ANALYTICAL METHOD OF ACTIVE INGREDIENT IN GLUE-LINE-TREATED PLYWOOD

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ABSTRACT

A rather efficient method for quantitative analysis of the active ingredient in a glue-line-treated plywood was found by using formic acid and toluene in combination as the extraction solvents. A recovery rate of more than 95% was achieved.

Keywords: Plywood, analytical method, extraction, toluene, formic acid.

INTRODUCTION

Wood preservation is an important problem for hardwood such as lauan, meranti, etc. because attack by *Lyctus* is becoming serious, as plywood made from such materials is becoming widely used from the standpoint of resource-saving and cost performance.

Although there are three or four ways of treating plywood with insecticidal and/or fungicidal materials, the glue-line treatment method using glue containing a reasonable amount of an active ingredient is the most effective and promising. This method is simple and does not require any additional equipment to conventional systems. Also the plywood thus produced has proved to have the same adhesive strength as that from conventional systems. Also the plywood thus produced has proved to have the same adhesive strength as that from a conventional system. The active ingredient in the plywood prepared by this method, however, is so difficult to recover for analysis that it was suggested (Tamura and Akihisa 1978) that most of the active ingredient is occluded in the glue layer. It has been reported (Nishimoto 1978) that only 20–40% of chlordane is recovered by benzene extraction from plywood in which urea or melamine-urea formaldehyde resin is used as the glue component. Inoue et al. (Inoue 1979; Yagishita et al. 1979) improved the recovery rate by using benzene as a Soxhlet extraction solvent; the amount of chlordane is determined colorimetrically, and the extraction efficiency reaches to 20–50%. This method became the one of the Japan Agricultural Standard (JAS). The low percentage recovery, however, does not seem to be sufficient for quantitative analysis for purpose of quality control in large factory production, or for determining behavior (distribution, storage stability and so on) of the active ingredient in the plywood.

In this paper we want to report a more suitable extraction solvent system—formic acid coupled with toluene, achieving more than 95% in extraction ratio (Maeda et al. 1983a, b; Nishimoto et al. 1982).

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TABLE 1. *Analytical conditions of gas chromatography.*

	Sumithion	Chlordane	Sumicidin
GC equipment	Shimadzu GC-7AG	Shimadzu GC-5A	Shimadzu GC-5A
Detector	Flame-photometric	Electron capture	Electron capture
Column	Glass (3 mm × 1.1 m)	Glass (3 mm × 1.5 m)	Glass (3 mm × 1.0 m)
Phase	3% Silicone XE-60	10% Silicone DC-200	3% Silicone OV-101
Carrier	Chromosorb W AW DMCS (60–80 mesh)	Gas-chrom Q (100–120 mesh)	Gas-chrom Q (100–120 mesh)
Temperature (C)			
Column oven	180	220	230
Injection part	200	250	250
Detector	200	260	270
Carrier gas	Nitrogen	Nitrogen	Nitrogen
Flow rate ml/min)	50	40	100

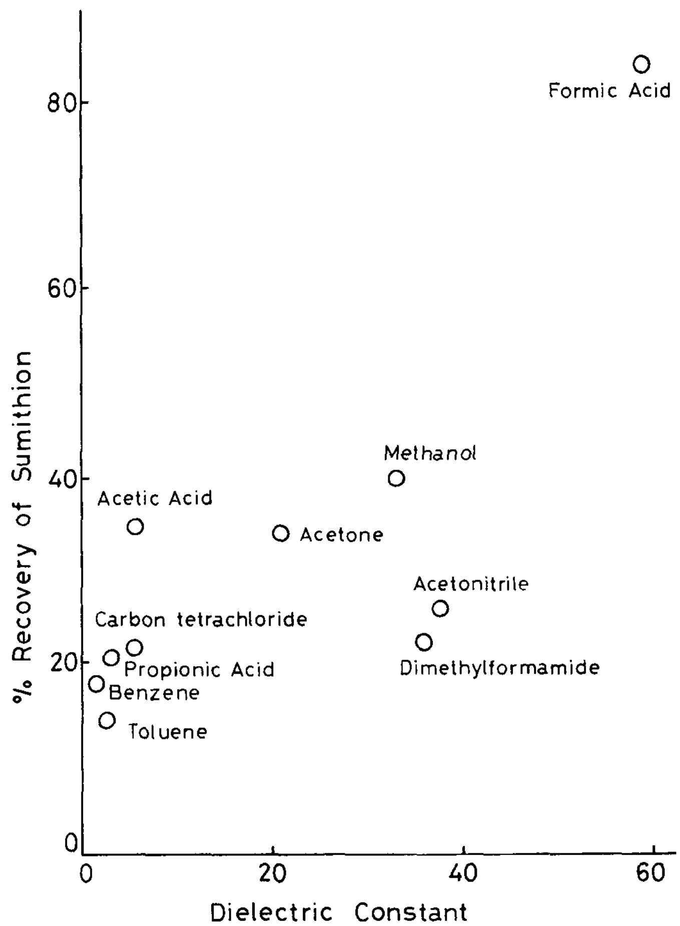

FIG. 1. Relation of % recovery of Sumithion versus dielectric constant of extraction solvent.

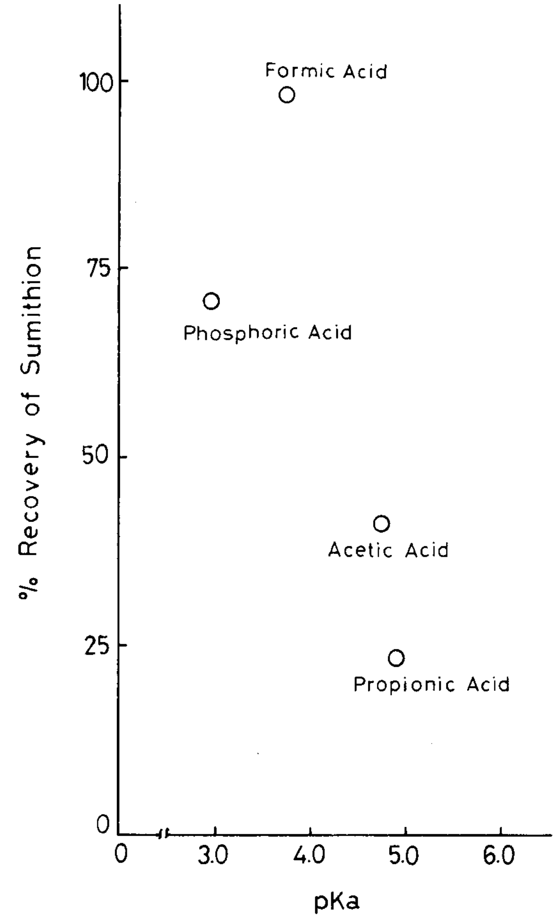

FIG. 2. Relation of % recovery of Sumithion versus negative logarithm of acid dissociation strength of extraction solvent (acid/toluene = 5 ml/100 ml).

EXPERIMENTAL

Materials

Chemicals for analysis.—Authentic samples of 0,0-dimethyl 0-(3-methyl-4-nitrophenyl)phosphorothioate (Fenitrothion, Sumithion®) and α-cyano-3-phenoxybenzyl α-*iso*-propyl-4-chlorophenyl acetate (Fenvalerate, Sumicidin®) were synthesized in the pesticide Synthetic Laboratory, Pesticides Research Laboratory, Sumitomo Chemical Co., Ltd. Standard chlordane technical grade was supplied from Velsicol Pacific Ltd. Solvents and all other chemicals for analysis were of reagent grade and were used without further purification.

Materials for preparation of plywood.—Materials used for plywood preparation are all commercially available. Insecticide: Rumbert® 60 EC (Fenitrothion 60 EC, Sumitomo Chemical Co., Ltd.), Sumicidin® 20 EC (Sumitomo Chemical Co., Ltd.) and Chlordane 60 EC (Shinto Paint Co., Ltd.). Synthetic resin: Urea (UA-125®, Sumitomo Bakelite Co., Ltd.) and Melamine (MA-209®, Sumitomo Bake-

TABLE 2. *Stability of Sumithion in various kinds of solvents.*

Solvent	Residual % of Sumithion after accelerated storage	
	40 C, 30 days	60 C, 30 days
n-Hexane	99.9	97.6
Benzene	99.5	99.1
Toluene	99.6	98.5
Chloroform	99.4	99.3
Acetonitrile	100.0	[a]
Methanol	88.0	49.8
MIBK[b]	100.0	[a]
Cyclohexanone	99.7	90.7
Phenol	[a]	98.7
DMF[c]	7.8	0.0

Initial concentration of Sumithion was 1 w/w (%).
[a] Not measured.
[b] Methyl *iso*-butyl ketone.
[c] Dimethylformamide.

lite Co., Ltd.). Veneers: Lauan, Meranti, *Shorea* sp. (Dipterocarpaceae) supplied by Shinto Paint Co., Ltd.

Preparation of the plywood.—Veneers (180 × 180 mm square, 4.5 mm thick, water content 7–8%) were assembled to the three-ply panels (1.0 + 2.5 + 1.0 mm). The plywood containing various amounts of insecticides was prepared by the following procedures: 1) *Preparation of the glue according to recipe A.* Urea resin 74.4%, ammonium chloride 0.4%, wheat powder 14.9%, insecticide in a form of emulsifiable concentrate 0.83% as an active ingredient (A.I.) in the case of application of 600 g A.I./m^3 and water, balancing to 100%. *Preparation according to recipe B.* Urea resin 35.7%, melamine resin 35.7%, ammonium chloride 0.4%, wheat powder 14.2%, insecticide in a form of emulsifiable concentrate 0.83% as an active ingredient, and water balancing to 100% (w/w). 2) Application of the glue (30 g/900 cm^2) to the plywood. 3) Cold pressing (10 kg/cm^2) at room temperature for 20 min. 4) Hot pressing (10 kg/cm^2) at 115–120 C for 90 sec.

Analysis

Sampling from the test plywood.—Each 1–2 gram of wood powder was obtained according to the method similar to Inoue's (1979). Shavings, planed off from the

TABLE 3. *Effect of solvent combination to extraction efficiency.*

Combination of solvents (5 ml/100 ml)	% Recovery of Sumithion
Formic acid/toluene	98
Formic acid/carbon tetrachloride	95
Formic acid/*n*-hexane	83
Formic acid/methanol	81
(Formic acid)	(84)
Acetic acid/toluene	41
Propionic acid/toluene	23
Phosphoric acid[a]/toluene	20
(Toluene)	(18)

[a] 10 w/w (%) in water.

TABLE 4. *Analysis of chlordane, Sumicidin and Sumithion by different techniques. (Comparison of analytical procedure.)*

Active ingredient	Analytical procedure				% Recovery of active ingredient
	Extraction solvent		Determination		
	Benzene (Soxhlet)	Formic acid/ toluene	C[a]	GC[b]	
Chlordane		o		o	97
		o	o		92
	o		o		18
	o			o	20
Sumicidin		o		o	97
Sumithion		o		o	98
	o			o	23

[a] Colorimetry.
[b] Gas chromatography.

diagonal part of the test pieces (150 × 150 mm), maintaining uniformity, were pulverized by means of a coffee mill into fine particles less than 0.5 mm in diameter to give the test powder.

Determination of content.—One hundred ml of the solvent for extraction was added to 1–2 gram of the test powder, and mixed well. After the mixture had stood for 8 h, it was shaken again vigorously before analysis and stood for another 30 min; a part (10 ml) of clear solution from the upper layer was taken and the content of the insecticide was determined by gas chromatography under experimental conditions shown in Table 1, or by a colorimetric method (Inoue 1979; Yagishita et al. 1979).

Extraction of the insecticide from the glue.—Glue containing 0.458% (w/w) of Sumithion was prepared according to recipe A shown earlier, replicated on a glass plate (about 1 mm thick), dried at 115–120 C for 15 min, crushed, and pulverized into very fine particles less than 250 microns. Then 10 ml of the solvent for extraction was added to 500 mg of the fine powder in a test tube made of glass (10 mm in diameter). The mixture was shaken for 2 h, and the amount of extracted Sumithion was measured. The degree of swelling of the thermosetting resin powders after absorbing the solvent was also measured.

Stability test of Sumithion in the extraction solvent.—About 1% (w/w) solutions of Sumithion in various kinds of solvent were stored at 40 C and 60 C for 30 days. Residual amounts of Sumithion in the solvent were determined by gas chromatography.

Determination of penetration of the applied insecticide into the veneers.—Layers from the surface to 0.18 mm deep (surface layer), from 0.18 to 0.75 mm (middle layer), from 0.75 to 1.28 mm (resin layer), and from 1.28 to 1.78 mm (core layer) were sliced off by a plane from test pieces (40 × 150 mm); and the shavings were pulverized into fine powder just as mentioned earlier. The Sumithion content in each layer was determined by gas chromatography equipped with a flame-photometric detector (FPD).

RESULTS AND DISCUSSION

Sumithion percentage recoveries obtained for various kinds of extraction solvent are plotted against their dielectric constant in Fig. 1, and acid strength in

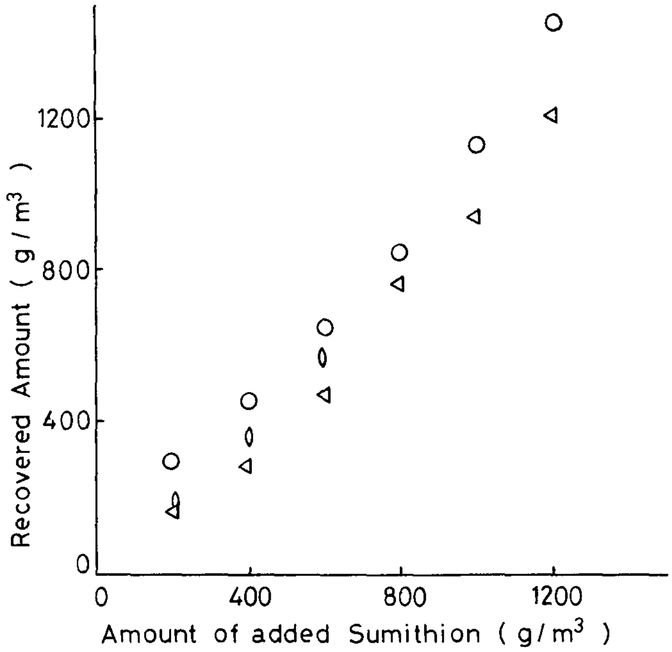

FIG. 3. Amount of recovered Sumithion from various kinds of plywood. Symbol ◁: Plywood made of red lauan using urea resin glue (Recipe A), Symbol ○: Plywood made of red lauan using melamine-urea resin glue (Recipe B) and Symbol ◊: Plywood made of white meranti using urea resin glue (Recipe A).

Fig. 2, respectively. Formic acid as an extraction solvent was found to be the most effective, giving 85–95% recovery in contrast to 20% for benzene. Although there is no clear relation between the percentage recovery and dielectric constant or acid strength, it was elucidated that good extraction solvents are highly dielectric or acidic. The drastic change in extraction efficiency in the organic acid series solvents from propionic acid to formic acid may suggest that molecular size is another important factor. Power of the solvent to dissolve Sumithion does not seem to be important, because the insecticide is quite soluble in all the solvents examined.

Compatibility of Sumithion with these solvents is not so importnat that chemical decomposition does not occur during analytical procedures, because, except in the case of dimethylformamide, an almost quantitative amount of the active ingredient was recovered after an accelerated storage test of Sumithion in various kinds of solvents as shown in Table 2.

It is very interesting that when 5 ml of formic acid (a suitable amount to wet the wood powder sample) and 100 ml of toluene were used in combination, although these two solvents are not missible with each other, the best result was obtained (Table 3). It is clear that when formic acid and toluene are used in combination as the extraction solvents, Sumithion is extracted almost quantitatively from the plywood.

As shown in Table 4, fenvalerate and chlordane were also extracted successfully by this method (formic acid + toluene). A value of 97% in the case of chlordane

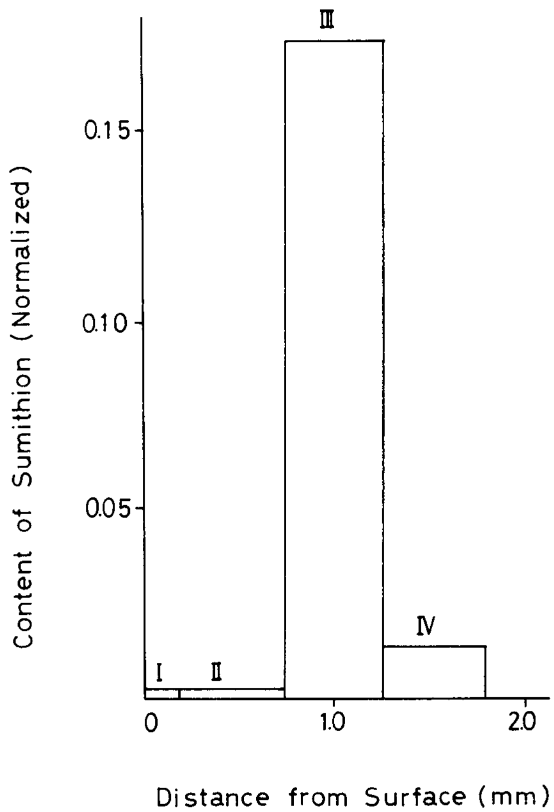

FIG. 4. Vertical distribution of Sumithion in plywood. (I): Surface layer, (II): Middle layer, (III): Resin layer and (IV): Core layer.

should be compared with that of 18% obtained by a conventional method (benzene extraction, colorimetric determination), which is well in accord with the reported values of 20–30% (Nishimoto 1979; Inoue 1979). There is no significant difference between measuring methods—that is colorimetry and gas chromatography—but large differences between extraction solvents, benzene and formic acid/toluene. Thus the high percentage recovery achieved in this study in comparison with conventional methods can reasonably be attributed to the high extraction efficiency.

From these results, we can conclude that the analytical method presented here, where formic acid and toluene are used for extraction solvents, is more suitable than conventional ones, and seems to be more widely applicable to a variety of the plywoods in which the content of the insecticide, or kind of insecticides, resins, and veneers may be different, as shown in Fig. 3. Moreover, in the case of these acidic extraction conditions, the amount of the extracted materials such as waxes, nonvolatile oil from the wood composition, which sometimes disturb the analysis, is very small.

As a result of finding this excellent extraction solvent, we could analyze the penetration of the active ingredient into the veneer as shown in Fig. 4. The applied

TABLE 5. *Swelling test of thermosetting resin powder.*

Solvent (10 ml)	Volume (ml) of resin powder (% swelling)						Extracting rate of Sumithion (formic acid = 100)
	Initial	1 h	2 h	3 h	6 h	22 h	
Toluene	0.75	0.75 (0)	0.75 (0)	0.80 (7)	0.80 (7)	0.80 (7)	13
Benzene	0.75	0.75 (0)	0.80 (7)	0.80 (7)	0.80 (7)	0.80 (7)	12
Acetone	0.60	0.60 (0)	0.60 (0)	0.60 (0)	0.60 (0)	0.60 (0)	14
Methanol	0.60	0.60 (0)	0.60 (0)	0.60 (0)	0.60 (0)	0.70 (17)	15
Formic acid	0.75	1.20 (60)	1.60 (113)	1.60 (113)	1.80 (140)	2.20 (193)	100
Acetic acid	0.80	0.80 (0)	0.80 (0)	0.80 (0)	0.80 (0)	0.80 (0)	12
Phosphoric acid	0.70	0.80 (14)	0.80 (14)	0.90 (29)	0.90 (29)	0.90 (29)	12
Water	0.80	0.80 (0)	0.80 (0)	0.80 (0)	0.80 (0)	0.90 (13)	0

Sumithion is, as expected, highly localized in the resin (glue) layer. It is interesting that though the amount of Sumithion at the surface layer is very small, it is enough for controlling *Lyctus brunneus* Stephens (Ito et al. 1983).

Table 5 shows that the thermosetting resin swells most effectively when formic acid is added. So it was supposed that the role of formic acid would be to expand the resin networks where most of active ingredient applied was occluded and that the role of toluene would be to extract the active ingredient efficiently from the expanded resin networks.

SUMMARY

A rather efficient method for quantitative analysis of the active ingredient in a glue-line-treated plywood was found by using formic acid and toluene in combination as the extraction solvent. A recovery rate of more than 95% was achieved, which should be compared with, at best, 50% by the conventional benzene Soxhlet extraction method of Japan Agricultural Standard (JAS). It was also shown that this method could have wide application, because the recovery rate was almost independent of the kind of active ingredients, woods and resins. Formic acid was presumed to have an important role to expand the thermosetting resin networks in which most of the treated active ingredient was occluded.

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