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PP#8E2092: Chlorpyrifos in Tomatoes. Evaluation of Analytical Method and Residue Data.

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Thru: Chief, RCB, HED, (TS-769)

Dow Chemical Company proposes a tolerance for combined 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 tomatoes at 0.5 ppm.

Chlorpyrifos is to be used on tomatoes grown in Mexico which is intended for export to the United States. Chlorpyrifos is also to be used on tomatoes grown in Israel which is intended for processing to juice and/or paste which may be exported to the United States.

Tolerances for chlorpyrifos are established on a variety of commodities at levels of 0.05-1.5 ppm (§180.342). These include tolerances on meat, fat, and meat byproducts of turkeys at 0.2 ppm; eggs, meat, fat, and meat byproducts of poultry at 0.01 ppm; and in milk fat at 0.25 ppm (reflecting negligible residues of 0.01 ppm in whole milk).

Conclusions

1. The nature of the residue is adequately delineated.

2. Adequate analytical methods are available for enforcement purposes.

3. Residues in or on tomatoes or tomato byproducts (juice, paste) are not likely to exceed the proposed tolerance.

4. Residues could occur in the eggs, milk, meat, fat, and meat byproducts of livestock [§180.6(a)(2)]; however, such residues would be adequately covered by the existing tolerances.

Recommendations

Toxicological considerations permitting, we could recommend for the proposed tolerance contingent upon the response to the following request.

The petitioner should be requested to document how the pesticide usage is regulated in the exporting country. This includes the submission of registered labels or evidence of application for a registration for those countries with registration laws.

Detailed Considerations

INFORMATION ON PRODUCT IMPURITIES IS NOT INCLUDED

Proposed Use

Chlorpyrifos is formulated as LORSBAN(R) 4E, an emulsifiable concentrate containing 4 lb a.i./gallon, and is proposed for aerial or ground, foliar applications on tomatoes.

Mexico: up to 3 aerial or ground applications at 0.96 kg/hectare (about 0.86 lb act/A) with a 1-day PHI for fresh fruit intended for export to the U. S.

Israel: up to 4 ground sprays at 10-day intervals at 0.96 kg/hectare (0.86 lb act/A) with a 14-day PHI for harvest of tomatoes intended for processing to juice and/or paste, some of which may be exported to the U.S.

The formulations inert ingredients are cleared for use under §180.1001.

The manufacturing process for technical chlorpyrifos and its impurities have been discussed in previous petitions (PPs4F1445, 6F1673). The impurity [redacted] The chlorpyrifos formulations will contain [redacted] at a maximum level of about [redacted] Because of the relative quantities involved and the dilution factors, the impurity [redacted] and the remaining impurities are not expected to produce a residue problem.

Nature of the Residue

We have discussed the nature of plant and animal residues in PP 4F1445 and PP 3F1306. Metabolism studies with radiolabelled chlorpyrifos and its metabolite 3,5,6-trichloropyridinol (TCP) show that chlorpyrifos is absorbed from soil and foliar applications and translocated in plants (beans, corn). Chlorpyrifos is metabolized and/or degraded in soil and plants to yield TCP which could be conjugated. (The residue method could determine bound residues). TCP is metabolized via dechlorination and formation of diols and triols and subsequent cleavage of the pyridine ring. The oxygen analog of chlorpyrifos has not been noted.

The nature of plant residues is adequately delineated.

Analytical Methods

Chlorpyrifos- a sample is extracted by blending with acetone, filtering, and evaporation of the solvent. The residue is cleaned-up using either a silica gel or florisil column with hexane as the diluting solvent. The eluate is evaporated to dryness, and the residue is taken up with acetone. Chlorpyrifos is determined in an aliquot by gas-liquid chromatography (GLC) using a flame photometric detection system.

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The presence of chlorpyrifos in a sample is confirmed by alkaline hydrolysis of the final solution. The hydrolysis yields TCP. The trimethylsilyl derivative of TCP is formed by treatment with N,O-bis (trimethylsilyl) acetamide, BSA. The derivative is then determined by GLC using an electron capture detection system.

Untreated (control) samples had <0.01 ppm equivalent residues of chlorpyrifos. Control samples were fortified with chlorpyrifos at levels of 0.01-0.50 ppm. Recoveries were 78-104%.

3,5,6-Trichloro-2-pyridinol (TCP) - a sample is extracted by heating with alcoholic sodium hydroxide which hydrolyzes any chlorpyrifos present to TCP. (The method involves an assay for total TCP. Thus, chlorpyrifos is determined separately, and TCP originally in the sample is determined by difference). The mixture is filtered, and an aliquot is concentrated, acidified with hydrochloric acid, and the TCP extract is cleaned up on an alumina column using ether as the eluting solvent. The TCP residues are extracted into sodium bicarbonate which is acidified and extracted with benzene.

An aliquot of the benzene extract is treated with BSA to form the pyridinol trimethylsilyl derivative. The derivative is determined by GLC using an electron capture detector.

Untreated (control) samples had <0.05 ppm TCP-equivalent residues. Control samples were fortified with TCP at levels of 0.05-0.50 ppm. Recoveries were 80-104%.

Successful method trials have been performed with chlorpyrifos on peaches at levels of 0.025 ppm and 0.05 ppm and beef fat at levels of 0.1 ppm and 0.5 ppm (PP3F1306, memo 6/12/73, J. E. Hayes). A successful trial has been performed on bananas with TCP at levels of 0.05 ppm and 0.10 ppm (PP3F1370, memo 9/25/73, F. D. R. Gee) and beef fat at levels of 0.1 ppm and 0.5 ppm (PP3F1306, memo 11/1/73, F. D. R. Gee).

We believe the results of the method trials can be extended to include tomatoes.

Adequate methods are available for enforcement purposes.

Residue Data

Mexico- samples were collected from plots which had received 1-3 foliar applications at the proposed rate and harvested at intervals of 1-14 days after the last application. Overall residue levels were <0.05-0.59 ppm. Residue levels at the proposed 1-day PHI were 0.12-0.37 ppm.

The data indicate that apparent levels for combined residues will not exceed the proposed tolerance (0.5 ppm).

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Mississippi - the proposed use does not include tomatoes grown and treated in the U. S. These data are being evaluated to indicate residue patterns, in general. Samples which had received 1-5 ground applications at 0.86 lb act/A were collected at intervals of 0,3, and 7 days after the last application. Overall residues due to 1-5 applications were <0.05-0.64 ppm (0-day) and <0.05-0.78 ppm at 3-7 days due to 5 applications.

The data indicate that residues increase with an increase in the number of applications and decrease with an increase in the PHI.

Israel - samples were collected at intervals of 0-21 days after the last application from plots treated as proposed. Fresh tomatoes had residues of <0.12-0.74 ppm (0-day), <0.11-0.42 ppm (7-day), 0.06-0.18 ppm (14-day, proposed PHI), and <0.05-0.25 ppm (21-day). The tomatoes were processed to juice and paste. The juice had residues of <0.06-0.09 ppm and the paste had residues of <0.15-0.25 ppm at the 14-day PHI. The level in the paste shows a slight concentration; however, the concentration is not considered significant.

We conclude that combined residues of chlorpyrifos and its metabolite in tomatoes and its byproducts (juice and paste) are not likely to exceed the proposed tolerance.

Meat and Milk

Tomato pulp is occasionally used as a livestock feed item. Therefore, we conclude that residues could occur in the eggs, milk, meat, fat, and meat byproduct of livestock [§180.6(a)(2)]; however, such residues would be adequately covered by the existing tolerances.

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