THE CONTROL OF STORED PRODUCTS INSECTS WITH PIRIMIPHOS-METHYL

J. McCALLUM DEIGHTON
Plant Protection Ltd
Jealott's Hill Research Station
Bracknell, Berks
ENGLAND

ABSTRACT: Pirimiphos-methyl, 2-diethylamino-6-methylpyrimidin-4-yl dimethyl phosphorothionate, a broad spectrum insecticide with a mammalian LD50 > 2000 mg/kg, is being developed for use against insects attacking stored produce. The lowest doses of pirimiphos-methyl giving complete kill of susceptible and malathion-resistant strains of insects are approximately the same as those for fenitrothion, but lower than those for malathion, bromophos, iodofenphos, tetrachlorvinphos, or dichlorvos. This relative order of effectiveness is unchanged when comparing the lower doses which allow some adults to lay eggs but kill the resultant progeny. Of all the insecticides tested, only γ-BHC was as effective against *Rhyzopertha dominica* as against the other insect species used.

Pirimiphos-methyl will protect grain from insect attack and will also eradicate infestations of the larvae of primary grain insects. It has good claims to be considered, in some respect, uniquely suitable as a stored product insecticide.

2-diethylamino-6-methylpyrimidin-4-yl-dimethylphosphorathionate was first synthesized and evaluated in our laboratories in 1967. This chemical has a wide spectrum of insecticidal activity combined with a low mammalian toxicity (LD_{50} > 2000 mg/kg for rats). It was originally coded PP511, and later given the common name pirimiphos-methyl. The wide spectrum of activity, combined with an unusually low toxicity to mammals (Table 1) made use in stored products a possibility.

TABLE 1. Acute oral LD_{50} levels for pirimiphos-methyl.

Species	LD_{50} (mg/kg)	95% confidence limits (mg/kg)
Rat (female)	2050	1840-2260
Mouse (male)	1180	1030-1360
Guinea pig (female)	1000-2000	-
Rabbit (male)	1150-2300	-
Cat (female)	575-1150	-
Dog (male)	1500	-
Greenfinch	200-400	-
Quail	140	-
Hen	30-60	-

This paper summarises the activity of pirimiphos-methyl in this field. The techniques used and more detailed results will be published elsewhere.

INTRINSIC ACTIVITY: The LC_{50}, or LD_{50}, is the figure normally quoted when comparing the effectiveness of insecticides in the laboratory. This has limited practical value where insect pests of stored grain are concerned. A more meaningful evaluation, and one comparable to the situation in the field, can be made by comparing the lowest dose required to kill all insects of a certain species within a specified time when they are exposed continuously to treated grain. This we have called the minimum effective dose (MED).

The MED's for pirimiphos-methyl and several other insecticides are shown in Table II. In these tests the insect mortality was assessed after the insects had been kept in treated wheat at 25°C and 70% relative humidity for 7 days, except for *Rhyzopertha dominica* which was assessed after thirteen days. Treated wheat was examined for F_1 progeny of primary grain insects after ten weeks (Table III).

TABLE II. MED's in ppm for technical grade insecticides against susceptible strains of stored produce insects.

	pirimiphos-methyl	malathion	bromophos	iodofenphos	tetrachlorvinphos	fenitrothion	dichlorvos	γ BHC
S. granarius	0·25-0·5	1-3	2-3	< 1	> 20	0·25-0·5	2-3	0·5-1
S. oryzae	0·5-0·75	2-3	3-4	2-3	5-7·5	1-2	3-4	1-5
S. zeamais	0·25-0·5	1-2	3-4	1-2	5-7·5	0·5-0·75	1-2	1-5
O. surinamensis	0·1-0·25	< 0·5	2-3	2-3	7·5-10	0·25-0·5	1-2	> 15
C. ferrugineus	0·25-0·5	2-3	0·1-0·25	0·25-0·5	5-7·5	0·25-0·5	> 3	1-5
R. dominica	<7·5	> 20	> 20	> 20	12·5-15	12·5-15	5-7·5	1-5
T. castaneum	0·5-0·75	4-5	4-5	2-3	15-17·5	1-2	3-4	> 15

TABLE III. Minimum doses of technical grade material in ppm preventing the development of a living F_1 generation.

	pirimiphos-methyl	malathion	bromophos	iodofenphos	tetrachlorvinphos	fenitrothion	dichlorvos
S. granarius	0·25-0·5[a]	4-5	2-3	1-2	17·5-20	0·25-0·5	3-4
S. oryzae	0·75-1	4-5	3-4	2-3	5-7·5	1-2	> 4
S. zeamais	0·75-1	2-3	3-4	1-2	7·5-10	0·75-1	3-4
R. dominica	< 10	15-17·5	> 20	-	< 10	< 12·5	5-7·5

[a] Fresh deposits on wheat, assessments 10 weeks after treatment.

EFFECT ON RESISTANT STRAINS: Several authors have examined the types of organo-phosphorus resistance found in *Tribolium castaneum* [1],[2],[3] and [4], and it has been generally accepted, until recently, that two types of organo-phosphorus resistance occurred, namely, malathion specific and malathion-non-specific. These types of resistance are exemplified by the Kano and CTC 12 strains of *Tribolium castaneum* respectively. In the first strain resistance to malathion can be suppressed with tri phenyl phosphate, whereas a similar suppression of resistance does not occur with the second strain. Using the MED we have examined the resistance of these two types of resistant strains of *T. castaneum* to pirimiphos-methyl, malathion and other insecticides (Table IV). The level of cross-resistance by the CTC 12 strain to pirimiphos-methyl is of the order of 2-4 times and there is no cross-tolerance by the malathion-specific resistant strain. The figures for bromophos and iodofenphos when tested on the CTC 12 strain are different from those of Champ & Campbell-Brown [3] who found, when using a different testing techniques, that the CTC 12 strain of *T. castaneum* had a negative cross-tolerance to these two insecticides. Our results show

TABLE IV. MED's in ppm for technical grade insecticides against susceptible and organo-phosphorus-resistant strain of *T. castaneum*.

	pirimiphos-methyl	malathion	bromophos	iodofenphos	tetrachlorvinphos	fenitrothion	dichlorvos
Susceptible strain	0·5-0·75	4-5	4-5	2-3	15-17·5	1-2	3-4
Kano strain	0·5-0·75	> 20	4-5	7·5-10	15-17·5	1-2	4-5
CTC 12 strain	1-2	> 20	17·5-20	> 20	> 20	> 7·5	7·5-10

that the CTC 12 strain of *T. castaneum* has considerable cross-tolerance to the same two insecticides. Our results also indicate that the Kano strain of *T. castaneum* exhibits cross-tolerance to iodofenphos. The resistance pattern of both of these strains has been checked using the method described by Champ and Campbell-Brown [3].

Dr. Seth of Plant Protection Ltd has shown that pirimiphos-methyl is very effective against malathion-resistant *T. castaneum* infesting rice in Malaysia. Strain of *T. castaneum* from Malawi, resistant to malathion and cross-resistant to bromophos, are also known to be susceptible to pirimiphos-methy [5].

SPECTRUM OF ACTIVITY: Many stored produce Lepidoptera and mites have a low level of susceptibility to malathion. In laboratory tests, using *Ephestia cautella*, the following comparison was obtained when adult moths were placed on treated hessian, cut from sacks, and kept in open and closed containers at 25°C and 70% RH (Table V).

Soderstrom and Armstrong [6] have shown that pirimiphos-methyl is very active against *Plodia interpunctella* and a comparison of their results and those obtained by Spitler and Hartsell [7] using malathion indicates that pirimiphos-methyl is the more active of the two against this moth. When tested against *Ephestia cautella* infesting bags of maize, pirimiphos-methyl was superior to malathion [8].

Complete kill of the grain mite, *Acarus siro*, was obtained

TABLE V. Percentage mortality of adult *E. cautella* after exposure for 24 hours on deposits of several ages.

Chemical and Rate	Deposits aged			
	1 month		3 months	
	Open dish	Closed dish	Open dish	Closed dish
pirimiphos-methyl				
0·5 g ai/m^2	100	100	-	100
0·1 g ai/m^2	100	100	-	100
malathion				
0·5 g ai/m^2	100	100	-	100
0·1 g ai/m^2	100	100	-	36

24 hours after the mites were sprayed with 0·25% pirimiphos-methyl, whereas 1·0% fenitrothion only gave complete kill after 48 hours. Sprays of 0·5% fenitrothion resulted in 87% kill after 48 hours, and many mites were still alive 48 hours after treatment with a spray of 2·5% malathion. A dosage level of 4 ppm pirimiphos-methyl from a 2% dust formulation resulted in complete control of a complex of mite species infesting a 200 ton parcel of grain. The mite complex included *Acarus siro*, *Tyrophagus* spps, *Glycyphagus* spps and *Cheyletus* spps. Ten weeks after treatment there were only three *Cheyletus* spps in eighteen samples of 200 gm each from the treated wheat, whereas in six samples of 200 gm from an untreated portion there were 1808 *Acarus siro*, 36 *Tyrophagus* spps, 28 *Glycyphagus* spps, and one *Cheyletus* spps. Pirimiphos-methyl was shown to have considerable activity against *Acarus siro*, *Tyrophagus putrescentiae*, and *Glycyphagus destructor* by Wilkin and Hope [9] and against the first two species by Zdárková and Horak [10].

PROTECTION OF GRAIN FROM INSECT ATTACK: Pirimiphos-methyl can be formulated either as a dust or an emulsion for admixture with grain. Initial tests, comparable to those reported by Kane and Green [11] for other insecticides, showed that 4 ppm active ingredient, from either of the two types of formulation, on wheat and barley was more effective than 10 ppm malathion in protecting the grain for up to 6 months when the grain was subjected to a severe infestation pressure by *Oryzaephilus surinamensis*, *Sitophilus granarius* and *T. castaneum*.

Following these tests, the results from a large number of field trials in England have shown that 4 ppm pirimiphos-methyl is very effective in preventing insect infestation of wheat and barley. This is exemplified in a field trial where 25 ton parcels of wheat were treated with a 25% emulsion concentrate or a 2% dust formulation of pirimiphos-methyl at 4 ppm active ingredient. Samples have been taken for bioassay and residue analysis for up to

5 months and have given the following results (Table VI). This test is still continuing. When samples were taken for residue analysis, part of the sample was milled, baked into bread, and examined for any taint. In none of the samples, nor in the samples from a further five trials, was any taint detected, although residues were present.

TABLE VI. Percentage mortality of insects after 4 days, and residues in ppm from samples of wheat treated with pirimiphos-methyl.[a]

Treatment	Initial[b] residue	1 month residue	2 months residue	Time after treatment: 3 months residue	3 months % bioassay mortality[c] Tc[d]	Os	Sg	Cf	5 months % bioassay mortality Tc	Os	Sg	Cf	6 months % bioassay mortality Tc	Os	Sg	Cf
25% EC	3·29	3·19	2·74	2·63	100	100	100	100	100	100	100	100	100	99	100	100
2% dust	2·22	2·09	1·56	1·43	96	100	85	99	100	100	100	100	100	99	100	100

a. Treated with 4 ppm active ingredient.

b. Residue analysis on sub-sample from twenty-seven probe samples.

c. Insects exposed for 4 days to 100 gm sub-sample from twenty-seven probe samples.

d. *T. castaneum*, *O. surinamensis*, *S. granarius*, *C. ferrugineus*.

Trials have been, and are being, conducted in many countries, including the major grain producing countries, and these have shown that pirimiphos-methyl is very effective in protecting all cereals, and also other stored produce, from insect attack.

ERADICATION OF INSECTS FROM GRAIN: Pirimiphos-methyl can be used not only to protect grain from infestation, but also to eradicate insects from grain. Pirimiphos-methyl and many other insecticides will control adult insects in grain, and pirimiphos-methyl will also eradicate a population of primary grain insects from wheat, etc.

The eradicant action against adult insects in grain can best be seen when a specific number of insects is added to grain which is then treated. In such tests which we have done, a specific number of insects was added to wheat in sacks, the insects allowed to find their optimum situations within the sacks, and the sacks then sprayed with pirimiphos-methyl, malathion, or fenitrothion. One week later the wheat was sieved and insect mortality calculated (Table VII).

To be able to eradicate an established infestation of primary grain pests, an insecticide must kill not only the adults, but also the immature insects. To demonstrate this activity, wheat of 14% moisture content was infested with *Sitophilus granarius* adults and these were allowed to lay eggs in the grains for one week. The adults were removed and, at intervals after the oviposition, portions of the grain were either left untreated or were treated with several concentrations of pirimiphos-methyl, malathion or dichlorvos. The numbers of adults emerging from the treated samples were counted when the F_1 generation, and later the F_2

TABLE VII. Percentage mortality of insects seven days after spraying exterior of sacks containing wheat and infested with known number of insects.

Chemical and Rate	Percentage mortality		
	T. castaneum	*S. granarius*	*O. surinamensis*
<u>pirimiphos-methyl</u>			
0·25 g ai/m^2	93	93	99
0·5 g ai/m^2	100	100	100
1·0 g ai/m^2	100	100	100
<u>malathion</u>			
1·0 g ai/m^2	95	67	97
1·5 g ai/m^2	96	69	97
2·0 g ai/m^2	97	74	100
<u>fenitrothion</u>			
0·25 g ai/m^2	98	95	100
0·5 g ai/m^2	95	90	96
1·0 g ai/m^2	97	83	100

generation, were emerging from the untreated grain.

When treatments were applied nine days after oviposition both pirimiphos-methyl and dichlorvos had a considerable effect and whilst the higher rates of dichlorvos killed almost all the larvae, those which did survive the treatment developed into normal viable adults which, in turn, gave rise to an F_2 generation. The lowest rate of dichlorvos had little effect on the number of adults emerging and eventually a large F_2 population developed (Table VIII). Whilst the lowest rate of pirimiphos-methyl did not reduce the number of larvae maturing to adults in the F_1 generation to the same extent as the higher rates of dichlorvos, nevertheless, those insects which emerged died rapidly and did not give an F_2 generation. Higher rates of pirimiphos-methyl both reduced the number of larvae maturing to adults, and also killed those adults emerging so that, again, an F_2 population explosion was prevented. The malathion treatments gave results mid-way between those for pirimiphos-methyl and dichlorvos.

All the treatments applied 25 days after egg laying reduced the numbers of adults produced (Table IX). Whether or not this reduction was due to the death of developing larvae within the grain, or to the death of the adults prior to emergence, was not determined. Pirimiphos-methyl was superior to either malathion or dichlorvos in that not only were the numbers of adults produced lower than for these two other chemicals, but these adults died before an F_2 population could be produced. Whilst the malathion

TABLE VIII. Production and mortality of F_1 and F_2 generations of *S. granarius* from infested wheat[a] treated with different chemicals.

Chemical and Rate	Total number of adults after 9 wks[b]	12 wks	18 wks	Number of adults alive after 9 wks	12 wks	18 wks
pirimiphos-methyl						
2% dust 3 ppm	33	33	33	0	0	0
6 ppm	12	12	12	0	0	0
12 ppm	1	4	5	0	0	0
25% EC 3 ppm	28	35	35	0	0	0
6 ppm	15	16	16	0	0	0
12 ppm	7	7	7	0	0	0
malathion						
25% EC 5 ppm	36	42	49	29	26	32
10 ppm	24	52	54	0	0	0
20 ppm	35	49	49	0	0	0
dichlorvos						
50% EC 3 ppm	23	38	562	24	38	561
6 ppm	2	2	48	2	2	48
12 ppm	2	3	3	2	2	3
Untreated	56	71	702	56	68	693

a. Wheat of 14% moisture content treated 9 days after egg laying.
b. Time after egg laying.

and dichlorvos treatments reduced the numbers of adult *S. granarius* only the highest-rate of malathion prevented a large F_2 population from developing.

Similar figures were obtained when the treatments were applied 33, 41 and 46 days after egg laying. This eradicant effect is probably due to a combination of the activity of pirimiphos-methyl in the vapour phase on the pre-adult stages, and on the adults prior to emergence, and to the persistence of pirimiphos-methyl in the pericarp which either kills the adults as they are trying to emerge or kills them soon after emergence. Unpublished work from the USA has shown that the vapour phase/fumigant activity of pirimiphos-methyl is at least as good as that of carbon tetrachloride, and it could be inferred in our tests, therefore, that *S. granarius* larvae were killed inside the grains.

TABLE IX. Production and mortality of F_1 and F_2 generations of *S. granarius* from infested wheat[a] treated with different chemicals.

Chemical and Rate	Total number of adults after 7 wks[b]	12 wks	18 wks	Number of adults alive after 7 wks	12 wks	18 wks
pirimiphos-methyl						
2% dust 3 ppm	101	116	116	4	0	0
6 ppm	75	86	90	0	0	0
12 ppm	34	43	44	0	0	0
25% EC 3 ppm	128	133	134	0	0	0
6 ppm	93	98	98	0	0	0
12 ppm	41	42	42	0	0	0
malathion						
25% EC 5 ppm	98	123	585	60	20	363
10 ppm	87	135	411	45	34	302
20 ppm	99	135	137	17	0	1
dichlorvos						
50% EC 3 ppm	113	319	770	113	315	708
6 ppm	103	244	901	102	242	861
12 ppm	75	130	882	75	126	855
Untreated	147	-	933	147	-	933

a. Wheat of 14% moisture content treated 25 days after egg laying.
b. Time after egg laying.

Where similar tests were done with 18% moisture content wheat the relative effectiveness of pirimiphos-methyl was even greater, since the weevils unaffected by the treatments increased much more rapidly than in the drier wheat used previously, and also since the pirimiphos-methyl was more stable on the higher moisture content grain than either malathion or dichlorvos (Table X).

Similar results were obtained in the laboratory by Coulon et. al. [12] when pirimiphos-methyl was compared with malathion, dichlorvos, iodofenphos and bromophos against immature *S. granarius*, of varying age, in wheat and Champ et. al. [13] obtained comparable results for malathion and dichlorvos against *Sitophilus oryzae*.

CONCLUSIONS: Pirimiphos-methyl has a very promising potential for use in the control of insects in stored produce.

TABLE X. Production and mortality of F_1 and F_2 generations of *S. granarius* from infested wheat[a] treated with different chemicals.

Chemical and Rate	Total number of adults after 8 wks[b]	10 wks	14 wks	Number of adults alive after 8 wks	10 wks	14 wks
pirimiphos-methyl						
2% dust 3 ppm	208	208	212	4	2	0
6 ppm	132	132	132	0	0	0
12 ppm	24	24	24	0	0	0
25% EC 3 ppm	196	196	236	22	21	61
6 ppm	164	192	192	0	0	0
12 ppm	34	36	36	0	0	0
malathion						
25% EC 5 ppm	213	213	697	202	199	681
10 ppm	230	230	625	172	172	567
20 ppm	205	211	463	145	135	402
dichlorvos						
50% EC 3 ppm	-	-	754	-	-	754
6 ppm	-	-	757	-	-	757
12 ppm	-	-	828	-	-	828
Untreated	357	-	1298	354	-	1282

a. Wheat of 18% moisture content treated 33 days after egg laying.
b. Time after egg laying.

The data presented show that pirimiphos-methyl is intrinsically very active against a wide range of storage insects, and is more active than either malathion, or other potential replacements for malathion except for fenitrothion. It is effective against malathion-resistant strains of *T. castaneum*.

Pirimiphos-methyl has the unique property of eradicating established populations of primary grain pests and of protecting grain from infestation. It would, therefore, seem that pirimiphos-methyl can not only be considered as a direct replacement for malathion, but might also be used to replace fumigation followed by admixture with malathion.

ACKNOWLEDGEMENTS: Thanks are due to the many colleagues who have contributed to the work herein described and to Dr. J. T. Braunholtz, Director of Research, ICI Plant Protection Ltd for permission to publish this paper.

REFERENCES:

[1] Dyte, C. E., and Rowlands, D. G., (1968) J. stored Prod. Res. 4: 157-173.
[2] Spiers, R. D., and Zettler, J.L., (1969) J. stored Prod. Res. 4: 279-283.
[3] Champ, B. R., and Campbell-Brown, M. J., (1970) J. stored Prod. Res. 6: 111-131.
[4] Dyte, C. E., (1972) Nature. London 238: 48-9.
[5] Pieterse, A. H., Schulten, G. G. M., and Kuyken, W., (1972) J. stored Prod. Res. 8: 183-191.
[6] Soderstrom, E. L., and Armstrong, J. W. (1974) J. econ. Ent. 66 (6): 1305-6.
[7] Spitler, G. H., and Hartsell, P. L., (1970) J. econ. Ent. 63 (5): 1502-5.
[8] Schulten, G. G. M., (1973) Intern. Pest Cont. 15 (2): 18-21.
[9] Wilkin, D. R., and Hope, J. A., (1973) J. stored Prod. Res. 8: 323-327.
[10] Ždárková, E., and Horák, E., (1973) J. econ. Ent. 66 (5): 1237-8.
[11] Kane, J. and Green, A. A., (1968) J. stored Prod. Res. 4: 59-68.
[12] Coulon, J., Barres, P., and Delorme, R., (1971) Phytiatrie-Phytopharmacie (Séance du 20 Octobre 1971).
[13] Champ, B. R., Steele, R. W., Genn, B. G., and Elms, K. D., (1969) J. stored Prod. Res. 5: 21-48.