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Original Article

Application of Fenitrothion Microcapsule for Insect-proof Plywood

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Fenitrothion microcapsule was compared with fenitrothion 60% emulsifiable concentrate in applicability to insect-proof plywood. Microencapsulated fenitrothion was more stable than fenitrothion formulated in emulsifiable concentrate in four kinds of adhesives, especially in highly alkaline adhesives such as alkaline phenol resin, in which nonencapsulated fenitrothion easily decomposed when the adhesive was hardened. The efficacy of plywood containing fenitrothion microcapsule against *Lyctus brunneus* was excellent. Fenitrothion microcapsule was more effective than fenitrothion emulsifiable concentrate to be used for insect-proof plywood, because it retained residual efficacy at a smaller dosage even after stored in severe conditions regardless of the sort of adhesives used with.

INTRODUCTION

Fenitrothion is one of the most widely used organophosphorous insecticides because it has high insecticidal activity against many kinds of insect pests as well as excellent safety for mammalia and environment. Because of its an excellent efficacy against *Lyctus brunneus* (Lyctus powder-post beetle), fenitrothion 60% emulsifiable concentrate (Ranbert®) has been used for insect-proof plywood.[1]

Four kinds of adhesives are generally used as glues for plywood, *i.e.*, melamine-urea resin, urea resin, modified phenol resin and alkaline phenol resin. However, it was difficult to apply fenitrothion emulsifiable concentrate to strongly alkaline adhesives such as alkaline phenol resin, because fenitrothion easily decomposed under strongly alkaline conditions.

Microencapsulation is one of the most suitable methods to solve this problem, because the wall of microcapsule is expected to prevent fenitrothion from contacting adhesives.[2,3] We prepared a fenitrothion microcapsule with polyurethane wall by interfacial polymerization and studied whether it would be applicable to insect-proof plywood.[4,5]

MATERIALS AND METHODS

1. Preparation of a Fenitrothion Microcapsule

Fenitrothion was microencapsulated by interfacial polymerization method with polyisocyanate and ethylene glycol.[6] The wall material was polyurethane and the mass median diameter was about 20 μm. The concentration of fenitrothion was 20 wt% in the final aqueous slurry.

2. Compatibility of Fenitrothion Microcapsule with Adhesives

Twenty grams of an adhesive, 0.12 g of the fenitrothion 20% microcapsule or fenitrothion 60% emulsifiable concentrate as an active ingredient and 0.1 g of a hardener were mixed with deionized water to make 21 g of mixture. One gram of the mixture was spread onto a Petri dish (i.d., 5 cm). After drying, the treated Petri dish was kept at the prescribed temperature for 20 min until the mixture hardened. Adhesives used in this study and hardening

Table 1 Adhesives used in this study.

Adhesive[a]	Type	pH	Hardener	Temp.[b] (°C)
Ohshika resin 210	Urea	7.0	NH_4Cl	120
Ohshika resin pwp-8	Melamine-urea	8.8	NH_4Cl	120
Dianol DM-465	Modified phenol	8.8	NH_4Cl	120
Dianol D-17	Alkaline phenol	10.8	HOT P-5[c]	140

[a] Supplied by Ohshika Shinko Co., Ltd. [b] Hardening temperatures in the compatibility test between adhesives and two formulations. [c] Supplied by Ohshika Shinko Co., Ltd.

temperatures are shown in Table 1.

Samples were grinded into powder with a mortar immediately after hardening or after storage at 50°C for 1 month. Five milliliters of formic acid and 40 ml of toluene were added to the powder and the slurry was kept at ambient temperature for 12 hr to extract fenitrothion from the powder. The fenitrothion content in the extracted solution was analyzed by GC under the following conditions: detector, FPD: column, 1.1 m and 3 mm i.d.; liquid phase, 3% silicone XE-60; support, Chromosorb W AW DMCS (60–80 mesh); column oven temperature, 180°C; injection temperature, 200°C; detector temperature, 200°C; carrier gas, nitrogen (50 ml/min).

3. Stability of Fenitrothion Microcapsule and Emulsifiable Concentrate in Alkaline Condition

Ten milligrams of fenitrothion microcapsule or fenitrothion emulsifiable concentrate as an active ingredient was mixed with 10 ml of 0.1 N NaOH solution in a glass ampoule. After the ampoule was stored at 120°C for the prescribed period, fenitrothion was extracted with 20 ml of ethyl acetate and 5 ml of formic acid. The fenitrothion content in the extracted solution was analyzed by GC under the same conditions described above.

4. Preparation of Insect-Proof Plywood

Plywood pieces used in this study were prepared by Ohshika Shinko Co., Ltd., under the following conditions:

1) Composition: 2 sharings 4.0 mm thick as face and back parts and 1 sharing 3.0 mm thick as core part. (The face and back of the core sharing were treated with *ca.* 400 g of an adhesive per one square meter, respectively.)

2) Dosage of fenitrothion per 1 m^3 of plywood: 300 g of fenitrothion microcapsule or 400 g of fenitrothion emulsifiable concentrate as active ingredient.

3) Cold press: 10 kg/cm^2 for 20 min at ambient temperature.

4) Hot press: 10 kg/cm^2 for 100 sec at 115°C for urea resin and meramine urea resin, at 125°C for modified phenol resin and at 140°C for alkaline phenol resin.

5. Storage Stability of Insect-Proof Plywood

After stored at 40°C for 3 months, the insect-proof plywood was cut into two equal parts diagonally. The cut surface was shaved with a hand plane and the wooden powder was collected. *ca.* 1–2 g of the powder was weighed and mixed with 5 ml of formic acid and 40 ml of toluene, and the mixture was kept at ambient temperature for 12 hr to extract fenitrothion.[7,8] The fenitrothion content in the extracted solution was analyzed by GC under the same conditions described above.

6. Boring Prevention Test

Immediately after preparation or after storage at 60°C for 2 months, an aluminum pannel (8 cm×5 cm) with 32 holes (3.5 mm i.d.) was attached to a piece of plywood (8 cm×5 cm). A mature larva of *Lyctus brunneus* (Lyctus powder-post beetle) was inoculated into each hole of the aluminum pannel and the holes were packed with artificial diet powder, and another piece of plywood (8 cm×5 cm) was mounted onto the aluminum pannel.[9] Boring-preventive effect was examined by investigating whether the plywood was bored by newly emerged *Lyctus brunneus* after incubation for

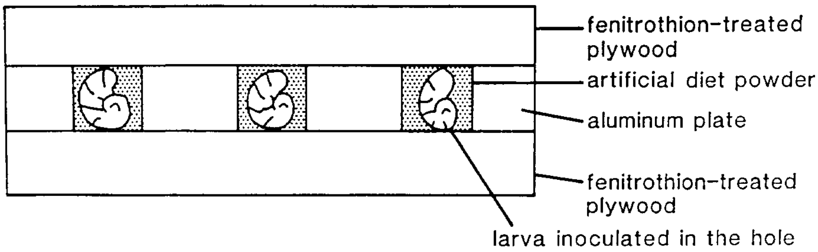

Fig. 1 Method for the boring prevention test.

2 months in the dark at 25°C and 70% humidity (Fig. 1).

RESULTS AND DISCUSSION

1. Stability of Fenitrothion in Adhesives

In the case of fenitrothion 60% emulsifiable concentrate, remaining fenitrothion immediately after hardening was much lower than the feeding amount as shown in Fig. 2. The order of adhesives with high content of remaining fenitrothion was as follows; melamine-urea resin, urea resin, alkaline phenol resin and modified phenol resin. On the other hand, encapsulated fenitrothion was much more stable than that applied as emulsifiable concentrate, especially in modified phenol resin and alkaline phenol resin.

Figure 3 shows the stability of fenitrothion after stored at 50°C for 1 month. The amount of remaining fenitrothion was not so lower than that immediately after hardening in all adhesives.

From the results in Figs. 2 and 3, the relative ratio (RR) of remaining fenitrothion in microcapsule to that in emulsifiable concentrate under the same experimental conditions was calculated by the following Eq. (1).

$$\mathrm{RR}\ (\%) = \frac{\text{(remaining fenitrothion in microcapsule)}}{\text{(remaining fenitrothion in emulsifiable concentrate)}} \times 100 \qquad (1)$$

As shown in Table 2, the RR was more than 100% in all the conditions and the order of adhesives with high RR was as follows; modified phenol resin, alkaline phenol resin, urea resin and melamine-urea resin. That is, the RR increased with a decrease in the stability of fenitrothion applied as emulsifiable concentrate. This result shows that microencapsulation is effective to stabilize of fenitrothion, especially in case non-encapsulated fenitrothion decomposes a great deal. On the other hand, the RR after storage was similar to that immediately after heat curing for the same adhesive. This shows that storage stability of fenitrothion applied as microcapsule form in the adhesive is not so much different from that applied as emulsifiable concentrate.

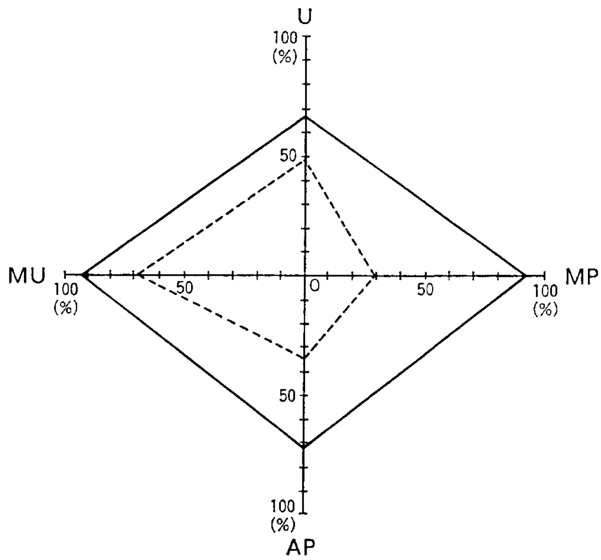

Fig. 2 Percentage of remaining fenitrothion in adhesives to the feeding amount immediately after heat curing.

Fenitrothion: ——, fenitrothion 20% microcapsule; ······, fenitrothion 60% emulsifiable concentrate. Adhesive: U, urea resin; MU, melamine-urea resin; MP, modified phenol resin; AP, alkaline phenol resin.

As shown in Table 3, the microencapsulated fenitrothion is more stable than non-encapsulated fenitrothion in the alkaline aqueous solution. The reason seems to be that microencapsulated fenitrothion was protected from direct contact with the alkaline medium by

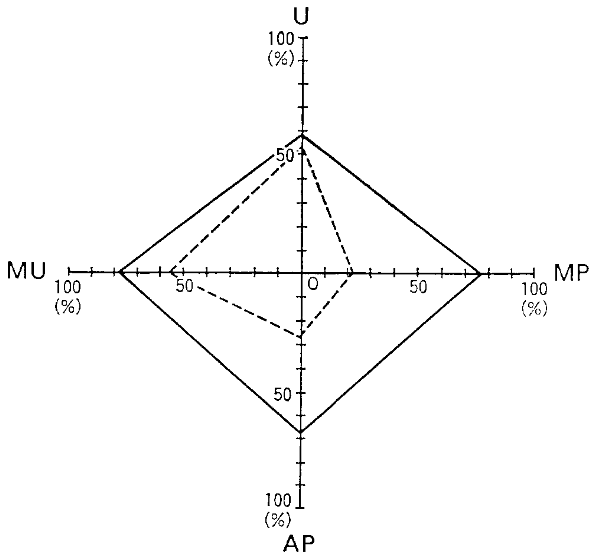

Fig. 3 Percentage of remaining fenitrothion in adhesives to the feeding amount after storage at 50°C for 1 month.

Symbols are the same as Fig. 2.

Table 2 Relative stability of fenitrothion microcapsule to fenitrothion emulsifiable concentrate in adhesive.

Adhesive	RR value (%)[a)] Immediately after preparation	RR value (%)[a)] After storage at 50°C for 1 month
Urea[b)]	139	109
M urea[c)]	135	139
M phenol[d)]	317	350
A phenol[e)]	215	252

a) Relative ratio calculated by the following equation;

$$RR = \frac{(\text{remaining fenitrothion microcapsule}) \times 100}{(\text{remaining fenitrothion emulsifiable concentrate})}$$

b) Urea resin. c) Melamine-urea resin.
d) Modified phenol resin. e) Alkaline phenol resin.

the wall. The difference in the stability of fenitrothion in the two formulations in the alkaline solution is supposed to be the cause of the difference in the stability during the hardening process. The wall prevents the microencapsulated fenitrothion from direct contact with adhesive slurry.

After heat curing, however, adhesives are no

Table 3 Stability in alkaline aqueous solution.

Storage conditions: Temperature (°C)	Storage conditions: Period (min)	Decomposed fenitrothion (%): Micro-capsule[a)]	Decomposed fenitrothion (%): Emulsifiable concentrate[b)]
120	30	2.0	10.0
120	60	6.6	14.1

a) Fenitrothion 20% microcapsule.
b) Fenitrothion 60% emulsifiable concentrate.

longer aqueous slurry but solidified. Thus, droplets of fenitrothion emulsifiable concentrate dispersed in an adhesive are supposed to be covered with polymerized adhesives and no longer to meet with alkaline aqueous slurry. This, in a sense, is the same situation of the microencapsulated fenitrothion. That is supposed to be a reason why the storage stability of fenitrothion applied as emulsifiable concentrate is almost the same as that applied as microcapsule in adhesive during storage.

2. *Application to Insect-Proof Plywood*

Figures 4 and 5 show percentage of the remaining fenitrothion in the insect-proof plywood immediately after preparation and after storage at 40°C for 3 months.

Stability of fenitrothion applied in emulsifiable concentrate decreased with an increase

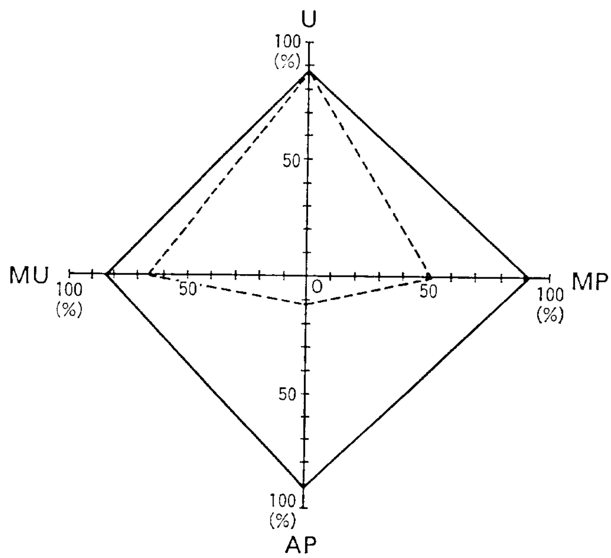

Fig. 4 Percentage of remaining fenitrothion in plywood to the feeding amount immediately after preparation.

Symbols are the same as Fig. 2.

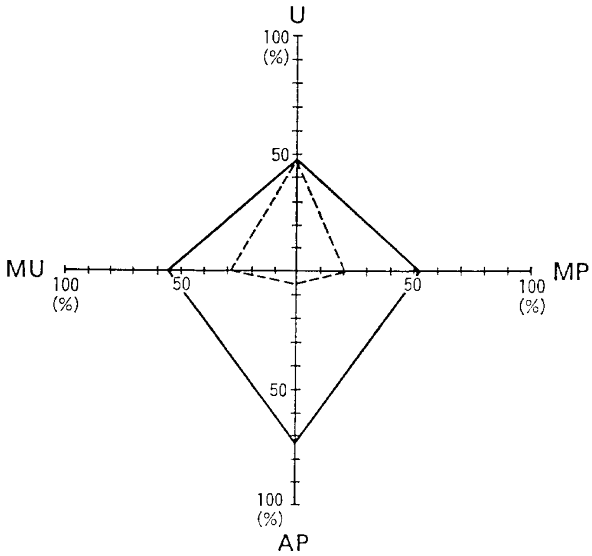

Fig. 5 Percentage of remaining fenitrothion in plywood to the feeding amount after storage at 40°C for 3 months.

Symbols are the same as Fig. 2.

Table 4 Relative stability of fenitrothion microcapsule to fenitrothion emulsifiable concentrate in plywood.

Adhesive	RR value (%)[a]	
	Immediately after preparation	After storage at 40°C for 3 month
Urea[b]	102	102
M urea[c]	124	189
M phenol[d]	173	236
A phenol[e]	767	1480

[a] Relative ratio calculated by the following equation;

$$RR = \frac{\text{(remaining fenitrothion in microcapsule)} \times 100}{\text{(remaining fenitrothion in emulsifiable concentrate)}}.$$

[b] Urea resin. [c] Melamine-urea resin.
[d] Modified phenol resin. [e] Alkaline phenol resin.

Table 5 Boring prevention test.

Formulation	Adhesive	Number of damaged plywood pieces[g]	
		Initial	After storage
EC[a]	Urea[c]	0	0
	M Urea[d]	0	0
	M Phenol[e]	0	1
	A Phenol[f]	0	1
MC[b]	Urea[c]	0	0
	M Urea[d]	0	0
	M Phenol[e]	0	0
	A Phenol[f]	0	0
Untreated	Urea[c]	3	4
	M Urea[d]	3	—
	M Phenol[e]	4	—
	A Phenol[f]	3	4

[a] Fenitrothion 60% emulsifiable concentrate.
[b] Fenitrothion 20% microcapsule.
[c] Urea resin.
[d] Melamine-urea resin.
[e] Modified phenol resin.
[f] Alkaline phenol resin.
[g] Total 4 pieces of plywood were observed.

in the pH of adhesives and the temperature of hot pressing in preparation. On the other hand, percentage of microencapsulated fenitrothion remaining were high regardless of the sort of adhesives not only immediately after preparation but also after storage. The RR value in Table 4 showed that microencapsulation improved the stability of fenitrothion in the alkaline phenol resin as shown in the test result of compatibility between adhesives and two formulations.

Table 5 shows the result of the boring prevention test. Plywood with an adhesive but without fenitrothion was all bored by *Lyctus brunneus*. The plywood treated with fenitrothion emulsifiable concentrate was prevented from boring at the initial stage, but after stored at 60°C for 2 months, one plywood piece out of 4 replications with melamine urea resin and alkaline phenol resin was damaged by *Lyctus brunneus*. Of course, as the storage conditions at 60°C for 2 months is too severe compared with the actual conditions under which plywood is normally used, the efficacy of the emulsifiable concentrate is supposed to be acceptable.

On the other hand, plywood containing fenitrothion microcapsule was completely protected from boring by *Lyctus brunneus* even in the condition where plywood containing fenitrothion emulsifiable concentrate was penetrated, in spite that the dosage of fenitrothion microcapsule as an active ingredient (300 g/m^3) was lower than that of fenitrothion emulsifiable concentrate (400 g/m^3). The improved stability of the microencapsulated fenitrothion during the hardening process in preparation, especially in the alkaline phenol resin, may have affected the result of the biological test described above.

The way of action of fenitrothion microcapsule in plywood against *Lyctus brunneus* has not been examined yet. However, *Lyctus brunneus* is supposed to break microcapsule and contact with fenitrothion as cockroaches and termites do.[10]

In conclusion, it was found that microencapsulated fenitrothion was considerably useful for the insect-proof plywood because of reducing the dosage and keeping the residual efficacy even under severe storage conditions independent of the kind of adhesives.

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要　約

フェニトロチオンマイクロカプセルの防虫合板への適用性

川島操子，大坪敏朗，津田重典
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フェニトロチオンマイクロカプセルの防虫合板への適用性をフェニトロチオン乳剤と比較して検討した．マイクロカプセル化されたフェニトロチオンの4種の合板用接着剤中での安定性は，いずれも乳剤化された場合のそれを上回った．とくにアルカリフェノール型樹脂のような強アルカリ性の接着剤中において，その安定化効果は顕著であった．それに伴い，マイクロカプセルを用いた防虫合板のヒラタキクイムシに対する効果は，乳剤を用いた場合よりも優れたものとなった．フェニトロチオンマイクロカプセルは，乳剤と比較して，乳剤よりも低薬量で，使用接着剤の種類に無関係に安定した効果を示す優れた製剤であることが確認された．