PP# 3F1370

SEP 25 1973

PP #3F1370. Chlorpyrifos in or on bananas. Evaluation of analytical methods and residue data.

Coordination Branch
and Toxicology Branch, RD

Dow Chemical Company proposes a tolerance for residues of the insecticide chlorpyrifos [0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in or on bananas at 0.25 ppm of which not more than 0.05 ppm shall be present in the plup after the peel is removed and discarded.

There are no permanent or current temporary tolerances for this chemical. Permanent tolerances are pending for residues in peaches and field corn from application, and in fat, meat, etc., of cattle and turkeys from dermal application (PP #3F1306).

Conclusions

1. The nature of the residue is understood.

2. The petitioner's gas chromatographic methods are adequate for determining residues of the parent and its metabolite 3,5,6-trichloro-2-pyridinol.

3a. The proposed 0.25 ppm tolerances is adequate for combined residues of the parent and TCP in whole bananas. Residues are confined to the peel and are comprised of the parent only.

b. No real residues of either the parent or TCP are expected in banana pulp.

4. This use is classified in Category 3 of Section 180.(a).

Recommendations

The petitioner should be informed that since the proposed use will be used outside of the United States, we will require a statement as to what regulatory mechanism is available to control the use in the country or countries of use.

Contingent on the submission of the above statement and pharmacological consideration permitting, we recommend for the proposed tolerance.

Detailed Considerations

Formulations

Technical chlorpyrifos has a minimum purity of 94% and a maximum of 6% impurities. The impurities are: [redacted]

PRODUCT IMPURITY INFORMATION IS NOT INCLUDED

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[redacted]

Two formulations are to be used. They are:

1. Lorsban(R) 5G, a 5% granular insecticide.

2. Polyethylene-D, polyethylene containing 1% chlorpyrifos.

The inerts are exempt from requirements of tolerances.

Proposed Use

1. Lorsban 5G Granular Insecticide is used for the control of banana root borers. Apply in a uniform band (barrier) 6 inches wide around the base of each banana plant at the rate of 3 grams per plant (equivalent to 60 grams of formulation). Apply when needed but not more than once every 6 months.

2. Polyethylene-D (Polyethylene containing Chlorpyrifos Insecticide) is used for the control of insects, e.g., aphids, thrips and fruit-scarring beetles. Install the chlorpyrifos impregnated polyethylene bags around the stems after all of the fruit bunches have formed and allow to remain there until harvest (about 80 days).

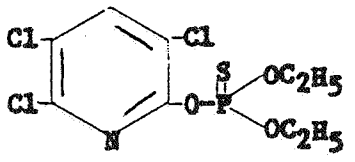
A single bag is used per stem. Bags are not replaced if damaged.

Each bag contains approximately 1/3 gram of chlorpyrifos.

Since this use is for bananas, and obviously will be used outside of the United States, we will require a statement as to what regulatory mechanism is available to control the use in the country or countries of use.

Nature of the Residue

Structural formula:



Little or no residue is expected from translocation. Residues may occur on whole bananas from surface contamination. No real residues of either the parent or TCP are expected in the edible banana pulp.

No new metabolism data are submitted in this petition. Reference is made to the data in PP #3F1306, "Chlorpyrifos in various commodities." We concluded in PP #3F1306, March 1, 1973, that the metabolism in plants is understood. Residues of concern are comprised primarily of the parent, and the hydrolysis product, 3,5,6-trichloro-2-pyridinol (TCP), is the primary metabolite. We reaffirm that conclusion.

Analytical Methods

Analyses were made by gas chromatography. The methods for the parent and TCP are discussed below.

Chlorpyrifos

Dow's Method ACR 72.14 was used to determine the parent in banana peel, pulp, and whole bananas. In this method, the residue is extracted from the tissue by blending with acetone. The extract is filtered and the filtrate is evaporated to remove the acetone leaving the residue and several mls of co-extracted water. The residue is partitioned into hexane and a silica gel column cleanup is used. The hexane is evaporated to dryness with a jet of dry air on a water bath. The residue is redissolved in a known volume of acetone and an aliquot is analyzed by gas chromatography, using flame photometric detection. Recovery averaged 91% from whole bananas, 88% from banana peel, and 88% from banana pulp at 0.01-5.0 ppm fortification levels.

Except for the silica gel column cleanup, the method is similar to DOW's Method 71.14 which was successfully tested on peaches by the Analytical Methods Section in connection with PP #3F1306. Therefore, no method trial was recommended for this method. We consider the gas chromatographic method to be adequate for enforcement purposes.

TLC is available for confirmation [J. Ag. & Food Chem., 15, 182-186 (1967)].

3,5,6-Trichloro-2-Pyridinol (TCP)

TCP is extracted from the tissues with methanol and chromatographed on an acidic alumina column using a hydrochloric acid solution to elute the compound. TCP is partitioned into benzene, followed by sodium bicarbonate partitioning, acidification with hydrochloric acid, and finally partitioning into benzene. An aliquot of the benzene phase is treated with BSA, (N,O-bis (trimethylsilyl)acetamide, to form the pyridinol trimethylsilyl derivative

which is determined by gas chromatography using an electron capture detector. Recovery by the petitioner averaged 85% for whole bananas, 88% for banana peel, and 86% for banana pulp at fortification levels of 0.05-1.0 ppm.

The method for TCP in bananas (Dow Method ACR 72.13) is similar to the methods which the Analytical Methods Section tested on peaches and beef fat in connection with PP #3F1306. AMS obtained low recoveries by Method ACR 71.11 for peaches (58-64%) and Method ACR 70.19 for beef fat (38-46%). AMS concluded that TCP was not quantitatively eluted from the alumina cleanup in the presence of peach or beef fat extractives. Subsequent to the tryout, we learned that the cleanup procedure in Method 72.13 included an essential step which the petitioner had inadvertently omitted from Methods ACR 71.11 and ACR 70.19 (see B. Puma's memo of 6/31/73 conference re PP #3F1306). For this reason, we recommended that AMS test Method ACR 72.13 on bananas and ACR 70.19 (revised) on beef fat.*

AMS has informed us that the method for TCP in bananas gave satisfactory results in the tryout. Recoveries from whole bananas were 88 and 94% at 0.05 ppm, and 91 and 98% at 0.10 ppm. Controls were <0.005 ppm. We therefore conclude that the method is adequate for enforcement.

Residue Data

Storage stability data show no loss of TCP or parent when spiked samples were stored in a freezer for 4.5 and 9 months, respectively.

The base of banana plants were treated once and twice at 3 grams per plant. Bananas were collected at 1 day, 2 weeks, 1, 3, and 6 months after treatment. Gross sample values for the parent and TCP did not differ from controls (<0.005 ppm-0.01 ppm) for the whole banana, banana peel, or banana pulp.

Bananas were grown for about one to three months in chlorpyrifos impregnated polyethylene bags containing 0.25 to 0.66 grams of chlorpyrifos per bag. At normal harvest time, residues of the parent were <0.005-0.14 ppm in whole banana, <0.005-0.21 ppm in banana peel, and non-detectable, i.e., same as control <0.005 ppm, in banana pulp.

No detectable (<0.01 ppm) residue of TCP was found in any sample.

From these data, we conclude that the combined residues of chlorpyrifos and TCP will not exceed the proposed tolerance for whole bananas, and that no real residue of either component is expected in the pulp.

* The re-testing of the method for beef fat is discussed in PP #3F1306.

Transfer of Residues to Meat, Milk, Poultry, and Eggs

No feed item is involved. Thus, the proposed use is classified in Category 3 of Section 180.6(a).

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