DETERMINATION OF CYPERMETHRIN CONTENT IN OSCILLATING PRESSURE TREATED RUBBERWOOD

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SALAMAH SELAMAT, WAN ASMA IBRAHIM, HABIBAH MOHAMAD & FAEZAH ABOOD. 1993. Determination of cypermethrin content in oscillating pressure treated rubberwood. Rubberwood samples at three different moisture contents were treated with cypermethrin by oscillating pressure method. The amount of cypermethrin in the wood was determined immediately after treatment and after drying by calculation and by high performance liquid chromatography (HPLC). Results showed that the amount of cypermethrin detected by HPLC was much lower than that by calculation. Rubberwood samples of low moisture contents gave better penetration of cypermethrin. Cypermethrin was detected only in the first layer (1 *cm*) of the treated green samples at all drying conditions. For the samples treated at lower moisture contents, cypermethrin was detected in all three layers taken. However, the amount of cypermethrin detected decreased as the drying time increased.

Key words : Rubberwood - oscillating pressure method - cypermethrin - HPLC

SALAMAH SELAMAT, WAN ASMA IBRAHIM, HABIBAH MOHAMAD & FAEZAH ABOOD. 1993. Penentuan kandungan sipermethrin dalam kayu getah yang diawit dengan kaedah tekanan berulang. Contoh kayu getah yang terdiri dari tiga kadar kandungan kelembapan air yang berlainan diawet dengan bahan awet sipermethrin menggunakan kaedah tekanan berulang. Kandungan sipermethrin di dalam kayu berawet ditentukan sebaik sahaja selepas rawatan dan selepas dikeringkan dengan cara kiraan dan kaedah kromatografi cecair berkuasa tinggi (High Performance Liquid Chromatography, HPLC). Keputusan menunjukkan bahawa kandungan sipermethrin yang dikesan dengan menggunakan kaedah HPLC lebih rendah dari kaedah kiraan. Contoh kayu getah yang mempunyai kandungan kelembapan air yang rendah menghasilkan penembusan sipermenthrin yang baik. Sipermethrin juga dikesan hanya pada lapisan pertama (1 *cm*) pada semua contoh kayu yang diawet dalam keadaan kelembapan tinggi pada semua keadaan kekeringan. Sipermethrin dikesan pada kesemua lapisan (3 lapisan) dalam kayu yang diawet dalam keadaan kelembapan air yang rendah. Walau bagaimanapun kandungan sipermethrin yang dikesan berkurangan sekiranya masa kekeringan dipanjangkan.

Introduction

Boron treatment by the dip-diffusion and full-cell processes are two common methods used for the protection of rubberwood against insects. Boron compounds have been found to be suitable for the treatment of both green and partially seasoned timber as they readily diffuse into the timber (Salamah *et al.* 1987, 1988). These compounds do not discolour wood but they readily leach from the treated wood (Anonymous 1979, Zaitun & Salamah 1990). Due to this, alternative insecticides such as synthetic pyrethroids have been tested for use in wood preservation.

Pyrethroids possess low mammalian toxicity and do not pose environmental hazards. The compounds are strongly absorbed by soil and are non-leachable and biodegradable (Briggs *et al.* 1983). Apart from being an agricultural insecticide, pyrethroids have also been treated on logs and timbers (Berry 1979) and have been found effective against marine borers (Rutherford *et al.* 1982), termites (Yoshimura *et al.* 1989) and wood boring insects (Baker & Berry 1980).

Oscillating pressure treatment is an effective method of treating timbers using non-diffusible preservatives especially for refractory timbers (Wilkinson 1979). This method has been practised in Malaysia for the treatment of rubberwood with synthetic pyrethroids. However, the efficiency in terms of penetration and retention of the compounds has not been assessed. The stability of the chemical after penetration into the wood must be ensured for the treated wood to be adequately protected during service. Its permanence inside the wood at various stages of drying after treatment can be assessed by determining its retention values. The results obtained can be used as a guideline to determine the required concentration of the treatment solutions before treatment for various types of timber.

The objective of this study was to assess the penetration and retention of cypermethrin in rubberwood following treatment by the oscillating pressure method (OPM) and to monitor the cypermethrin content at various stages of drying after treatment.

Materials and methods

Preparation of rubberwood samples for treatment

In this study three sets of rubberwood samples dried at different conditions were used as shown in Table 1. The sample size was 50 × 50 × 1200 *mm*. The six replicates of the wood samples used for each drying of condition were selected from a batch of 20 pieces. The samples selected were free from dirt, bark and any natural or drying defects. The samples were end-coated with epoxy paint and weighed before treatment.

Table 1. Conditions of rubberwood samples subjected to oscillating treatment

Sample	Number of replicates	Conditions	Average moisture content (% w/w)
Set 1	6	Freshly cut from newly felled log (green)	77.7
Set 2	6	Kiln dried (partially dry)	25.0
Set 3	6	Kiln dried (dry)	17.0

Preservative solution

The formulation of cypermethrin used in this study was in the form of an emulsifiable concentrate at 0.2% w/v.

Treatment method

An oscillating pressure method was used for the treatment of rubberwood. This process involves repeated applications of high and low pressures during impregnation. The high pressure was 14.062 *kg* cm^2 (200 *lb* in^2), and the low pressure was in the vacuum range of 0.98 *mm* Hg. The treatment time was two hours with 40 cycles of oscillating high and low pressures. The treatment was carried out in a wood preservation mill in Kedah. Gross retention was calculated from the weight gain and solution concentration data.

Preparation of sample for chemical analysis

The wood samples of length 120 *cm* were sawn immediately after treatment into various sections as shown in Figure 1a. Sections B and B1 of each sample were used for the determination of the amount of cypermethrin in the sample. Section B1 was cut into three layers and labelled as layer 1, 2 and 3 (see Figure 1b). Section B and every layer of section B1 were then chipped and ground with a hammermill separately. Special care was taken to avoid any contamination between the three layers of ground samples.

Preparation of sample for further drying after treatment

The remainder of section X from each set of the treated sample was subjected to air drying for four and eight weeks under shade (26°*C*). The remainder from section Y of the same sets was subjected to oven drying (40°*C*) (maximum temperature without shade at the Institute).

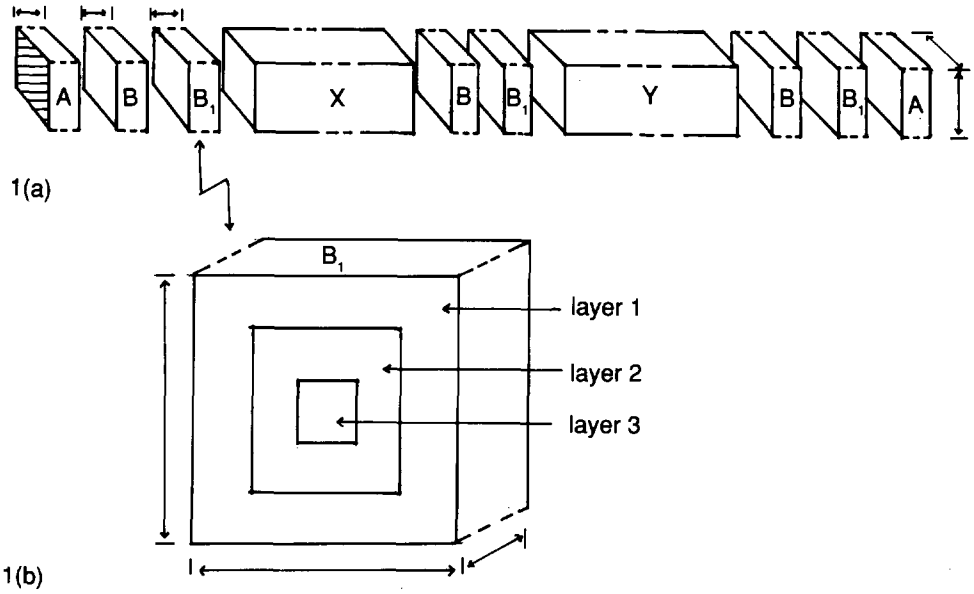

Figure 1. Sampling for analysis. [A: discarded; B: Cypermethrin determination for the whole cross section; B_1: Cypermethrin determination for each layer; X: Dried in oven at 40°C; Y: Dried in air (at room temperature)]

After each sample had been exposed for four weeks drying time, a 5 *cm* length was sawn from one end of the sample which was then cut into three layers (similar to Figure 1b). The remaining portion was end-coated and left for eight weeks drying time after which the same procedure of sample preparation was followed for the chemical analysis.

Preparation of sample for HPLC analysis

Exactly 2.0 *g* of air dried samples were extracted in a soxhlet extractor with 125 *ml* hexane HPLC grade on a heated water bath for 3 *h*. After extraction, the extract was filtered through a 0.5 *micron* PTFE membrane filter and concentrated by evaporation. The concentrate was then transferred into a weighed 10 *ml* volumetric flask, made up to the volume with hexane, and the flask reweighed. Each sample was analysed by a HPLC immediately after preparation.

The HPLC conditions were as follows;

HPLC	:	Shimadzu SCL.6B
Column	:	Spherisorb 5 *microns* silica
Mobile phase	:	Hexane/tetrahydrofuran (99.5 : 0.5)
Flowrate	:	1.5 *ml* min^{-1}
Wavelenght	:	254 *nm*
Range	:	0.32 AUFS
Injection volume	:	10 *ul*

Table 2. Factors and levels taken for statistical analysis

No.	Factors	Level (total no.)
1	Sample condition	green, partial dry, dry (3)
2	Drying condition	airdried, ovendried (2)
3	Drying times	0, 4, 8 weeks (3)
4	Sample layer	1, 2, 3 (3)

Statistical analysis

Analysis of variance was carried out to determine if there was any significant difference between the sample conditions and chemical retention, and between all factors taken as shown in Table 2. The means of the main effect (factors) were compared in order to detect any significant difference and to identify the best among them using Duncan's Multiple range test at 5% level of significance.

Results and discussion

Table 3 shows the uptake of cypermethrin solution by the rubberwood samples and the cypermethrin retention in samples of different moisture contents. The mean weight gain retention values for the green, partially dry and dry samples were 0.383, 0.775 and 0.927 *kg* m^3 respectively. The actual amounts of cypermethrin determined by HPLC were 0.078, 0.173 and 0.759 *kg* m^3 for green, partially dry and dry samples respectively. These results indicate significantly greater loading values of treatment solution and cypermethrin retention as the wood moisture content decreased ($p<0.05$). The actual amounts of cypermethrin in the wood was also greatly influenced by the moisture content. However, the actual amounts of cypermethrin detected by HPLC in the wood samples were 4.92, 4.48 and 1.22 times lower for green, partially dry and dry samples respectively, as compared to weight gain retention. The amounts of cypermethrin in the wood samples based on weight gain and HPLC analysis fulfill all the recommended toxic values against *Hylotrupes bajulus, Anobium punctatum* (Berry 1983, 1984) and drywood termites (Oliveira 1983) as shown in Table 4. These values are also much higher than the recommended value given for local use which is 0.06 *kg* m^3 (Anonymous 1987). However, as the above toxic values are not based on local insect strains, the recommended value should be increased since the weather for this country is very conducive to the growth of insects and other biodeterioration agents (Hong *et al.* 1982).

Cypermethrin content in the various depths of the wood after drying

The results obtained from chemical analysis carried out on the treated green samples subjected to different drying times and conditioning show that cypermethrin was present only in the first layers of the samples taken for all

Table 3. Uptake of treatment solution and active ingredient by rubberwood samples of different moisture contents

Sample number	Sample condition	Moisture content (% w/v)	Chemical absorption (*g*)	Gross loading ($g\ cm^3$)	R1 ($kg\ m^3$)	R2 ($kg\ m^3$)
1	green	70.5	668.4	0.223	0.446	0.096
2	green	77.5	521.2	0.174	0.348	0.086
3	green	86.1	476.3	0.159	0.318	0.057
4	green	75.8	641.6	0.205	0.410	0.067
5	green	77.2	573.5	0.191	0.382	0.086
6	green	79.0	594.3	0.198	0.396	0.076
mean		77.7	574.7	0.192	0.383	0.078
1	partial	24.2	1121.7	0.384	0.768	0.196
2	partial	27.6	1050.1	0.350	0.700	0.161
3	partial	28.0	1184.3	0.395	0.790	0.147
4	partial	23.7	1184.1	0.395	0.790	0.155
5	partial	24.3	1214.6	0.405	0.810	0.176
6	partial	27.6	1247.0	0.426	0.852	0.204
mean		25.9	1167.0	0.389	0.775	0.173
1	dry	13.7	1374.9	0.458	0.916	0.699
2	dry	19.4	1317.2	0.439	0.878	0.838
3	dry	18.1	1368.5	0.456	0.912	0.712
4	dry	16.0	1412.6	0.471	0.942	0.649
5	dry	20.0	1401.4	0.467	0.934	0.813
6	dry	16.2	1468.5	0.490	0.980	0.844
mean		17.2	1390.5	0.464	0.927	0.759

Note:
R1 = Extrapolated retention of cypermethrin
R2 = Retention of cypermethrin in treated samples determined by HPLC.

Table 4. Toxic values of cypermethrin ($g\ m^3$) against larvae of wood boring beetles (Berry 1983) and termites (Oliveira 1983)

House longhorn beetle *(Hylotrupes bajulus)*	Common furniture beetle *(Anobium punctatum)*	Drywood termite *(Cryptotermes* sp.*)*
1.1 - 5.7 (freshly hatched larvae)	0.76 - 1.59* (eggs laying and larval survival)	165
6.7 - 13.4 (matured larvae)	20.3 - 39.3 (matured larvae)	

* Berry 1984.

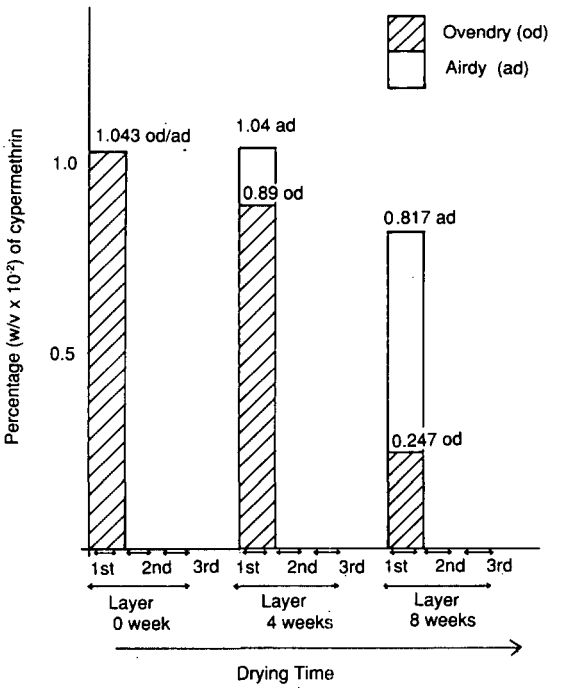

Figure 2. The percentage of cypermethrin detected in rubberwood samples treated in the green condition after air and oven drying

drying conditions (Figure 2). For air dried samples the values decreased from 1.043 before drying to 1.040 and 0.817% after four and eight weeks drying times respectively. However, on oven drying the values decreased more to 0.890 and 0.247% after four and eight weeks drying times respectively.

In the partially dry and dry treated samples, cypermethrin was detected in all three layers immediately after treatment as shown in Figures 3 and 4. The amount detected also decreased in each layer as the drying time increased. After eight weeks of both air and oven drying, cypermethrin was no longer detected in the second and third layers. This indicated the loss of preservative due to drying.

The amounts of cypermethrin retained immediately after treatment and after four weeks of drying at a depth of 1 *cm* from the surface (first layer) of the samples were sufficient for protection against wood borers (Anonymous 1987) for all sample conditions. However, in the second layer the amount was sufficient only for samples which had not undergone any drying after treatment as shown in Figures 3 and 4.

Statistical analysis showed that there is an interaction between all the four factors (sample condition, drying conditions, drying time and sample layers) in terms of the cypermethrin content (Table 5). The Duncan's Multiple Range Test result based on sample condition showed that the dry sample (the lowest

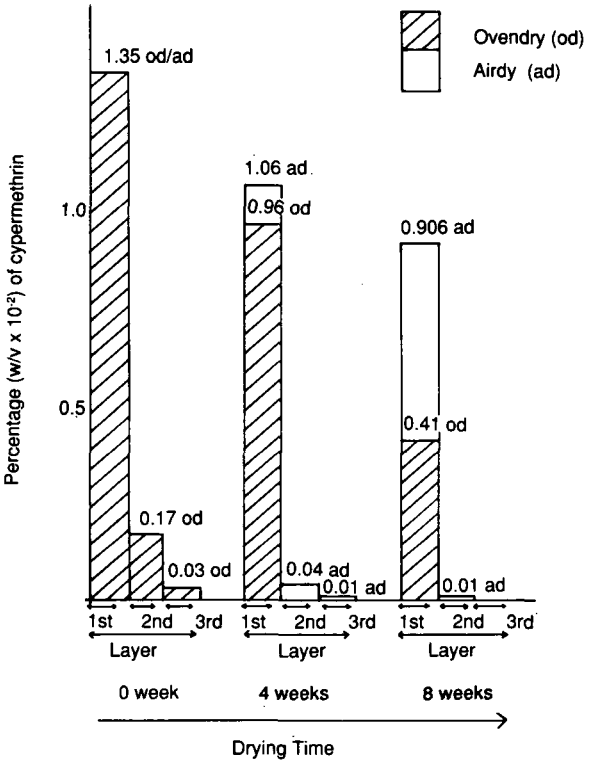

Figure 3. The percentage of cypermethrin detected in rubberwood samples treated in the partially dry condition after air and oven drying

Table 5. Analysis of variance (ANOVA) for the amount of cypermethrin detected in treated rubberwood at different sample condition (SAMCON), drying condition (DRYCON), drying time (WEEK) and sample layer (LAYER)

Source	DF	Anova SS	Mean Square	F Value	Pr > F
SAMCON	2	0.00055540	0.00027770	95.12	0.0001
DRYCON	1	0.00002560	0.00002560	8.77	0.0038
WEEK	2	0.00080588	0.00040294	138.01	0.0001
LAYER	2	0.00310584	0.00155292	531.91	0.0001
SAMCON*DRYCON	2	0.00000009	0.00000005	0.02	0.9840
SAMCON*WEEK	4	0.00062155	0.00015539	53.22	0.0001
SAMCON*LAYER	4	0.00043011	0.00010753	36.83	0.0001
DRYCON*WEEK	2	0.00001621	0.00000811	2.78	0.0666
DRYCON*LAYER	2	0.00000000	0.00000000	0.00	1.0000
WEEK*LAYER	4	0.00087493	0.00021873	74.92	0.0001
SAMCON*DRYCON*WEEK	4	0.00000497	0.00000124	0.43	0.7896
SAMCON*DRYCON*LAYER	4	0.00008533	0.00002133	7.31	0.0001
DRYCON*WEEK*LAYER	4	0.00001105	0.00000276	0.95	0.4401
SAMC*DRYC*WEEK*LAYER	8	0.00010748	0.00000768	2.63	0.0025

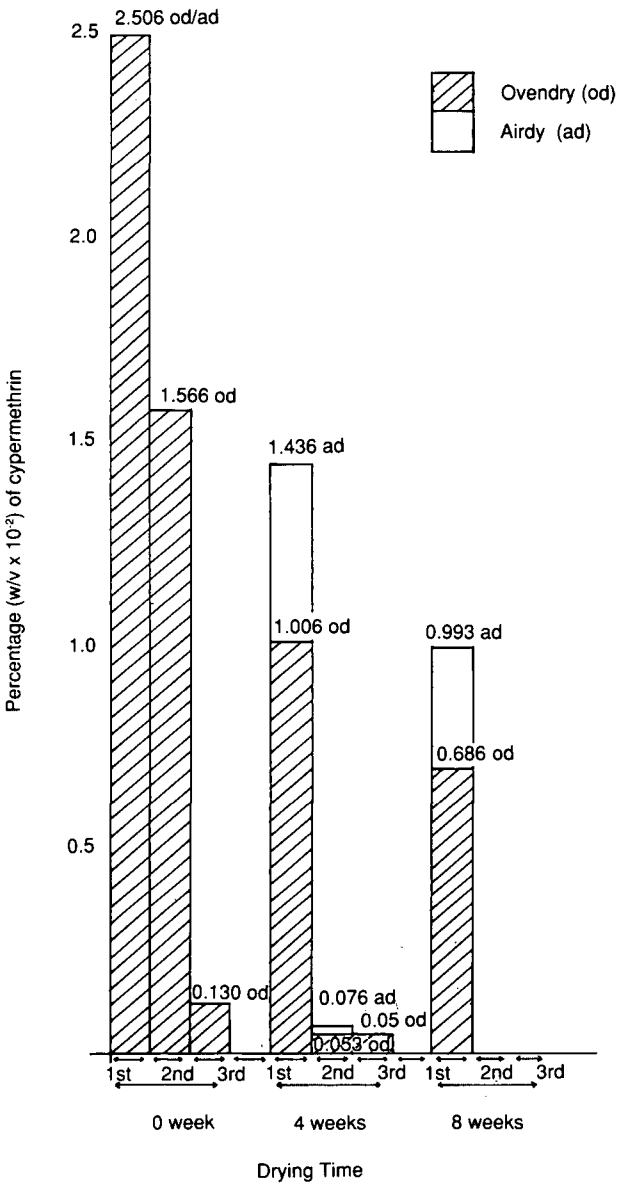

Figure 4. The percentage of cypermethrin detected in rubberwood samples treated in the dry condition after air and oven drying

moisture content) is significantly better than partially dry and green samples at all levels of factors tested. This result also shows that the air dried sample is significantly better than the oven dried sample at all levels of factors tested except for layer 3. Analysis based on the drying time shows that the treated samples at zero week drying is significantly better at all levels of factors taken except for layer 3. However, analysis based on layer shows that layer 1 is significantly better than layers 2 and 3 at all levels of factors tested but there was no significant difference between layers 2 and 3.

From this test the moisture content and drying times contributed the most towards the retention of cypermethrin in the rubberwood samples.

Conclusion

From the above study, it was found that the same amount of cypermethrin detected right after treatment cannot be retained in the rubberwood during drying. This behaviour makes the cypermethrin formulation used in this study inferior to boron compounds which are widely used in the rubberwood industry. This, however, does not mean that cypermethrin is not suitable for rubberwood protection as it has been proven effective as an insecticide. A formulation that can compensate for the amount lost during drying may be able to provide a better retention in rubberwood. Further studies must be carried out on different types of formulation of cypermethrin in order to obtain the correct formulation that can be used effectively to treat rubberwood.

Chemical analysis is a vital tool in determining whether the required amount of cypermethrin in the wood is met. The determination of the actual amount of cypermenthrin in wood is essential to ensure the quality of the final product. For the determination of this critical value, a detailed study should be performed under local conditions before this chemical can be recommended locally. These factors will be beneficial to our local wood industries and support the government's aim in promoting downstream processing.

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