

COMBINATIONS OF OILS AND SIMILAR COMPOUNDS WITH  
INSECTICIDES: EFFECTS ON TOXICITY AND ON LEAF RESIDUES

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ABSTRACT

The effects of oils on the toxicity of insecticides to the house fly, *Musca domestica* L, and on the residue distribution of insecticides on cotton leaves were determined. At high oil to insecticide ratios, oils significantly increased the toxicity of permethrin and methyl parathion. When parathion was applied with oil to cotton leaves, a greater proportion was recovered on the leaf surface than when the insecticide was applied alone. The use of oils had less effect on permethrin residues which largely remained on leaf surfaces with or without oil additives.

INTRODUCTION

Efficacy of insecticides can be modified by use of particular additives. Toxaphene, when used as an additive, increased the amount of insecticide residues on cotton plants. For many years, control of cotton insect pests, such as *Heliothis* spp. (Nemec et al. 1968), was improved when insecticides were combined with toxaphene. Ware et al. (1975, 1980) and Bigley et al. (1981) found that toxaphene increased the initial deposit and residue life of parathion sprays applied to cotton. Similarly, Brown et al. (1982) found that fenvalerate residues were increased in the presence of toxaphene, whereas permethrin residues were reduced; both pyrethroids were synergized by toxaphene against various lepidopteran pests.

Following a ban on use of toxaphene in the United States, agricultural researchers have looked to other substances as toxaphene substitutes. Oils may prove to be advantageous toxaphene substitutes since they enhance insecticide efficacy (Bigley et al. 1981). Improved efficacy is supposedly due to two effects. First, oils synergize insecticides (Ochou 1985) either by expediting insecticide uptake by insects (Wigglesworth 1942, Ebeling 1974) or by improving distribution of insecticide over the integument (Quraishi and Poonawalla 1969, de Licastro et al. 1983). Second, oil alters the residue life and distribution of insecticide on plants (Ware et al. 1980). Alteration of residues on plants should presumably affect the insecticidal activity of insecticides.

This study determined the effect of mineral oils on the speed of action of insecticides against house flies. Also, we determined the effect of mineral oils and similar additives on the compartmentalization of insecticides on and within cotton leaves.

## MATERIALS AND METHODS

Biological Specimens. Test insects were male adult house flies, *Musca domestica* L., of a strain, Rutgers Diazinon-R, resistant to organophosphate and organochlorine insecticides. Flies were reared and maintained at the insect toxicology laboratory, Texas A&M University, College Station. Adults were fed a 1:1 (v:v) sugar:powdered non-fat milk mixture. Cotton plants (*Gossypium hirsutum* L., Stoneville 213) used for leaf residue studies were grown during the summer of 1985 in the toxicology laboratory.

Chemicals. Insecticides used were permethrin, 93.5% pure, technical grade, and methyl parathion and ethyl parathion, both 96+% pure. Additionally, radioactive-labeled samples of permethrin (54.8 mCi/mmol) and ethyl parathion (2.2 mCi/mmol) were used.

Mineral oils were Orchex<sup>®</sup> 796, Isopar<sup>®</sup> V, ER-7110, and ER-7020. Other additives tested were the long-chain paraffins, hexadecane and tetracosane, and ethylene glycol.

All compounds were prepared as weight-per-volume acetone solutions. Tetracosane, due to its poor solubility in acetone, was prepared in dichloromethane.

Toxicity Tests. These tests were conducted to determine if combining mineral oils with insecticides affected the time required for knockdown of flies. To determine effects on toxicity, 20 ml glass vials were coated on their inner surfaces with only the insecticide or with a mixture of insecticide plus additive. Permethrin or methyl parathion were each used at 10 µg/vial dosages. In treatments using insecticide plus additive mixtures, corresponding amounts of oils necessary to give insecticide:oil ratios of 1:0.1, 1:1, 1:10, 1:30 and 1:100 were tested. Total volume of each solution was adjusted to 0.5 ml by addition of acetone. Vials were intermittently rolled on their sides until the acetone, which dispersed the insecticides and additives on the vials' inner surfaces, had evaporated. Additives used were Orchex 796, Isopar V, ER-7110 and ER-7020.

Following vial preparation, five house flies were placed in each vial and the vials were plugged with cotton. The time (in minutes) required for knockdown of three of the five flies per vial was recorded. That time was expressed as the  $KT_{50}$  (time necessary to produce 50% knockdown). If oils decreased the  $KT_{50}$ , then they increased the speed of insecticidal action.

Insecticide Compartmentalization in Cotton Leaves. To determine the effect of oils on the compartmentalization of insecticides on and within cotton leaves, radioactive-labeled insecticide alone and in combination with additives was applied to leaves of cotton plants. The proportion of total residues recovered from leaf surfaces was compared between treatments.

Permethrin solutions consisted of 5 µg mixtures of technical grade permethrin plus 5 µl radiolabeled permethrin (ca. 9100 dpm; ca. 37 ng) mixed in a 1% soap-water solution. Parathion solutions consisted of a 50 µg mixture of technical grade ethyl parathion plus radiolabeled ethyl parathion (ca. 8200 dpm, ca. .45 µg) mixed in a 1% soap-water solution. In insecticide-additive mixtures, 5 µg of additive were also added to give 1:1 permethrin:oil and 1:0.1 parathion:oil ratios. Additives used were Orchex 796, hexadecane, tetracosane, and ethylene glycol. For all treatments, 50 µl were applied in droplet form by microsyringe to a single mature cotton leaf. Droplets of solution were immediately spread over the entire upper leaf surface by using the tip of a glass rod. Each leaf was sampled 0, 1, 2, 24 and 48 h post-treatment by punching a 1 in. diameter circular disc from a leaf. Leaf

discs were subjected to extraction techniques (Nigg et al. 1981) to recover residues distributed in various leaf compartments (i.e. surface, wax and cellular). Dislodgeable surface residues were rinsed from a leaf disc with a 7:3 (v:v) methanol:water mixture; residues within the leaf wax were removed by a 20 sec chloroform dip; and internal residues were obtained by homogenizing the leaf disc in a 1:1 (v:v) dichloromethane-acetone mixture. Each extraction portion yielded an insecticide-extraction solvent volume of about 5 ml. Solvent was evaporated and 5 ml of scintillation fluid (Scinti Verse 1, Fisher Scientific) were added to each extraction portion. Individual portions from each sampling time were analyzed on a LKB scintillation counter. Percentages of insecticide from the leaf surface for each sampling time were derived as fractions of the total counts recovered from all compartments of a leaf disc sampled at a particular time.

## RESULTS AND DISCUSSION

Toxicity Tests. Mineral oils altered the performance of permethrin and methyl parathion against house flies. The results differed among additives and between insecticides. All mineral oils tested significantly ( $p < .01$ ) reduced  $KT_{50}$ 's of permethrin against house flies at the 1:100 ratio (Table 1). In addition, knockdown times were significantly reduced with Orchex 796 and ER-7110 at the 1:10 and 1:30 ratios and with Isopar V at the 1:30 ratio. Similarly, Ochou (1985) obtained considerable enhancement of permethrin toxicity in house flies when he combined the insecticide with Orchex 796 at a 1:10 ratio.

Table 1. Knockdown Times (min + SD) for Male House Flies Exposed to Vials Treated with Permethrin Plus Mineral Oils.

Mineral oil <sup>a/</sup>	Ratio of Permethrin:Oil				
	1:0.1	1:1	1:10	1:30	1:100
Orchex 796	28.0 <sub>±</sub> 2.3	24.4 <sub>±</sub> 1.2	14.7 <sub>±</sub> 2.2 <sup>a</sup>	12.9 <sub>±</sub> 3.0 <sup>a</sup>	10.4 <sub>±</sub> 2.2 <sup>a</sup>
Isopar V	28.1 <sub>±</sub> 12.2	29.6 <sub>±</sub> 11.6	24.0 <sub>±</sub> 11.9	9.8 <sub>±</sub> 2.5 <sup>a</sup>	10.2 <sub>±</sub> 4.7 <sup>a</sup>
ER-7110	24.0 <sub>±</sub> 4.0	25.7 <sub>±</sub> 8.4	12.0 <sub>±</sub> 5.8 <sup>a</sup>	11.1 <sub>±</sub> 3.1 <sup>a</sup>	8.5 <sub>±</sub> 4.1 <sup>a</sup>
ER-7020	23.3 <sub>±</sub> 4.2	24.6 <sub>±</sub> 3.8	23.0 <sub>±</sub> 8.3	14.7 <sub>±</sub> 7.2	10.8 <sub>±</sub> 7.2 <sup>a</sup>

<sup>a/</sup> n=3 for all treatments. Knockdown times followed by an "a" were significantly different ( $p < .01$ ) from time for permethrin alone (20.1 ± 7.7 min).

$KT_{50}$ 's for methyl parathion were significantly ( $p < .01$ ) reduced when the insecticide was combined with Isopar V, ER-7110 and ER-7020 (Table 2). Isopar V reduced knockdown times of methyl parathion at 1:10, 1:30 and 1:100 methyl parathion:oil ratios. ER-7110 and ER-7020 reduced knockdown times at the 1:100 ratio. Orchex 796 did not significantly ( $p > .01$ ) reduce knockdown times of methyl parathion against flies. In similar tests, de Licastro et al. (1983) found increased toxicity of ethyl parathion when combined with various mineral oils at high ratios in tests with Triatoma infestans. When the knock-

down times of methyl parathion: mineral oil combinations were tested at the  $p=0.05$  level of significance, an inconclusive pattern regarding the toxicity of methyl parathion:oil combinations resulted. Therefore, statistical tests utilizing the  $p=0.01$  level of significance more accurately discriminated methyl parathion synergism (or the lack of it) by mineral oils.

Insecticide Compartmentalization in Cotton Leaves. Data on the proportion of  $C^{14}$ -insecticide recovered from leaf surfaces are presented in Tables 3 and 4.

Table 2. Knockdown Times in Minutes for Male House Flies Exposed to Vials Treated with Methyl Parathion Plus Mineral Oils.

Mineral oil <sup>a/</sup>	Ratio of Methyl Parathion:Oil				
	1:0.1	1:1	1:10	1:30	1:100
Orchex 796	28.6+5.5	23.2+1.7	27.5+11.1	19.8+4.4 <sup>b</sup>	23.4+13.2
Isopar V	21.3+3.6 <sup>b</sup>	24.0+1.7	20.4+3.8 <sup>a</sup>	14.4+2.3 <sup>a</sup>	10.2+4.7 <sup>a</sup>
ER-7110	26.9+2.2	21.5+0.9 <sup>b</sup>	26.0+2.3	23.4+6.6	19.8+2.5 <sup>a</sup>
ER-7020	22.3+4.4 <sup>b</sup>	24.1+4.6	23.7+6.6	20.0+8.5	15.2+2.4 <sup>a</sup>

<sup>a/</sup>  $n=3$  for ER-7110,  $n=4$  for all other treatments. Knockdown times followed by an "a" ( $p<0.01$ ) or "b" ( $p<0.05$ ) were significantly different from time for methyl parathion alone (29.3+6.4 min).

Table 3. Percent (+ S.D.)<sup>a/</sup> of  $C^{14}$ -Parathion Recovered From the Surface of Cotton Leaves at Various Sampling Times Following Application.

Additive	Sampling time (hours)				
	0	1	2	24	48
none	32 + 15	26 + 9	48 + 19	21 + 10	38 + 42
Orchex 796	69 + 20	79 + 9	68 + 22	56 + 25	38 + 42
Hexadecane	76 + 16	84 + 15	77 + 20	53 + 26	12 + 10
Tetracosane	84 + 14	80 + 23	80 + 12	50 + 23	26 + 15
Ethylene Glycol	66 + 37	65 + 29	66 + 28	40 + 20	27 + 30

<sup>a/</sup> Percentages are based on total  $C^{14}$ -parathion recovered per leaf disc sample and not the amount applied.

After ethyl parathion was applied in soap solution to the cotton leaf, little was retained on the leaf surface (Table 3). Less than 50%

(mean value) of the parathion recovered was from the leaf surface even when sampling occurred immediately after application, (i.e. 0 hours, within 5 minutes). The data imply that much of the parathion applied to a cotton leaf does not remain of the surface but penetrates the interior, decreasing its availability as a contact poison. Ineffectiveness of the 7:3 (v:v) methanol:water rinse as an extraction procedure is unlikely, since Nigg et al. (1981) determined this solvent system to be more effective than other solvent systems at removing parathion from citrus leaf surfaces. However, Nigg et al. (1981) found that movement of parathion into citrus leaves occurred at a much slower rate than that observed in this study with cotton. Also, Matsumura (1960) found that malathion was readily absorbed by bean leaves.

All test additives increased the proportion of ethyl parathion recovered on the surface of a cotton leaf. During the first 24 h, 50% or more of the total parathion recovered was from the leaf surface for all parathion additives. The only exception was with ethylene glycol at 24 h, which had 40.1% (mean value) of parathion recovered on the surface. Presumably, penetration of ethyl parathion into the leaf interior was slowed by the additive. However, the greater proportion of parathion partitioning on the leaf surface could be due in part to decreased loss by volatilization.

In contrast, when permethrin in soap solution was applied without oil to cotton leaves, more than 50% of the recovered permethrin was obtained from the leaf surface through 24 h (Table 4). Initial (i.e. 0 h) leaf samples showed that 86% of the permethrin was recovered from the surface. This agreed with Southwick et al. (1983) who found that permethrin surface residues were 80-90% of the total cotton leaf load.

Table 4. Percent ( $\pm$  S.D.)<sup>a/</sup> of C<sup>14</sup>-Permethrin Recovered From the Surface of Cotton Leaves Various Sampling Times Following Application.

Additive	Sampling time (hours)				
	0	1	2	24	48
none	86 $\pm$ 0	76 $\pm$ 10	74 $\pm$ 9	54 $\pm$ 25	41 $\pm$ 39
Orchex 796	83 $\pm$ 4	80 $\pm$ 13	76 $\pm$ 17	66 $\pm$ 15	37 $\pm$ 46
Hexadecane	69 $\pm$ 20	72 $\pm$ 33	91 $\pm$ 5	72 $\pm$ 10	67 $\pm$ 6
Tetracosane	82 $\pm$ 10	82 $\pm$ 10	85 $\pm$ 10	65 $\pm$ 21	60 $\pm$ 27
Ethylene Glycol	72 $\pm$ 14	76 $\pm$ 2	73 $\pm$ 4	67 $\pm$ 12	49 $\pm$ 13

<sup>a/</sup> Percentages are based on total C<sup>14</sup>-permethrin recovered per leaf disc sample and not the amount applied.

Additives had little effect on distribution of permethrin within the leaf. That is, high percentages of permethrin, when applied with additives, continued to be recovered on the leaf surface. Additives tested may have delayed the leaf penetration of permethrin through 48 h, though data were most variable at this final sampling time for all

treatments. Similarly, Southwick et al. (1986) demonstrated that ULV-oil formulations produced permethrin levels in soybean leaf interiors which were comparable to those of EC-water formulations.

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