ACTIVATING PYRETHROID INSECTICIDES

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Abstract

Certain adjuvants have been shown to enhance the activity of pyrethroid insecticides, in particular the synthetic pyrethroids. Typical of these pyrethroids are alpha-cypermethrin, lambdacyhalothin, betacyfluthrin and deltamethrin. Respectively these are the active insecticide ingredient in the emulsifiable concentrates, *Fastac* (Cyanamid), *Karate* (ICI), *Bulldock* EC (Bayer) and *Decis Forte* EC (AgrEvo) and the *Fastac* ultra low volume (ULV) . The preferred adjuvants are based on the alkyl esters of fatty acids with the higher levels of unsaturation which appear as more effective penetrants of the waxy protective surfaces of insects. The ethyl esters appear most effective. Another adjuvant is based on the alkyl esters of dibasic acids such as di-isooctylmaleate.

The adjuvant is added to an insecticide preferably at about 2 to 5% v/v. Selected nonionic esters of the fatty acids provide good emulsification and coupling effects to furnish a finished homogeneous product. Where the application of the insecticide is as a ULV formulation, the adjuvant may exceed 80%, as the adjuvant is also acting as the diluent of the insecticide.

The alpha-cypermethrin containing adjuvants produce quicker knockdown in adult mustard beetles than the same formulation applied alone. Similar results were obtained when the adjuvant was used as a carrier solvent indicating the adjuvants have potential as an pyrethroid insecticide carrier. This use evidenced 100% knockdown at a concentration of alpha-cypermethrin of 0.001% a.i. w/v. Effective treatments appear possible using less pyrethroid insecticide. Lambdacyhalothrin, betacyfluthrin and deltamethrin have similarly shown improved insecticidal performance with added adjuvants. The last two products were trialled with field crickets.

Introduction

To maximise crop yields it has become essential to eliminate or substantially reduce the damage that pests inflict on crops. To this end, the chemical industry has developed a range of pesticides to combat most insects. However, the man on the land daily faces the competing tension between the persistent pests which would reduce his crop yields and the environmental impact which can occur through use of pesticides. Accordingly, there has long been a continuing investigation into the best means to maximise pesticidal efficacy whilst minimising environmental damage.

Current general concerns to reduce pesticide input in farming have raised questions about how this can be achieved quickly, cost effectively and in a manner which is environmentally acceptable. It is now recognised that by integrating formulation and application procedures, increased efficacy of agrochemical treatments is possible thereby reducing the mass of application of active ingredient (a.i.) necessary to control weeds, pests and diseases (Ford et. al., 1987). Furthermore, integration of these procedures may lead to selective treatments based on broad spectrum products (Ford et. al., 1992).

The use of spray adjuvants is an illustration of how this approach is being applied by farmers who wish to reduce costs and protect the environment by reducing pesticide inputs on their farms. Most research to date concerns spray additives to enhance the performance of herbicides in crop protection. These materials include surfactants and petroleum oils which can be harmful to the environment. Materials derived from plant oils which are non-toxic, biodegradable and therefore less hazardous are being considered for use as adjuvants in farming operations as disclosed in International Patent Application No. PCT/AU94/00229 by Victorian Chemical Co. Pty. Ltd. and Wilbur-Ellis Company. In that patent application, ethylated esterified seed oils are used to improve the efficacy of herbicide, crop desiccant and defoliant treatments by softening the leaf waxes and enhancing penetration.

Four insecticides have been considered with the organic esters, namely the typical synthetic pyrethroids alpha-cypermethrin, lambdacyhalothin, betacyfluthrin and deltamethrin. Respectively these are the active insecticide ingredient in the emulsifiable concentrates, *Fastac* (Cyanamid), *Karate* (ICI), *Bulldock* EC (Bayer) and *Decis Forte* EC (AgrEvo). *Fastac* is also available as an ultra low volume (ULV) formulation for specialist low volume aerial application. The bulking agent is usually a paraffinic oil.

Materials and Methods

A series of investigations has been undertaken to show how the processes of dose transfer, penetration and distribution of the insectides are affected by the use of the adjuvants and how any changes might modify the effectiveness of the insecticides as a contact pyrethroid insecticide. The materials used, *Esterol 123*, *Esterol 112*, *Vicchem* EOP, *Vicchem* MOP and *Vicchem* DOP, are proprietary products made by the Victorian Chemical Company of Richmond, Victoria, Australia of which

Esterol 123 is substantially ethyl oleate material;
Esterol 112 is substantially methyl oleate material;

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Vicchem EOP and *Vicchem* MOP are respectively *Esterol 123* and *Esterol 112* emulsified with nonionics including esters of the fatty acids.
Vicchem DOP is di-isooctylmaleate emulsified with nonionics including esters of the fatty acids.
Alpha-cypermethrin is a commercially available emulsifiable concentrate *Fastac*™ EC, 100g a.i./litre. Alpha-cypermethrin is also commercially available as *Fastac* ultra low volume (ULV) containing 1% w/v alpha-cypermethrin, both ex Cyanamid, The ULV formulation was mixed with the oil adjuvant (co-diluent) *Shellsol™ D100* a highly refined petroleum solvent.
Lambdacyhalothin is a commercially available emulsifiable concentrate *Karate*™, 50g a.i./litre ex ICI
Betacyfluthrin is a commercially available emulsifiable concentrate *Bulldock*™ EC, 25g a.i./litre.ex Bayer
Deltamethrin is a commercially available emulsifiable concentrate *Decis Forte*™ EC, 27.5g a.i./litre ex AgrEvo.

SERIES 1 - Alpha-cypermethrin

Penetration studies using isolated insect cuticles

Penetration of topically applied alpha-cypermethrin (4 μl of an aqueous solution of *Fastac* EC containing 1% a.i. w/v) across isolated cuticles of final instar larvae of *Spodoptera littoralis* Boisd. was studied using a diffusion flow cell (Ford et. al., 1995). Changes in the solute concentrations in the receptor solvent were monitored at 220 nm wavelength at 10 second intervals. The penetration rates for *Fastac* EC (1% w/v of a.i. as above) with and without *Esterol 123*, *Vicchem* EOP or *Vicchem* DOP (1% v/v) were compared to establish whether these adjuvants modify cuticle permeability.

Droplet ageing on glass slides

Esterol 123, *Vicchem* EOP and *Vicchem* DOP were added to the *Fastac* EC already diluted to 1% a.i. w/v with distilled water to give final solutions containing 1, 5, 10 or 25% v/v of adjuvant. Droplets (20 μl) of each solution were applied to glass microscope slides and left to dry. For comparison, droplets of pure *Vicchem* EOP and *Vicchem* DOP were also prepared. The effect of deposit ageing was assessed throughout a 24 hour period.

Pick-up, penetration and redeposition of alpha-cypermethrin

Pick-up of alpha-cypermethrin from droplets placed on glass slides was investigated to determine whether addition of adjuvant enhanced dose transfer. Adult mustard beetles held dorsally by a suction pooter were placed in contact with the centre of a deposit for 2 seconds, removed to a petri dish and left for 2 hours before being immersed in Analar acetone to remove transferred pyrethroid insecticide. The beetles were removed and the washings analysed for alpha-cypermethrin using electron capture detection (ECD) on a Hewlett Packard 1580 gas chromatograph (GC). The washed beetles were then frozen in liquid nitrogen to remove tissue water, crushed and further extracted in acetone to determine the internal concentrations of penetrated alpha-cypermethrin using ECD GC.

Beetles were held as before in order to contact deposits containing the diluted EC (1% w/v alpha-cypermethrin) and known amounts of adjuvant (*Vicchem* EOP or *Vicchem* DOP). Redeposition of alpha-cypermethrin onto glass surfaces was followed for five successive contacts (2 sec per contact) in order to estimate the retained fraction. The contaminated beetles and glass surfaces were washed immediately with acetone and analysed for alpha-cypermethrin using a Hewlett Packard GCD (ion-selective mode).

Response of mustard beetles following contact with aged deposits

Beetles were held for 2 seconds in contact with deposits prepared earlier from solutions containing known amounts of alpha-cypermethrin and adjuvant. The treated insects were then confined to filter paper lined petri dishes. Knockdown and mortality were observed at frequent intervals after treatment.

Results

Penetration studies using isolated insect cuticles

Penetration profiles for EC formulations containing 1% w/v alpha-cypermethrin with and without *Esterol 123*, *Vicchem* EOP and *Vicchem* DOP (1% v/v) are presented in Figure 1. All four formulations penetrated the cuticle at matching rates to produce similar absorbency profiles with time. These profiles measure the penetration of all of the formulation components including the active ingredient.

The results suggest that these adjuvants make little difference to the overall permeability of the cuticle as a result of surface effects, for example by modifying the organisation of the epicuticular waxes as suggested for plant cuticles.

Droplet ageing on glass slides

On drying, the EC formulation formed a liquid deposit from which the pyrethroid insecticide crystallised slowly with time. Addition of *Esterol 123*, *Vicchem* EOP and *Vicchem* DOP slowed the ageing process and prevented crystallisation so that deposits remained liquid 24 hours after application to glass. In this fluid state, pyrethroid insecticide deposits are known to be more available for transfer to contacting insects.

Pick-up, redeposition and subsequent penetration of alpha-cypermethrin

Addition of the adjuvants *Esterol 123* and *Vicchem* EOP increased the amount of alpha-cypermethrin initially transferred following a single 2 second contact with deposits aged for four hours after application of 20 μl droplets to glass slides (Table 1). *Esterol 123* was the most effective treatment when the adjuvants were added at a concentration of 1% v/v; increasing the adjuvant concentration to 5% v/v increased the transfer of alpha-cypermethrin from the *Vicchem* EOP and *Vicchem* DOP formulations to the level attained by *Esterol 123* at 1% v/v.

Redeposition of alpha-cypermethrin following initial contact with deposits prepared from a solution of alpha-cypermethrin and *Vicchem* EOP (1% w/v) was investigated in a similar manner. Adult beetles were held in contact with deposits for 2 seconds, as before, and then brought into contact with 5 successive clean glass surfaces for the same time to allow any redeposition from the tarsi onto the glass to take place. The contaminated surfaces were washed with acetone and the washings analysed by GCD. Although initial contact with such deposits resulted in an average transfer of 3 μg/insect, no subsequent redeposition was detected. Thus, the initial amount transferred remained on the insect where it was available for poisoning.

Penetration of acquired alpha-cypermethrin was investigated following 2 second contacts of beetles with deposits formed from formulations containing different amounts of adjuvant. Analysis of the quantities recovered from the beetle surface and the internal extracts (Table 2) suggests an optimum adjuvant concentration (5% v/v) which gave maximal dose transfer and internal accumulation of alpha-cypermethrin 4 hours after contact. Thus, the adjuvant is seen to have some effect on cuticular penetration and the concentration sprayed is also significant.

Response of mustard beetles following contact with deposits of alpha-cypermethrin

The influence of ethylated esterified seed oils on the insect response was investigated and is depicted in Figures 2, 3 and 4. At the recommended field rate of 1% w/v alpha-cypermethrin, a *Fastac* EC formulation containing adjuvants such as *Esterol 123* produce quicker knockdown in adult mustard beetles, *Phaedon cochleariae* Fab., than the same formulation applied alone. Similar results were obtained when the adjuvant *Vicchem* EOP was used as a carrier solvent. Thus, *Vicchem* EOP has potential as an pyrethroid insecticide carrier (Figures 3 and 4). This use of *Vicchem* EOP, for example, gave 100% knockdown at a concentration of alpha-cypermethrin of 0.001% a.i. w/v. The same concentration of a.i. resulted in only 60-80% knockdown (the upper response limit) following contact with deposits containing *Fastac* EC, suggesting that use of the adjuvant as a carrier increases insecticidal efficacy (Figure 4). Thus, effective treatments are possible using less pyrethroid insecticide.

This study suggests that the use of adjuvants derived from ethylated esterified seed oils increases the efficacy of the contact pyrethroid insecticide alpha-cypermethrin in a dose-related manner. The effect results primarily from an increased transfer of pyrethroid insecticide to adult mustard beetles, *Phaedon cochleariae* Fab. following contact with residual deposits. The higher internal levels of toxin which are observed 4 hours after encountering a deposit and associated changes in the speed of intoxication probably reflect this enhanced pick-up, although changes in the rate of cuticular penetration cannot be entirely discounted. Use of *Vicchem* EOP as a carrier solvent for alpha-cypermethrin resulted in a more effective treatment than *Fastac* EC applied at an equivalent concentration (0.001% a.i. w/v). It should therefore be possible to reduce the quantity of pyrethroid insecticide sprayed either by adding an appropriate adjuvant to the tank mix or by reformulating alpha-cypermethrin in a novel carrier such as *Vicchem* EOP.

SERIES 2 - alpha-cypermethrin in bulking oils

Methods

Penetration studies using isolated insect cuticles, the pick-up, penetration and redeposition of alpha-cypermethrin and the response of mustard beetles following contact with aged deposits were as described in the Series 1 examples.

Results

Response of *Fastac* ULV blank and each adjuvant alone

The results from Figures 5 and 6, show that each oil induces knockdown in adult mustard beetles brought into contact with a 4 hour old deposit placed on a glass slide. Complete recovery was observed twelve hours after contact with the *Fastac* ULV blank. However, there was no significant recovery after contact with *Esterol 123, Esterol 112* or *Shellsol D100*. These results demonstrate that undiluted oils can themselves exert some insecticidal activity.

In Figures 7 and 8 show that a mixture containing 50% by volume 1% a.i. w/v *Fastac* ULV and 50% by volume *Shellsol D100* gave 100% knockdown and was faster acting than either the *Fastac* ULV blank or the *Shellsol D100* bulking oil. Neither of the alpha-cypermethrin blanks gave complete knockdown.

When *Esterol 123* was mixed in different proportions with commercial bulking oil, *Shellsol D100*, for use as for the ULV formulation *Fastac* (1% a.i.), changing the ratio of adjuvants but maintaining the *Fastac* at 50% v/v had no effect on the speed of knockdown as illustrated in Figures 9 and 10. This result shows that *Esterol 123* and *Shellsol D100* are equally effective as bulking oils for this formulation of alpha-cypermethrin.

However, all four mixtures of adjuvants gave 100% mortality after 12 hours, whereas that containing only *Shellsol D100* gave approximately 17% recovery of the mustard beetles. This result indicates that greater dose transfer of alpha-cypermethrin is obtained in the presence of the adjuvants.

In another experiment, *Fastac* ULV 1% w/v was diluted by 50% and 20% v/v, respectively with *Esterol 112* to give mixtures containing different concentrations of *Fastac* formulation components including alpha-cypermethrin. The results from Figures 11 and 12, confirm that mixtures containing a.i. are much faster acting than the blanks. Furthermore, the formulation containing the smallest amounts of *Esterol 112*, and therefore the greatest concentration of alpha-cypermethrin appears to be the fastest acting mixture. Only the mixtures containing a.i. gave 100% mortality.

The responses due to alpha-cypermethrin dissolved in *Vicchem* EOP, *Vicchem* MOP or *Fastac* EC blank prior to final dilution with water to give concentrations of a.i. of 0.001% and 1% w/v were also compared directly. The results show that at both concentrations of alpha-cypermethrin, the addition of adjuvants produced faster knockdown. The results at 0.001% w/v a.i. demonstrate the benefits of addition of adjuvants most clearly in Figures 13, 14 and 15.

The formulation containing alpha-cypermethrin dissolved in *Vicchem* EOP gave the most rapid knockdown, followed by that dissolved in *Vicchem* MOP; the *Fastac* blank gave the slowest knockdown. This ranking was also observed at the higher concentration of a.i. (1% w/v). Percentage mortality follows the same trend. At 0.001% a.i., *Fastac* EC alone gave only 47% kill 24 hours after contact. Addition of *Vicchem* EOP and *Vicchem* MOP always resulted in 100% kill with 0.001% a.i. alpha-cypermethrin.

SERIES 3 - lambdacyhalothrin

Methods

The materials and methods, the pick-up, penetration and redeposition of lambda-cyhalothrin and the response of mustard beetles following contact with aged deposits were as described in the Series 1.

Results

Each of the insecticides and adjuvant mixtures was very effective compared with the pyrethroid lambda-cyhalothrin alone as shown in Figure 16. The insecticide with *Esterol 112* and *Esterol 123* at 5% v/v were the most effective initially exhibiting a higher knock down rate than insecticide compositions having 1% of these adjuvants. However, all the adjuvant and insecticide mixtures showed superior knock down rates to the insecticide not mixed with the adjuvants. This shows that these adjuvants improve the insecticidal performance of lambda-cyhalothrin.

SERIES 4 - betacyfluthrin and deltamethrin

Methods

A series of laboratory bioassays was carried out on black field crickets to determine if *Vicchem* EOP (treated with 2.0% composition of *Vicchem* EOP) could improve the efficacy of the synthetic pyrethroids betacyfluthrin (*Bulldock* EC) and deltamethrin (*Decis Forte* EC) (Horne et. al., 1996).

The black field cricket (*Teleogryllus commodus*) is a chewing insect and the first instars (i.e. newly emerged crickets) from a laboratory culture were used to test these pyrethroids. The culture was maintained at 24^0C in a controlled-temperature room. The adults were reared from nymphs in ventilated plastic containers. The crickets were fed grain pellets throughout their life stages. Equal numbers of males and females were present and first instars were removed daily for bioassays.

Insecticides in all treatments were applied using a Potter tower (Burkard) to ensure consistent application rates. The tower was run at 40 kPa and delivered droplets at about 50 μm in diameter. Plain cabbage was used for the bioassays.

Cabbage leaves were sectioned and placed onto the base of a petri dish (9 cm diam). One side only was sprayed and the leaf section was air-dried for 20 min. in a fume-hood. Controls were sprayed with water only. Five sections (replicates) were prepared for each dose. A sharpened steel cutter (18 mm in diam) was used to cut 3 discs from each sprayed section and these were placed into the base of the glass petri disc (9 cm in diam.). First instars were placed into each disc using a camel hair brush, before replacing the lid. Each replicate contained 10 crickets. The bioassays were conducted at 25^0C and cricket mortality was assessed after 24 hours.

An initial comparison was made between sprayed leaf discs and the contact toxicity of the adjuvant and *Bulldock* EC, sprayed onto the glass only. The adjuvant and *Bulldock* EC were applied separately at varying rates in order to determine a dose response curve. Petri dish bases (9 cm diam.) were sprayed and then air-dried for 20 min. Controls were sprayed with water only. Five replicates were prepared and each plate was innoculated with 10 crickets. The bioassays were conducted at 25^0C and cricket mortality was assessed after 24 hours.

Results

Vicchem EOP shows insecticidal activity when crickets were placed onto bare treated glass as shown in Figure 17 and mortality increased with the increasing concentrations of *Vicchem* EOP.

No cricket mortality was recorded when the leaf discs were sprayed with either 0.5% or 2.0% *Vicchem* EOP. It would appear that this result is due to lower effective doses being available on the leaf discs than on bare glass, or because of penetration of the *Vicchem* EOP into the leaf tissue, or a combination of both factors.

Vicchem EOP at a concentration of 2.0% shifted the dose-response curve for the synthetic pyrethroids, *Bulldock* EC as illustrated in Figure 18 and for *Decis Forte* EC shown in Figure 19 revealing a significant increase in the relative efficacy of these pyrethroids.

Note

The authors express their appreciation to Professor Martyn Ford (University of Portsmouth, UK) for his earliest research.

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Horne P. and Smith M. Reports from the Institute for Horticulture Development, Dept. of Agriculture, Victoria, Australia (l996)(private communications)

TABLE 1. Recoveries (μg/insect) of alpha-cypermethrin from the transfer to adult mustard beetles following a single 2 second contact between the deposit and the tarsi.

Adjuvant concentration (% v/v)	0	1	5
Esterol 123	2.6	14.4	15.8
Vicchem EOP	2.6	6.1	14.5

TABLE 2. Recoveries (μg/insect) of alpha-cypermethrin from the surface and internal tissues of adults of *Phaedon cochleariae* Fab. following contact (2 sec) with deposits containing ethylated esterified seed oils.

Adjuvant conc (% v/v)	0	1	5	10	25
External					
Esterol 123	0.94	1.92	3.30	2.84	2.06
Vicchem EOP	0.94	1.96	3.52	2.08	3.62
Internal					
Esterol123	0.33	1.02	2.58	1.20	1.32
Vicchem EOP	0.33	0.33	5.90	3.72	1.59

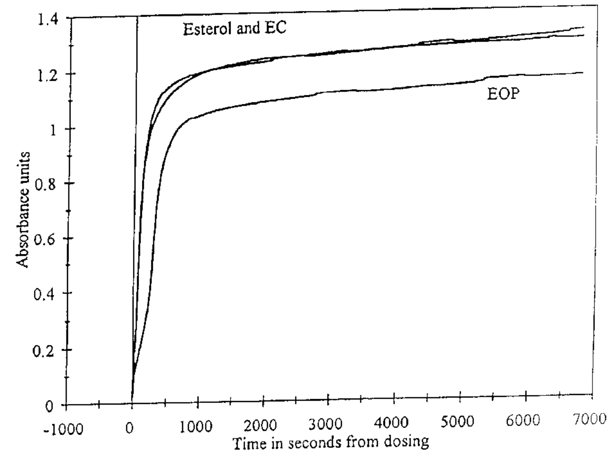

Figure 1 Penetration Profile of Insect Cuticle

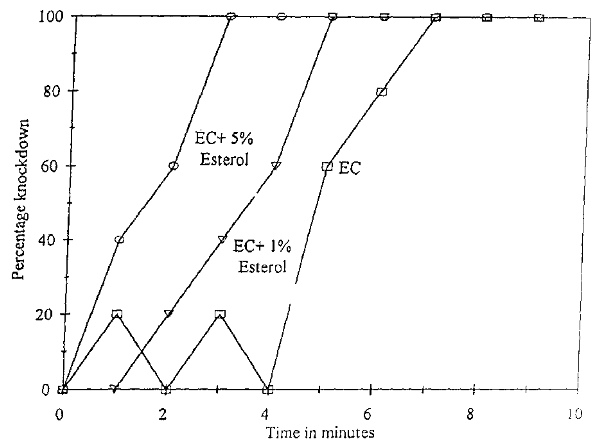

Figure 2 Insect knockdown response

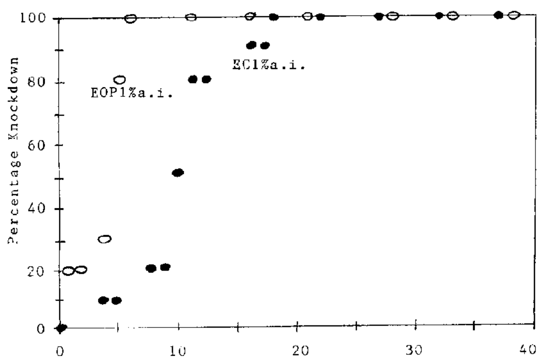

Figure 3 Insect knockdown response

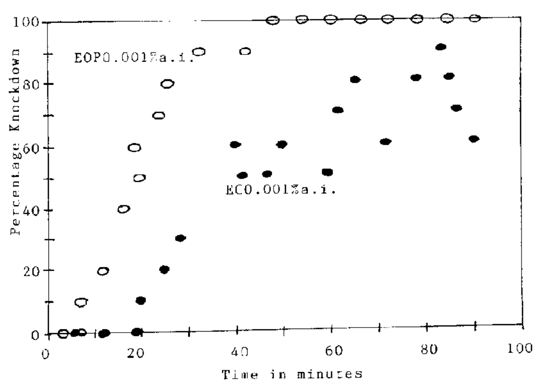

Figure 4 Insect knockdown response

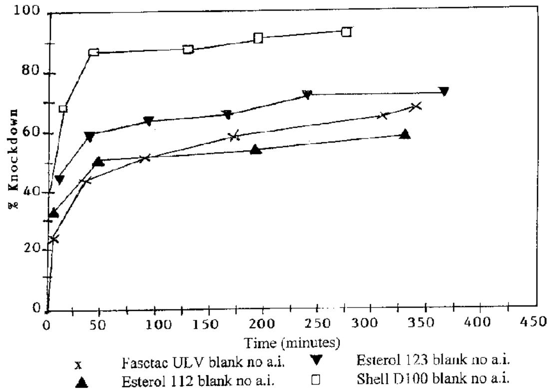

Figure 5 2 ULV Fastac formulations Blanks (no a.i.)

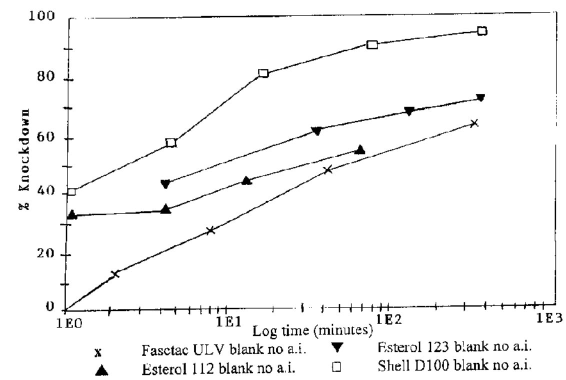

Figure 6 ULV Fastac formulations Blanks (no a.i.)

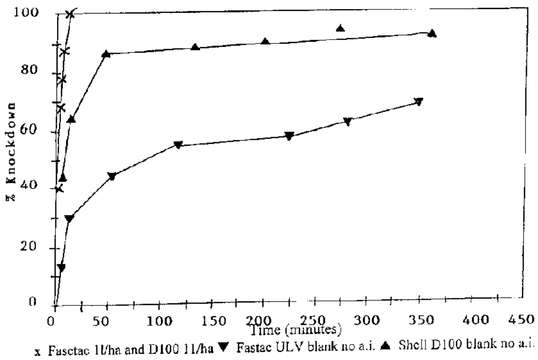

Figure 7 ULV Fastac formulations (Fastac 1l/ha + D100 1l/ha)

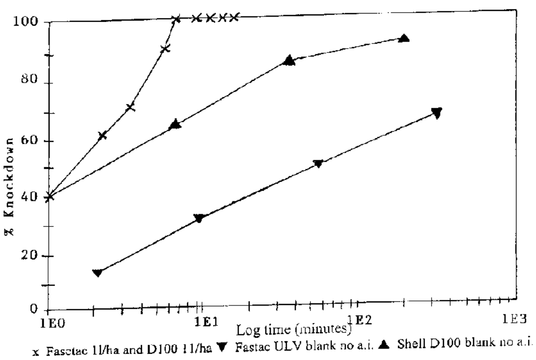

Figure 8 ULV Fastac formulations (Fastac 1l/ha + D100 1l/ha)

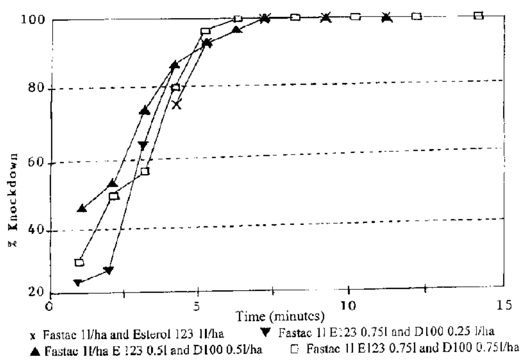

Figure 9 ULV Fastac formulations
(Fastac ULV – D100 and/or Esterol 123)

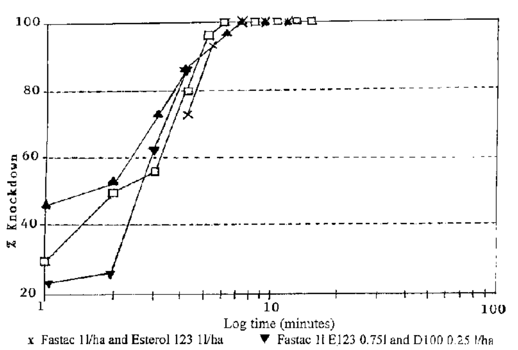

Figure 10 ULV Fastac formulations
(Fastac ULV + D100 and/or Esterol 123)

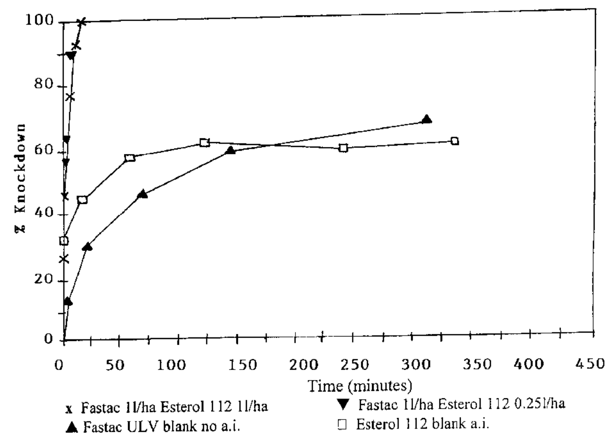

Figure 11 ULV Fastac formulations (Fastac 1l/ha + Esterol 112)

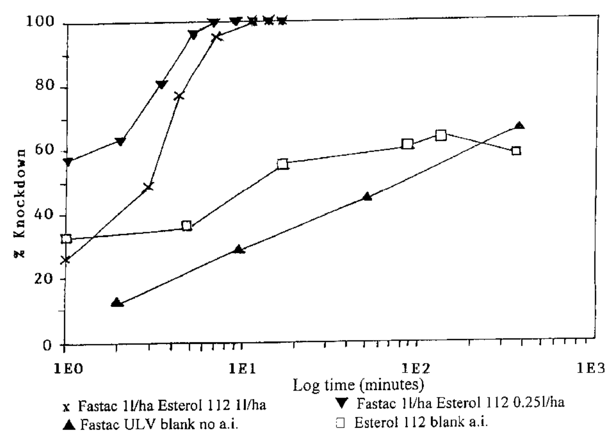

Figure 12 ULV Fastac formulations (Fastac 1l/ha + Esterol 112)

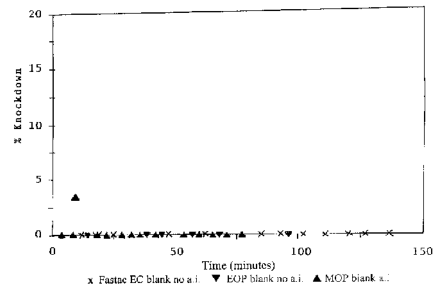

Figure 13 Fastac EOP & MOP blanks-no a.i.
(Concentrate diluted 1:10 with water)

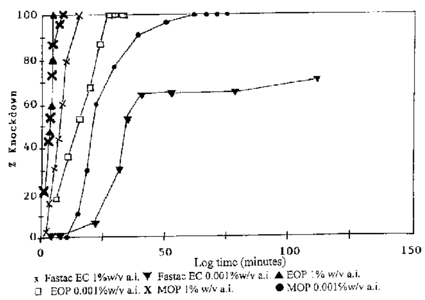

Figure 14 Fastac and EOP or MOP
(Concentrate diluted 1:10 with water)

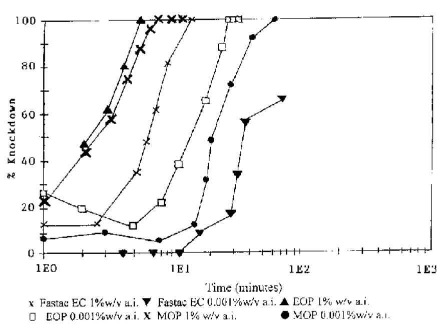

Figure 15 Fastac and EOP or MOP (Concentrate diluted 1:10 with water)

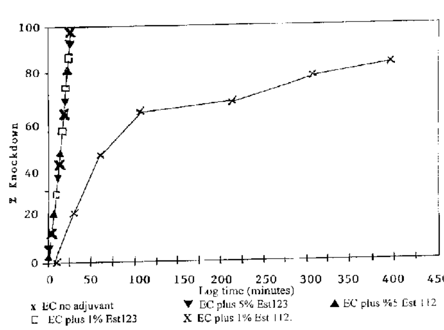

Figure 16 Esterol 123 and 112 (Modified EC Lambda-cyhalothrin)

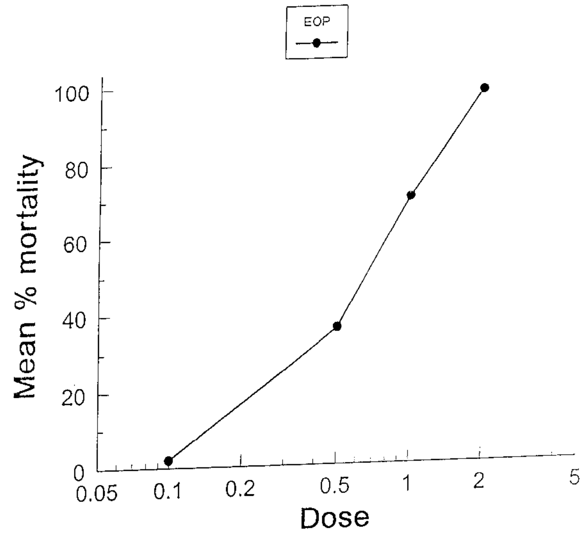

Figure 17 Field Cricket Mortality

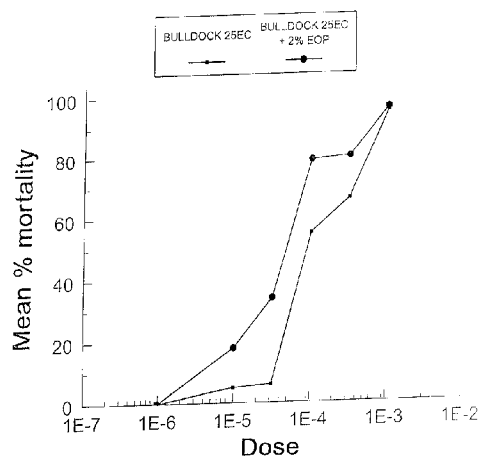

Figure 18 Field Cricket Mortality

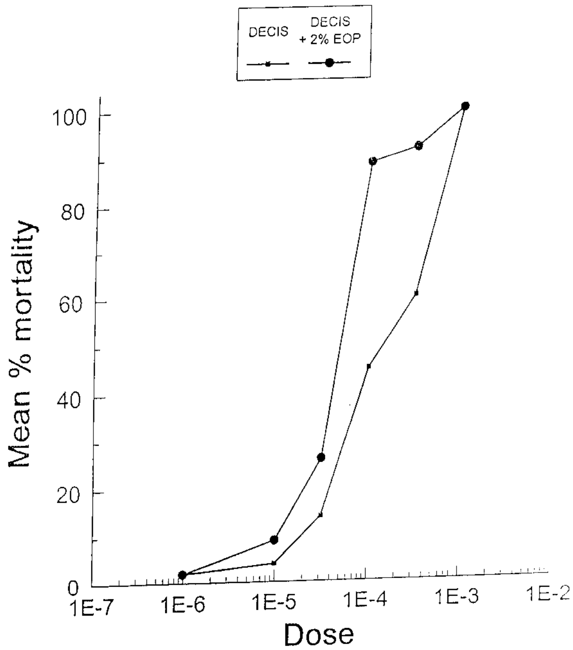

Figure 19 Field Cricket Mortality