



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MEMORANDUM

DEC 3 1982

Subject: PP# 3E2766: Chlorpyrifos on kiwi fruit. analytical method and residue data. OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES
Evaluation of

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and

Toxicology Branch
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The Dow Chemical Company proposes tolerances for the combined residues of the insecticide chlorpyrifos [0,0-diethyl 0-(3,5,6-trichloro-2-pyridinyl)phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in or on kiwifruit at 2.0 ppm.

Tolerances for chlorpyrifos have been established on numerous raw agricultural products, listed under 40 CFR 180.342, ranging from a low of 0.01 ppm on poultry (except turkeys) fat, meat and meat by products to a high of 15 ppm on peanut hulls.

Conclusions

1. The fate of chlorpyrifos in plants and animals is adequately understood with the parent compound and the metabolite 3,5,6-trichloro-2-pyridinol (TCP) the residues of concern.
2. Adequate methods are available to enforce the proposed tolerance.
3. Residues from the proposed use are not likely to exceed the requested tolerance of 2.0 ppm in or on kiwifruit.
4. Since there are no feed items involved, there will be no problem of secondary residues in meat milk poultry and eggs.
5. The petitioner should submit the composition of [REDACTED] so that we can determine whether it is cleared as an inert ingredient under 40 CFR 180.1001. If this inert is not cleared, the petitioner should seek clearance or delete it from the formulation.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

RECOMMENDATION

The petitioner should supply additional information clarifying the composition of the inert ingredient EMUL T200. If this inert is not cleared, the petitioner should seek clearance for preharvest use in or on raw agricultural commodities or delete it from the formulation. After this problem is resolved, we will be able to recommend that the proposed 20 ppm tolerance for the combined residues of chlorpyrifos in or on kiwifruit be established, TOX considerations permitting.

Detailed Considerations

Manufacturing Process

[REDACTED]

[REDACTED] has been cleared as an inert ingredient in 40 CFR 180.1001. We do not expect residue problems from the other technical impurities.

Formulation

For the purposes of this requested tolerance, three formulations of chlorpyrifos were used in the residue data: Lorsban 50 W, a wettable powder that is 50% active ingredient; Lorsban 40 EC, an emulsifiable concentrate that is 40% active ingredient; and Lorsban 50 EC that is 50% active. (None of these formulations are registered with the EPA).

The inert ingredients in Lorsban 50W are cleared for pre-harvest use under 40 CFR 180.1001. In both Lorsban 40 EC and 50 EC, one ingredient, [REDACTED] needs clarification. It is possible that this ingredient is acceptable under 40 CFR 180.1001, but the manufacturer has used nomenclature that prevents precise identification. The manufacturer must submit the composition of [REDACTED] so that the status of this inert ingredient can be determined.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

MANUFACTURING PROCESS INFORMATION IS NOT INCLUDED

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Proposed Use The proposed use is for kiwifruit grown in New Zealand. The pesticide registration act for New Zealand is submitted.

Lorsban 40 EC, 50 EC and 50 W are all used to control various pests infesting kiwifruit including lepidopterous leaf rollers (mainly ctenopseustis obliquana) and greedy scale (Hemiberlesia rapax).

The proposed use calls for application of Lorsban (EC or W) at green tip, then at two-week intervals from petal fall to mid-January. Applications are to continue at monthly intervals for the rest of the season. There is to be a 14 day PHI.

For Lorsban 40 EC or 50 EC, apply in sufficient water to obtain full spray coverage equivalent to 0.445 to .713 lbs active/acre.

For LORSBAN 50 W, apply in sufficient water to obtain full spray coverage at rates equivalent to 0.445 to 0.668 lbs active/acre.

Nature of the Residue

The nature of chlorpyrifos residues in plants (beans, corn) and animals (rats, cows, pigs chicken) has been discussed in PP#4F1445 and PP#3F1306

Plant metabolism studies with radiolabelled chlorpyrifos and its metabolite, 3,5,6-trichloropyridinol, show that chlorpyrifos residues on the surface of plants and in soil are absorbed and translocated. Chlorpyrifos degrades in soil and in or on plants thereby yielding 3,5,6-trichloropyridinol (TCP). TCP may then become conjugated with plant substrates.

Animal metabolism studies show that degradation occurs via oxidation and hydrolysis to water-soluble phosphoric acid derivatives; these derivatives are excreted primarily in the urine. The hydrolysis product, TCP, is excreted, or it is further degraded into smaller fragments. The significant residues of animal metabolism are the parent compound, chlorpyrifos, and its metabolite, 3,5,6-trichloro-2-pyridinol.

We conclude that the nature of the residue is adequately understood.

Analytical Method

Residues of chlorpyrifos are extracted from the kiwifruit sample by blending with acetone. After removing the acetone with a Synder column, the residue is partitioned into hexane. A hexane-acetonitrile partition and silica gel chromatographic column are used for cleanup. The resulting solvent is evaporated with a Synder column and a jet of dry air. The residue, redissolved in acetone, is analyzed by gas chromatography using flame detection.

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Recovery from samples fortified over the range 0.01 ppm to 10.0 ppm chlorpyrifos averaged $92 \pm 5\%$. The limit of detection is 0.01 ppm

Analysis for 3,5,6-trichloropyrinol was made by heating the sample with alcoholic sodium hydroxide which converted any chlorpyrifos present to TCP. Total pyrinol was then determined. Subtraction of the chlorpyrifos, determined in samples not treated with alcoholic sodium hydroxide, allowed the calculation by difference of TCP residue content (method ACR 71.19 (R)). Recoveries were $107 \pm 2\%$ for kiwifruit samples fortified over the range of 0.05 ppm to 20.0 ppm. The lower limit of detectability was 0.05 ppm for TCP.

Residue Data

Four field trials were conducted in New Zealand to determine the residues of chlorpyrifos and its metabolite (TCP) in or on kiwifruit treated with chlorpyrifos as either an emulsifiable concentrate (LORSBAN 40 EC, 40% A.I. or LORSBAN 50 EC, 50% A.I.) or a wettable powder (LORSBAN 50 W, 50% A.I.). The formulations were applied one to nine times at two to four week intervals as a foliar spray.

Rates ranging from 0.44 to 0.713 lbs of chlorpyrifos per acre were applied in the trials. The maximum residues of chlorpyrifos plus TCP in/on whole kiwifruit (treated nine times with .44 lbs a.i./acre) and harvested 14 days after the last application was 1.3 ppm. The maximum residues reflecting treatment 5 times to 0.71 lbs act/A was also 1.3 ppm. Therefore, the proposed tolerance of 2 ppm should encompass those results.

[The maximum total residue found was 2.7 ppm resulting from PHI = 1 day, 5 treatments of 0.67 lbs active/acre]

Residues in Meat, Milk, Poultry and Eggs

There are no feed items involved in this use; therefore there will be no problem of secondary residues in meat, milk, poultry and eggs.

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