A NEW FORMULATION LIQUID GRAIN PROTECTANT BASED ON DELTAMETHRIN AND CHLORPYRIFOS-METHYL

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Abstract The development of a new formulation liquid grain protectant is described. Initial Laboratory assays identified the preferred combination of actives and indicated target treatment rates. Subsequent formulation development produced two stable formulations with major benefits over traditional formulations of these actives. Both were tested in field trials at the Wellcome Research Station, 'Bangalla', Australia. Treatment was made at 0.2/4 ppm and 0.25/5 ppm (deltamethrin/chlorpyrifos-methyl), applied to 5 tonne lots of grain. Bioassays were conducted against a range of beetle strains at 'Bangalla' and at WEH laboratories, UK on samples taken at intervals during 12 months storage. Only against the highly resistant QTC279 strain of Tribolium castaneum was some loss in adult kill noted (after 6 months storage). There was negligible F_1 adult progeny development. Further field trials have been conducted by the Australian Wheat Board at 2 sites during 1988/9 and at 5 sites during 1989/90. In bioassays from the first trial the deltamethrin/chlorpyrifos-methyl combination has compared favourably at relatively low residue levels with standard products.

INTRODUCTION

In 1986 we were set the task of developing a new, non-irritant, cost-effective liquid grain protectant which would be effective against the broad spectrum of species and strains in the Australian grain handling industry.

In the absence of a broad spectrum active, in many parts of Australia there is a need to combine pyrethroid and organophosphate treatment in order to achieve control of Rhyzopertha dominica and other grain beetles, respectively.

Deltamethrin (DLTM) had been identified as a highly active pyrethroid, with a Codex ADI and relevant MRLs. At relatively high rates deltamethrin is active against a broad range of species but is very effective at low rates of application against R. dominica.

Chlorpyrifos-methyl (CPME) has entered the Australian grain protection market relatively recently, following the development of Fenitrothion resistance by Oryzaephilus surinamensis in some areas. Our tests had demonstrated that chlorpyrifos-methyl was effective against these resistant strains.

MATERIALS AND METHODS

Preliminary bioassays

Preliminary study utilized deltamethrin synergised with piperonyl butoxide. Previous evidence indicated that deltamethrin:piperonyl butoxide (DLTM:Pbo) in a 1:10 ratio was optimum (Duguet: personal communication). Synergised deltamethrin was mixed in 1:1 ratio with chlorpyrifos-methyl (i.e. DLTM:Pbo:CPME in 1:10:1 ratio) and tested in the laboratory against susceptible laboratory strains of Sitophilus oryzae, Tribolium castaneum and R. dominica. Comparison was made between the combination, synergised deltamethrin alone and chlorpyrifos-methyl alone. Batches of 50 g grain were spread out in foil-trays and each treated evenly by pipette with 5 ml of the appropriate solution in acetone. A series of doses were applied in each test; 3 replicates were made per dose. After allowing the solvent to evaporate, the treated grain was transferred to paper cups and 50 adult insects 1-2 weeks old of a given strain applied to each batch. The cups were covered with cotton cloth and held at 25°C, 50% relative humidity (RH) for 14 days. The insects were then sieved from the grain and mortality counted.

The data generated in these tests was input to a computer model developed by Le Patourel and Tayeb (1988) to determine the mixture composition required to protect grain (against the three species) for the minimum cost. This identified the most cost effective ratio at 1:10. On the basis of previous field data with these two actives a 1:20 ratio was also selected as an effective ratio.

Ratios of 1:10 and 1:20 DLTM:CPME with and without Pbo were then screened to establish whether Pbo was essential to the efficacy of the formulation. The presence of Pbo in the formulation under development caused stability problems and in combination with DLTM may enhance the irritancy of DLTM to spray operators.

The data were analysed by fitting probit curves to each species/strain combination and estimating the log LD50 and LD95 in each case.

Relative potencies derived from these data for the 1:20 ratio, which was selected for development are presented in figure 1. The addition of Pbo could not be justified solely on the basis of efficacy and was considered to be disadvantageous in other respects.

Formulation development

The traditional formulation types of oil solutions or emulsifiable concentrates employing DLTM as the active ingredient have met resistance from end-users due to the irritancy associated with the presentations. Conversely CPME has invariably been associated with oil solution or emulsifiable concentrate (EC) formulations due to stability problems encountered with other formulation types. Technical CPME is not commercially available and high concentration oil solution (e.g. Reldan* 50) is sold as a manufacturing concentrate.

The development of a CPME and DLTM combination formulation with reduced DLTM irritancy whilst maintaining CPME stability therefore posed a challenge. The approach adopted was to screen a diverse range of formulation types other than oil solution and EC presentations and to establish stability trends in the various presentations.

An established low irritancy formulation type for DLTM is the suspension concentrate for which several variations are commercially available. However, such a formulation type is not feasible for CPME, even assuming technical material was available on commercial scales, due to its low melting point (approximately 46°C). A mixed active suspension concentrate was therefore not a possibility.

Several other options were available for presentation of the CPME phase including microencapsulation; absorption onto a carrier for use in a dust, wettable powder or suspended carrier/active combination; or the production of a concentrated emulsion.

Encapsulation of CPME using interfacial polymerisation techniques failed to produce a stable product.

Stability data for CPME alone or in combination with DLTM was obtained on a range of carrier materials. For all cost effective carriers screened stability data was not acceptable and only by moving to non cost effective carriers could a stable formulation be developed. A liquid presentation was preferred, in any case.

Concentrated emulsion formulations were investigated employing a variety of surfactant systems. The stability profiles obtained from these emulsion systems indicated that the surfactants combination employed in producing the emulsion affected the resulting chemical stability in addition to the physical stability of the product.

The results of the screening exercise established only one promising line of enquiry, that being the development of a combination formulation based around a concentrated emulsion of CPME and containing the DLTM in suspension.

Stability data generated on the developed formulation (figures 2 and 3) showed acceptable stability at temperatures of 25°C and 38°C for up to 2 years and for 6-9 months at 50°C. Compatibility with a range of packaging materials is under investigation.

First Field Trials

The formulation was first trialled by spray admixture to grain in the laboratory in UK. Bioassay results on the grain stored in the laboratory for up to 9 months provided full justification for progressing to field trialling.

With the basic formulation (TF 2306) there was a tendency for phase separation to occur on prolonged standing. A variant (TF 2409) was produced in an attempt to overcome this problem. Both were evaluated at 0.2/4.0 and 0.25/5.0 ppm DLTM/CPME under field conditions during 1988 at the Wellcome Research Station, 'Bangalla' NSW. Comparison was made with standard treatments of 1/8/10 ppm Bioresmethrin/piperonyl butoxide/ Chlorpyrifos methyl and 1/8/12 ppm Bioresmethrin/piperonyl butoxide/ Fenitrothion. Five tonne quantities of grain were treated and stored in mini-silos. Samples were taken at intervals for analysis and bioassay in Australia.

At each sampling fifteen samples were taken from each silo bin, 5 from the grain surface, 5 spear samples taken one metre below the surface and 5 spear samples from two metres below the surface. All samples were mixed and weighed into glass jars; 150 g for S. oryzae and R. dominica bioassays and 300 g for T. castaneum and O. surinamensis. 110 vigorous 2-3 week old adult insects were added to each replicate and lids with gauze inserts secured. Assays were stored at 25°C, 55% RH. After 3 weeks the adult insects were removed by sieving and mortality counted. The grain was further sieved 7, 9 and 11 weeks later to remove and count F_1 adult progeny.

Bioassay data is presented in tables I and II.

Australian Wheat Board Trial 1988-9

The following information is presented with kind permission of the Australian Wheat Board (AWB).

Formulation TF2409 was trialled at two sites, Cecil Plains, Queensland and Wail, Victoria. It was applied to 545 tonnes and 400 tonnes grain, respectively. A tank mix combination of synergised bioresmethrin EC (BRM/Pbo 5/40% w/v) with chlorpyrifos methyl EC (CPME 50% w/v) was also trialled. Appropriately diluted formulation was sprayed on to the grain stream at the rate of one litre per tonne during turning of the grain from one bin to another using a conventional spray unit. The spray nozzle was positioned over a moving grain stream in the under cell area. Target treatment rates were TF2409 at 0.24/4.9 ppm DLTM/CPME and BRM/Pbo/CPME at 1/8/10 ppm.

Treated grain was sampled at each site at intervals from 12 points by means of a vacuum probe drawing samples from a depth of 2 metres below the grain surface. The samples were analysed for chemical residues by different procedures in cooperating laboratories. Results are presented in figure 4 for TF2409. Bioassays were also conducted on these samples at 'Bangalla' field station and other laboratories. A summary of the length of protection afforded by the two treatments, derived from the bioassay data is given in table III.

DISCUSSION

The formulation has been subjected to a progressive, staged development from initial laboratory assay, formulation development, laboratory-based formulation assays, through small- scale field trial and on to large-scale storage trials. The Australian Wheat Board trial has confirmed the efficacy of the formulation under Australian storage conditions against major Australian insect strains. Good control of S. oryzae strains was maintained for 6-9 months (the trial duration) at both sites. With T. castaneum there was variable and some poor activity in some assays against adults of the selected resistant QTC279 strain; kill of adult QTC285 resistant strain was also not always complete. However, with both strains F1 progeny production was negligible. This was also the case with O. surinamensis. The formulation was very effective in bioassays against R. dominica.

The formulation developed is a stable water-based concentrate. It is a low-odour, low-irritant formulation which is effective at relatively low rates of application of actives, thus going some way to meeting minimum residue requirements being demanded now of materials added to grain.

REFERENCE

Le Patourel and Tayeb (1988)
Journal of Stored Products Research 24, 207-214.

ACKNOWLEDGEMENTS

Deltamethrin is a product of Roussel-Uclaf.
Chlorpyrifos methyl is a product of DowElanco.

RESULTS

Table I Bangalla 1988 Bioassays with TF2306 and Bioresmethrin/Pbo/CPME

Species	Storage period (months)	TF2306 A%M	TF2306 %S	BRM/Pbo/CPME A%M	BRM/Pbo/CPME %S	Control A%M
S. oryzae BSO	0	100	99.7	100	100	0
	1.5	100	99.9	100	99.9	1
	3	100	99.98	100	99.98	0
	4,5	100	99.98	100	100	1
	6	100	100	100	99.98	0
	9	100	99.7	100	100	3
	12	100	99.9			0
R. dominica BRD	0	100	98.0	100	100	2
	1.5	100	99.1	100	100	3
	3	100	99.3	100	99.9	3
	4.5	100	99.7	100	100	5
	6	100	99.9	100	100	2
	9	100	99.9	100	100	6
	12	100	100			4
T. castaneum BTC	0	100	-	100	-	2
	1.5	100	99.1	100	100	0
	3	100	99.0	100	97.0	4
	4.5	100	100	100	100	6
	6	100	100	100	99.3	3
	9	100	99.9	28.0	100	5
	12	100	99.7			2
T. castaneum QTC 279	0	100	100	100	98.5	0
	1.5	100	100	100	100	4
	3	100	-	100	-	7
	4.5	99.0	100	100	100	13
	6	94.0	100	100	100	6
	9	97.0	100	86.0	100	0
	12	67.0	100			3
O. surinamensis BOS	0	100	-	100	-	2
	1.5	100	-	100	-	5
	3	100	100	100	100	2
	4.5	100	100	100	100	10
	6	100	100	100	100	3
	9	99.0	100	96.0	100	2
	12	93.0	100			2

Key A%M Adult mortality %

%S % suppression F_1 adult progeny compared to numbers emerging from controls. All progeny included in calculation, whether alive or dead.

Insufficient control progeny for valid calculation

Table II Bangalla 1988 Bioassays with TF2409 and Bioresmethrin/Pbo/Fenitrothion

Species	Storage period (months)	TF2409 A%M	TF2409 %S	BRM/Pbo/Fen. A%M	BRM/Pbo/Fen. %S	Control A%M
S. oryzae	0	100	100	100	100	0
	1.5	100	99.9	100	99.9	1
	3	100	100	100	100	0
	4.5	100	100	100	100	1
	6	100	100	100	100	0
	9	100	100	100	99.96	3
	12	100	99.96			0
R. dominica	0	100	98.5	100	99.8	2
	1.5	100	99.3	100	99.8	3
	3	100	99.5	100	100	3
	4.5	100	99.5	100	99.9	5
	6	100	100	100	100	2
	9	100	100	100	100	6
	12	100	100			4
T. castaneum	0	100	-	100	-	2
	1.5	100	99.1	100	100	0
	3	100	99.0	100	99.5	4
	4.5	100	100	100	100	6
	6	100	100	100	99.7	3
	9	100	99.9	100	100	5
	12	100	99.7			2
T. castaneum QTC 279	0	100	100	100	100	0
	1.5	100	98.1	100	100	4
	3	100	-	100	-	7
	4.5	100	100	100	100	13
	6	98.0	100	100	99.1	6
	9	98.0	99.8	66	99.8	0
	12	94.0	100			3
O. surinamensis	0	100	-	100	-	2
	1.5	100	-	100	-	5
	3	100	100	100	100	2
	4.5	100	100	100	100	10
	6	100	99.6	99	100	3
	9	100	100	49	100	2
	12	100	100			2

Table III AWB Trial: Summary of Control Duration in Months

Strain	Duration (months) CP	W	Interval of Protection (months) TF 2409 Cecil Plains	TF 2409 Wail	BRM/Pbo/CPME Cecil Plains	BRM/Pbo/CPME Wail
Sitophilus oryzae						
BSO						
adults	9	9	9m	9m	9m	9m
progeny			9m	9m	9m	9m
QSO56						
adults	9	9	>95% 6m	6m	9m	9m
progeny			>98% 6m	>97% 6m	9m	9m
CSO231						
adults	6	9	>94% 6m	6m	6m	9m
progeny			>97% 6m	>97% 6m	6m	9m
Tribolium castaneum						
BTC						
adults	9	9	9m	9m	>98% 9m	4.5m
progeny			9m	9m	9m	9m
QTC279						
adults	9	9	>95% 6m	6m	-	-
progeny			6m	6m	-	-
QTC285						
adults	6	9	77-100% 6m	4.5m	9m	>97% 6m
progeny			6m	9m	9m	9m
Rhyzopertha dominica						
BRD						
adults	9	9	>98% 9m	9m	9m	9m
progeny			9m	9m	9m	9m
Oryzaephilus surinamensis						
BOS						
adults	9	9	>94% 9m	95% 9m	4.5m	4.5m
progeny			9m	9m	9m	9m
QOS42						
adults	9	9	9m	3m	-	-
progeny			9m	6m	-	-

FIGURE 1

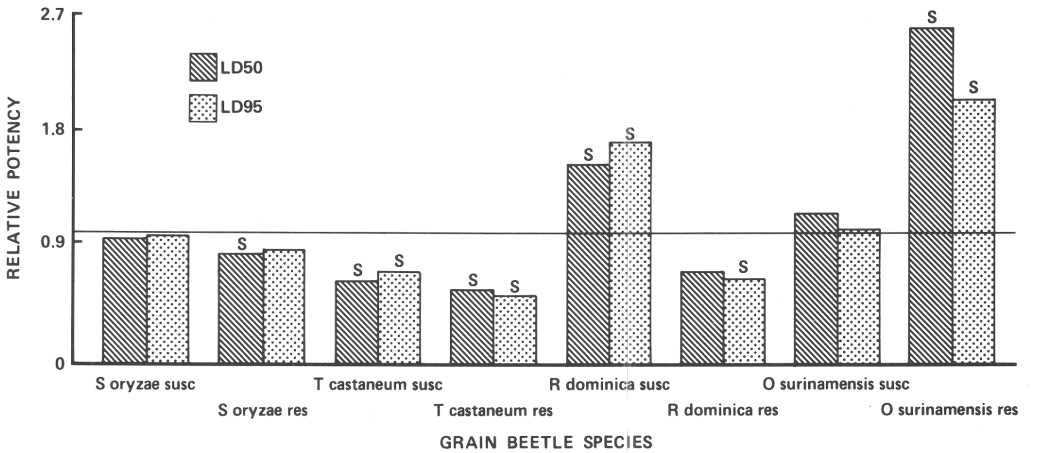


FIGURE 2

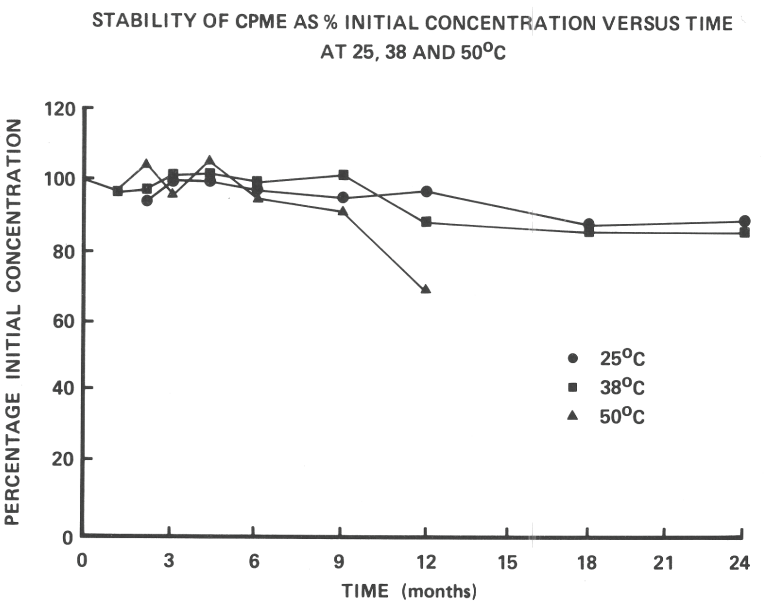


FIGURE 3

STABILITY OF DLTM AS % INITIAL CONCENTRATION VERSUS TIME AT 25, 38 AND 50°C

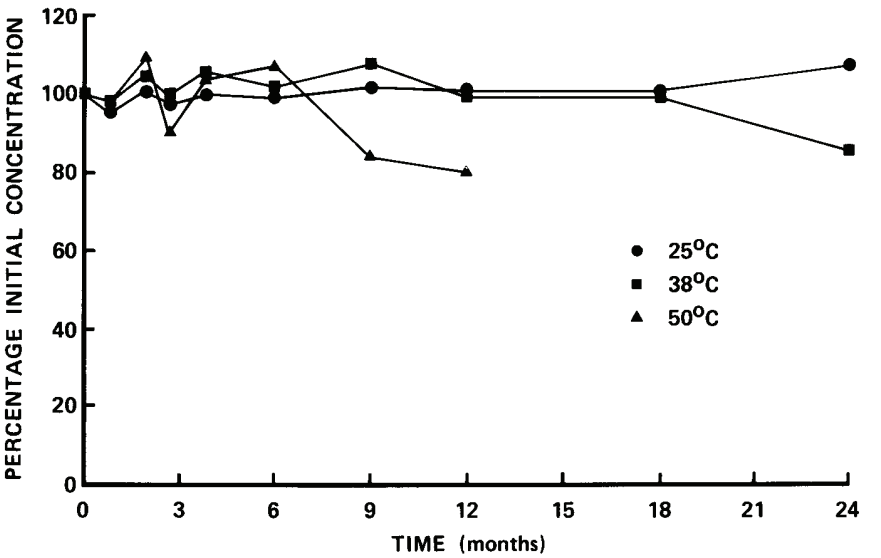
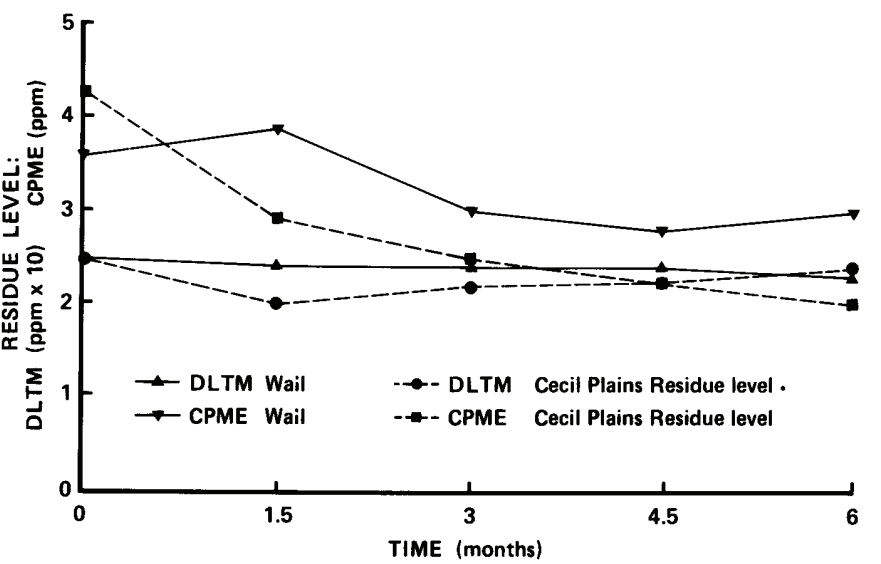


FIGURE 4

RESIDUE LEVELS OF DLTM AND CPME FOR TF2409 FROM CECIL PLAINS AND WAIL TRIALS



UNE NOUVELLE FORMULATION LIQUIDE D'INSECTICIDE DE CONTACT POUR GRAIN A BASE DE DELTAMETHRINE ET DE CHLORPYRIPHOS-METHYL

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RESUME

On y décrit le développement d'une nouvelle formulation d'insecticide de contact pour grain. Les premiers essais de laboratoire ont identifié les matières actives ainsi que leur combinaison optimale pour les insectes cibles choisis. Ils ont abouti à deux formulations stables présentant une amélioration nette par rapport aux formules classiques. Toutes deux ont été essayées sur le terrain à la station de Wellcome Research, "Bangalla", Australie. Le traitement a été fait à 0,2/4 ppm et à 0,25/5 ppm (deltaméthrine/chlorpyriphos-méthyl) appliqués sur des lots de cinq tonnes de grains. Les études d'efficacité ont été menées sur une série de souches de coléoptères à "Bangalla" et dans les laboratoires WEH, R.U., sur des échantillons de grains prélevés à intervalles pendant 12 mois de stockage. On n'a noté une diminution de l'efficacité sur les adultes que chez la souche QTC279 hautement résistante de *Tribolium castaneum* après 6 mois de stockage. Il n'y a pratiquement pas eu d'adultes en F1. D'autres essais sur le terrain ont été menés par l'Australian Wheat Board sur 2 sites dans les années 1988-1989 et sur 5 sites en 1989-1990. Dans le premier essai, la combinaison deltaméthrine/chlorpyriphos-méthyl a soutenu favorablement la comparaison avec les produits standards.