloses, its application to other woods is questionable.

Rubberwood is an attractive material for furniture and housing because of its low price, ease of working and appearance (Lew & Sim 1982, Hong & Sim 1999). However, it is particularly vulnerable to termite attack, possibly because of its high starch content (Azizol & Rahim 1989). It has a relatively high void volume and the rays and vessels appear to be largely free from obstruction. Nevertheless, treatment with preservatives such as trimethyl borate either in gaseous or liquid form and copper naphthenate in a hydrocarbon solvent still results in the insecticidal component being concentrated mainly in the outer layers of the wood after drying (Muhammed et al. 2009).

It is well established that in wood which has been impregnated with aqueous boric acid, part of the solute undergoes redistribution during subsequent drying process (Zaidon et al. 1998). As a result, the boric acid equivalent concentration increases in the periphery of the wood and decreases in the centre. Although the conditions are markedly different, the impregnation of rubberwood with non-aqueous preservative fluids and subsequent drying produce similar concentration differences, suggesting that redistribution processes occur here.

Unlike the extensive knowledge which is available on the flow of water in wood (Siau 1984), there appears to be little quantitative information on the movement of non-aqueous liquids in wood during drying. Accordingly, we investigated the behaviour of several non-aqueous liquids in rubberwood on being subjected to different drying procedures. For comparison, we

also examined how an aqueous solution behaved under similar conditions.

MATERIALS AND METHODS

Preparation of wood samples and copper solutions

Air-dried samples of rubberwood with the grain parallel to the length were cut with a band-saw into square cross-section blocks (50 × 50 × 125 mm or 50 × 50 × 25 mm) which were sanded until smooth. The blocks were oven dried at 105 °C to constant weight and the end faces were sealed with plastic padding so that liquids could penetrate only through the radial and tangential surfaces and not through the more highly permeable transverse surfaces. They were stored in a closed container. Some of the smaller blocks were also used unsealed.

Addition of a solution of copper sulphate pentahydrate (3.93 g) in water (50 ml) to a solution of naphthenic acid (acid value 180; 9.76 g) and sodium hydroxide (1.26 g) in water (100 ml) gave a dark green mixture. The mixture was added to cyclohexane (80 ml), which is a good, low boiling-point solvent. The organic layer was separated, freed from water by azeotropic distillation using a Dean and Stark apparatus and diluted to 100 ml with cyclohexane to give a solution containing 1% w/v copper. The concentration of copper was checked using atomic absorption spectrometry (Muhammed et al. 2009).

An aqueous solution containing 1% w/v copper was prepared by dissolving copper sulphate pentahydrate (39.29 g) in distilled water and diluting it to 1 litre.

Impregnation of rubberwood with solutions of 1-bromopropane and copper naphthenate in cyclohexane

A rubberwood block (50 × 50 × 25 mm), which had been end-coated to seal both transverse surfaces, was placed in a glass vessel which was evacuated to 0.1 mm Hg (Petty 1975). A 1:1 v/v solution of 1-bromopropane (boiling point 71 °C) in cyclohexane (boiling point 81 °C), of similar volatilities, was allowed into the vessel and the block was kept immersed in the liquid at atmospheric pressure until no further uptake of the solution occurred (~7 hours).

In a separate experiment, two unsealed rubberwood blocks (A and B; 50 × 50 × 25 mm) were impregnated with a solution of copper naphthenate in cyclohexane (containing 1% w/v copper) in a similar manner. The blocks were removed and each of the transverse surfaces of block A was immediately covered with aluminium foil backed with a thin layer of rubber and a metal plate as shown in Figure 1. The two seals were held firmly in place by a clamp. The four radial/tangential surfaces of block B were covered in a similar fashion (Figure 2). Both blocks were dried, initially at 50 °C and finally at 105 °C.

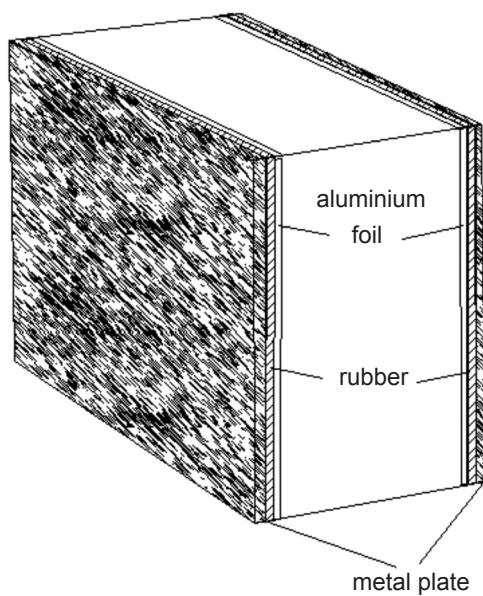


Figure 1 Block with transverse surfaces covered

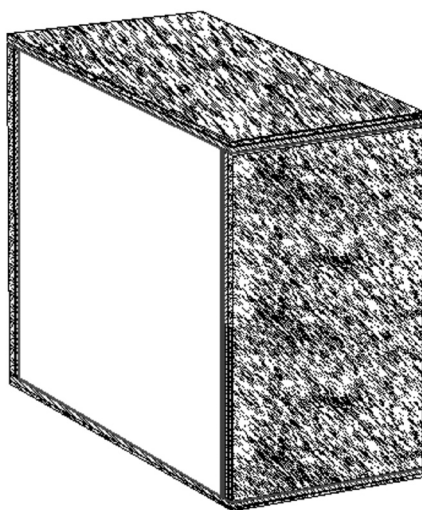


Figure 2 Block with radial and tangential surfaces covered

Location of bromine- and copper-containing compounds in rubberwood by X-radiography

The block impregnated with 1-bromopropane solution in cyclohexane was allowed to dry slowly in the air at 20 °C for 18 days during which time it was examined periodically by X-radiography through its transverse surfaces. The X-ray equipment, a single phase, fully rectified standard diagnostic unit, was set at the lowest accelerating voltage available (50 kV_p). The beam was unfiltered in order to maximise the low-energy component. The photon intensity (20–23 keV at peak) was adjusted to produce maximum contrast in the resulting radiographs which were recorded on film.

The dried blocks impregnated with copper naphthenate were subjected to X-radiography via their transverse faces in a similar manner.

Distribution of liquid in rubberwood during drying after impregnation with cyclohexane

An end-sealed rubberwood block (50 × 50 × 125 mm) was impregnated with cyclohexane using the vacuum/immersion procedure described above. The block was removed, wiped, weighed and immediately sawn to obtain the two coated ends. The remaining portion was quickly sawn into four similar blocks (each 50 × 50 × ~20 mm) labelled C–F. Each block was weighed and at once placed in a closed container saturated with cyclohexane vapour to minimise evaporation of the absorbed solvent. Block C, which was not allowed to dry, was sawn quickly into strips (each 10 × 10 × ~20 mm) that were numbered 1–5 according to their positions in the block as shown in Figure 3. The strips were weighed, oven dried finally at 105 °C and re-weighed. The difference in weights gave the weight of cyclohexane present in each strip.

The transverse surfaces of block D were covered with aluminium foil as in Figure 1 and the block was allowed to dry in the air at 20 °C until 26% of the weight of solvent had been lost. The block was then cut in a similar manner to give strips, each of which was weighed, dried at 105 °C and re-weighed. Blocks E and F had their transverse surfaces covered in the same way, and were allowed to dry at 20 °C until 42 and 59% respectively of the weight of solvent had been lost and each was then treated in a similar manner to block D.

Distribution of copper in impregnated rubberwood after drying by two different procedures

An end-sealed block of rubberwood (50 × 50 × 125 mm) was impregnated with a solution of copper naphthenate in cyclohexane (containing 1% w/v copper) using the vacuum/immersion procedure described earlier. The block was removed, wiped and weighed, and the coated ends were immediately sawn off. The remaining piece was quickly sawn into two equal portions, G and H (each 50 × 50 × ~60 mm). To prevent evaporation of the solvent via the transverse surfaces, portion G was covered at each end with aluminium foil as in Figure 1 so that evaporation could occur only via the four radial/tangential surfaces. The four sides of portion H were covered in the same way, (Figure 2) exposing only the transverse surfaces through which evaporation of the solvent could take place. The two blocks were allowed to dry in the air at 20 °C for 16 hours and then at 50 °C for 10 days (to constant weight). The dried blocks were sawn into strips (10 × 10 × ~60 mm) and these were numbered as shown in Figure 3, separately ground to woodmeal (40 mesh) and analysed for copper using atomic absorption spectrometry (Muhammed et al. 2009).

This experiment was repeated using an aqueous solution of copper sulphate containing 1% w/v copper in place of the cyclohexane solution of copper naphthenate. Evaporation of the solvent was again restricted either to the radial and tangential surfaces (block I) or to the transverse surfaces (block J). All measurements were made in duplicates.

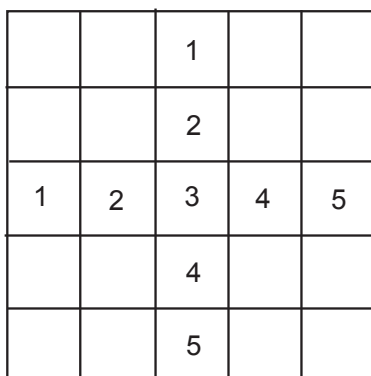


Figure 3 Block portions for cyclohexane and copper analyses

RESULTS AND DISCUSSION

Qualitative examination of the distribution of volatile and non-volatile solutes during drying

A solution of 1-bromopropane in cyclohexane has not previously been used in wood impregnation. To be sure that it would behave in rubberwood in a similar manner to solutions of copper naphthenate in white spirit (Muhammed et al. 2009), the fractional volumetric absorption of the solution was determined using an unsealed block (50 × 50 × 25 mm). The original weight of the block was 42.00 g and after impregnation it contained 25.61 g of the solution. Using the average of the two liquid densities (1.3539 and 0.7791 g cm⁻³ respectively), the latter corresponded to a volume of 24.01 cm³. The void volume of the block is given by (V – Vd/1.46) where V is the volume of the block (62.50 cm³), d is the density of rubberwood (0.672 g cm⁻³) and 1.46 is the density of cell-wall material, which gives a value of 33.73 cm³. The fraction of the void volume filled with the mixture was 24.01 × 100/33.73, i.e. 71.2% which was in substantial agreement with the value (66.38%) previously found for rubberwood using a solution of copper naphthenate in white spirit (Muhammed et al. 2009). The impregnation with 1-bromopropane/cyclohexane solution clearly follows a similar pattern.

The ‘heavy’ bromine atom (At. No. 35) is an efficient absorber of X-rays which readily permit the location of bromine-containing compounds in wood. Initially the block impregnated with the solution of 1-bromopropane and cyclohexane was uniformly opaque to X-rays but after drying at 20 °C for eight days, the radiograph showed that a narrow peripheral portion of the block had become X-ray transparent (Figure 4a). As drying continued, this zone expanded and after 18 days only the central portion of the block remained opaque to X-rays (Figure 4b). This indicated that the centre still had a relatively high concentration of 1-bromopropane while the outer parts had very little.

Copper (At. No. 29) also absorbs X-rays. The radiographs of the two blocks which had been impregnated with a solution of copper naphthenate in cyclohexane and then dried differed markedly. Block A, having had its radial/tangential surfaces exposed, showed strong absorption round the

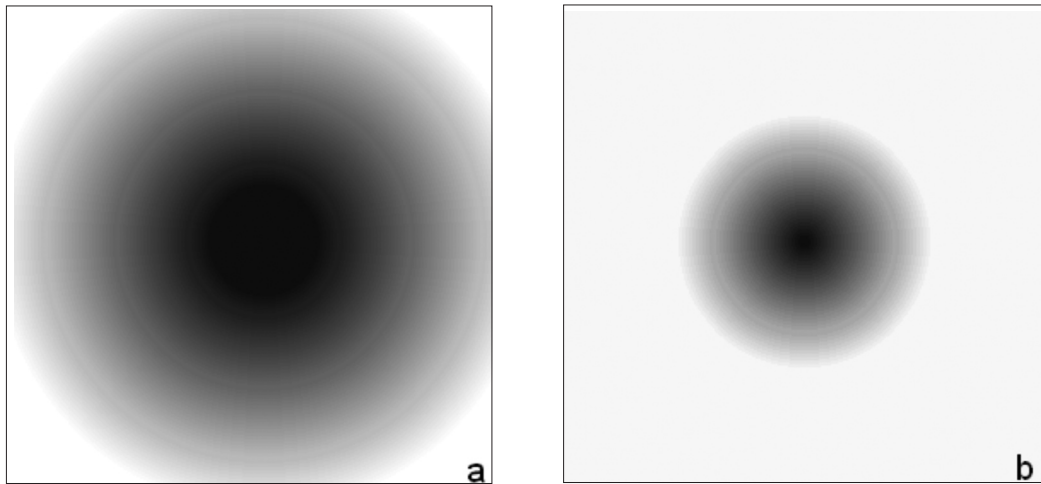


Figure 4 (a) Radiograph of block impregnated with 1-bromopropane and cyclohexane and dried for eight days at 20 °C and (b) radiograph after drying for 18 days at 20 °C



Figure 5 Radiograph of block impregnated with a solution of copper naphthenate in cyclohexane and dried at 50 °C

periphery (Figure 5). This corresponded to a high concentration of copper, with much weaker absorption in the centre which clearly contained less of the metal. In contrast, block B, having had its two transverse surfaces exposed, was completely opaque to X-rays, indicating that a relatively high concentration of copper was present across the whole of the transverse section.

Quantitative measurement of the distribution of solvent and solute during drying

The difference in behaviour during the drying process between the volatile solute 1-bromopropane and the involatile solute

copper naphthenate appeared at first sight to be contradictory. Therefore, quantitative measurements of the distribution of the solvent cyclohexane and the solute copper naphthenate using different drying procedures were considered desirable.

Of the four blocks (C–F) (Figure 6) which had been impregnated with cyclohexane, block C, which had not been allowed to lose any of the liquid, contained the highest concentrations (29.7%), of cyclohexane in the more accessible peripheral portions (1 and 5). Even the central portion 3 contained a substantial amount (22.7%), showing that cyclohexane had penetrated to the centre of the block (Figure 6). After evaporation of increasing amounts of their liquid content, each of the remaining blocks D, E and F showed rapid decrease in the amounts remaining in the outer portions (1 and 5) and a much slower decline in the inner portions (2, 3 and 4). This behaviour closely resembles that encountered earlier in the radiography of the blocks impregnated with the 1-bromopropane/cyclohexane solution.

The blocks which had been impregnated with a solution of copper naphthenate in cyclohexane via their radial and tangential surfaces showed distributions of copper which were dependent on the drying procedure employed (Table 1). Evaporation of the solvent via the radial and tangential surfaces resulted in the copper concentration being higher in the peripheral portions of block G. Drying through the transverse surfaces produced a nearly uniform distribution across the transverse section of block H (Table 1).

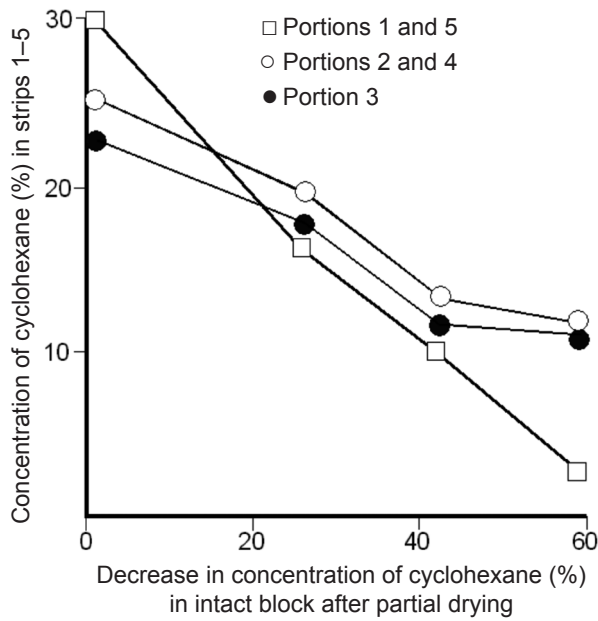


Figure 6 Distribution of cyclohexane in rubberwood during drying at 20 °C

Since the transverse surfaces are so much more permeable than the other surfaces, comparatively little lateral movement of the solution would be expected to occur during evaporation. The observed copper concentrations indicated that the impregnating solution had penetrated to the centre of the block.

Substitution of an aqueous copper sulphate solution in place of copper naphthenate in cyclohexane produced closely comparable results (Table 2) showing that both swelling and non-swelling solvents behaved in a similar manner in rubberwood.

CONCLUSIONS

Rubberwood, having a high fractional volumetric absorption value, is readily impregnated with solvents or preservative solutions leading to comparatively high concentrations throughout the wood. During subsequent drying, the liquid at or near the surface of the wood evaporates quickly and is slowly replaced by liquid moving from deeper within the wood. Any involatile solute is deposited in the peripheral region. Both aqueous and non-aqueous liquids appear to behave in a similar fashion.

These results are of course in conflict with the idea that the higher levels of preservative found in the outer layers of treated wood are a consequence of the difficulty of penetration of the wood by the preservative solution. The redistribution of preservative during drying of the treated wood has obvious commercial implications.

Table 1 Distribution of copper in rubberwood after impregnation with copper naphthenate in cyclohexane and subsequent drying

Block	Portion of block ^a	Copper content (% w/w)
G	1	0.56 (0.02)
	2	0.28 (0.03)
	3	0.25 (0.04)
	4	0.28 (0.04)
	5	0.55 (0.03)
H	1	0.56 (0.01)
	2	0.55 (0.01)
	3	0.51 (0.01)
	4	0.52 (0.01)
	5	0.52 (0.01)

Evaporation via the radial and tangential surfaces only in block G and via the transverse surfaces only in block H

^aSee Figure 3; Standard deviations in parentheses

Table 2 Distribution of copper in rubberwood after impregnation with aqueous copper sulphate and subsequent drying

Block	Portion of block ^a	Copper content (% w/w)
I	1	0.82 (0.01)
	2	0.47 (0.02)
	3	0.27 (0.02)
	4	0.43 (0.04)
	5	0.74 (0.02)
J	1	0.68 (0.03)
	2	0.59 (0.01)
	3	0.53 (0.03)
	4	0.61 (0.04)
	5	0.65 (0.01)

Evaporation via the radial and tangential surfaces only in block I and via the transverse surfaces only in block J

^aSee Figure 3; Standard deviations in parentheses

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