6-29-93

MEMORANDUM:

SUBJECT: **PP#3E4192**. Chlorpyrifos in/on Sugarcane. Evaluation of Residue Data and Analytical Methodology. CBTS# 11397. DP Barcode D188233. MRID#'s 426454-00, -01.

FROM: José J. Morales, Chemist
Tolerance Petition Section II
Chemistry Branch I -- Tolerance Support
Health Effects Division (H7509C)

THROUGH: Elizabeth T. Haeberer, Section Head
Tolerance Petition Section II
Chemistry Branch I -- Tolerance Support
Health Effects Division (H7509C)

TO: Hoyt Jamerson, PM 43
Emergency Response And Minor Use Section
Registration Support Branch
Registration Division (H7505C)

IR-4 and the Agricultural Experiment Stations of Florida and Hawaii are requesting a tolerance for residues of the insecticide chlorpyrifos in or on sugarcane at 0.01 ppm.

Revised tolerances reflecting residues of chlorpyrifos per se for the racs listed in 40 CFR §180.342 (a) and (b); and 40 CFR §185.1000 appear in the Federal Register Notice of 4/1/93.

Tolerances had been previously established for the combined residues of the insecticide chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridil)phosphorothioate and its metabolite 3,5,6-trichloro-2-pyridinol (TCP), on various racs and commodities of animal origin from 0.05 ppm in bananas, pulp with peel removed; beans, snap; nectarines; peaches; pears; and plums to 15.0 ppm in alfalfa, hay; peanut hulls; and soybean, straw [40 CFR §180.342 (a)] (see discussion in "Nature of the Residue" section of this memo).

Tolerances with regional registration were established for the combined residues of the insecticide chlorpyrifos and its metabolite TCP in or on the raw agricultural commodities dates, grapes and leeks at 0.5 ppm and in asparagus at 5.0 ppm [40 CFR §180.342 (b)].

Tolerances with regional registration are established for residues of chlorpyrifos per se in or on the raw agricultural commodities cherimoya, feijoa and sapote at 0.05 ppm [40 CFR §180.342 (c)].

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Food additive tolerances were established for residues of chlorpyrifos and its metabolite TCP in or on the processed commodities citrus oil at 25.0 ppm; corn oil at 3.0 ppm; mint oil at 10.0 ppm and peanut oil at 1.5 ppm as a result of application of the insecticide to the growing crops [40 CFR §185.1000].

Feed additive tolerances were established for residues of chlorpyrifos and its metabolite TCP in or on the feeds apple pomace, dried at 12.0 ppm; beets, sugar, molasses at 15.0 ppm; beets, sugar, pulp (dried) at 5.0 ppm; citrus pulp, dried at 5.0 ppm; corn soapstock at 1.0 ppm; grape, pomace, dried at 2.0 ppm; sorghum milling fractions at 1.5 ppm; and sunflower seed hulls at 0.5 ppm as a result of application of this insecticide to the growing crops [40 CFR §186.1000].

CBTS recommended for the establishment of tolerances for residues of chlorpyrifos per se in the following animal commodities as a result of PP#3F2884: milk fat (reflecting 0.01 ppm in whole milk) at 0.25 ppm; meat of cattle, goats, hogs, and sheep at 0.05 ppm; meat byproducts of cattle, goats, hogs, and sheep at 0.05 ppm; fat of cattle at 0.30 ppm; fat of goats, hogs, and sheep at 0.20 ppm; and meat, meat byproducts and fat of horses at 0.25 ppm. CBRS recommended for the establishment of tolerances for residues of chlorpyrifos per se in the following racs as a result of PP#4F3008/1H5295: tomatoes at 1.0 ppm; bean hay at 0.10 ppm; pea hay at 0.10 ppm; soybean hay at 0.10 ppm; and tomato pomace at 65 ppm.

Chlorpyrifos is a List A chemical. The Product and Residue Chemistry Chapters of the Registration Standard were issued on 2/29/84. The Second Round Review (SRR) for these chapters is dated 11/18/88.

CONCLUSIONS

1. The manufacturing process for chlorpyrifos has been reviewed for the Registration Standard and the Second Round Review of 11/18/88. Additional information concerning the chlorpyrifos manufacturing-use products has been requested by the Registration Standard. These requirements should be addressed by the petitioner in future submissions.

2. The nature of the residue in plants and animals is adequately understood. The residue of concern is the parent compound, chlorpyrifos.

3. Adequate methodology is available for enforcement purposes and for analysis of parent chlorpyrifos in sugarcane.

4. The FDA Pestrack data base (PAM Vol. I, Appendix, date 11/6/90) indicates that complete recovery has been obtained for chlorpyrifos under FDA multiresidue methods.

5. Geographical representation of residue data is adequate for the proposed use on sugarcane.

6. CBTS will translate the available storage stability data of chlorpyrifos in sorghum, mint, alfalfa, corn, and sugar beets to support the subject tolerance petition.

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7. Residue data on sugarcane stalks, "A" molasses, bagasse, and refined sugar show that nondetectable residues (<0.01 ppm) were obtained after chlorpyrifos treatment.

8. No residue data were sent for sugarcane forage. In the absence of residue data for this feed item, the registrant should impose a label restriction against feed use of forage. A revised Section B is needed. Alternatively, the petitioner may submit residue data on sugarcane forage in order to support the subject tolerance petition.

9. No residue data were sent for blackstrap molasses from Florida and Hawaii. Considering that a 8 month PHI is proposed, that chlorpyrifos is translocated only to a limited degree from soil or from treated leaves, that under prolonged exposure to UV chlorpyrifos undergoes extensive degradation, and that nondetectable residues were obtained in cane and "A" molasses, CBTS will not require blackstrap molasses data in support of this petition. Concentration of residues above the rac tolerance is not expected.

10. Since residues of chlorpyrifos per se are below the detection limit, we expect no significant increase in the dietary burden of poultry and ruminants.

11. An International Residue Limit (IRL) Status Sheet is appended to this review. There are no Codex, Canadian or Mexican limits established for chlorpyrifos per se on sugarcane. Therefore, no compatibility problems exist.

RECOMMENDATION

CBTS recommends against the establishment of the proposed tolerance for reasons given in Conclusion 8.

DETAILED CONSIDERATIONS

PRODUCT CHEMISTRY

The manufacturing process for chlorpyrifos has been reviewed for the Registration Standard and the Second Round Review of 11/18/88. Additional information concerning the chlorpyrifos manufacturing-use products has been requested by the Registration Standard. These requirements should be addressed by the petitioner in future submissions.

PROPOSED USE

Two registered formulations of chlorpyrifos are proposed for use: Lorsban® 4E and Lorsban® 15G. Lorsban® 4E (EPA Reg. No. 62719-23) is an emulsifiable concentrate containing 40.7% of ai (equivalent to 4 lbs. of active ingredient per gallon) and 59.3% of inerts. Lorsban® 15G (EPA Reg. No. 62719-34) is a granular insecticide containing 15.0% of ai and 58.0% of inerts. Clearance of the inert ingredients is under the purview of Registration Division.

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The following directions apply for Lorsban® 4E: for lesser cornstalk borer control apply Lorsban® 4E at 6.6 to 9.9 fl. oz. per 1000 ft. of row (0.2 to 0.3 lbs. ai/1000 ft. of row) in a 2 ft. wide band over the row shortly before planting or shortly before rattoon emergence. Apply in sufficient water to assure thorough coverage (at least 30 gallons of water per acre) using power operated ground spray equipment. Immediately after application, incorporate to a 1 to 2 inch depth using a disk, field cultivator, drag chains, tines, or equivalent equipment. Use the high rate in fields with a history of serious lesser cornstalk borer injury. An additional treatment may be applied before the canes are 10 inches high. Use power operated ground spray equipment to apply Lorsban® 4E in a band over the plant rows. Apply at a rate of 6.6 to 9.9 fl. oz. per 1000 ft. of row (0.2 to 0.3 lbs. ai/1000 ft. of row) in a 2 ft. wide band over the row. Do not make more than two applications of Lorsban® 4E per year. If Lorsban® 4E or Lorsban® 15G is used at planting time, one additional Lorsban® 4E treatment may be applied later. Do not use more than 3 quarts of Lorsban® 4E per acre per application. Do not apply within 8 months of harvest.

The following directions apply for Lorsban® 15G: for lesser cornstalk borer control apply Lorsban® 15G at 22 to 33 oz. per 1000 ft. of row (0.2 to 0.3 lbs. ai/1000 ft. of row) in a 2 ft. wide band over the row, shortly before planting or shortly before rattoon emergence. Use equipment that will evenly distribute the granules over the area to be treated. For at-plant treatment, the recommended granule placement is a T-band, with granules distributed into the planting slot and in a 2 ft. wide band over the plant row. Immediately after application, incorporate the granules to a 1 to 2 inch depth using a disk, field cultivator, drag chains, tines or equivalent equipment. Use the high rate in fields with a history of serious lesser cornstalk borer injury. Do not make more than one application per year or apply more than 20 lbs. of Lorsban® 15G per acre per year. Do not apply within 8 months of harvest.

NATURE OF THE RESIDUE

Plants

According to the Second Round Review, no further data were required to determine the nature of the residues in plants (Table A). The residues of concern were considered to be chlorpyrifos and its metabolite TCP. However, in an addendum to the residue chemistry chapter (D. Edwards, HED, to C. Kent, RD, 1/13/89) it was stated that TCP could be excluded from the tolerance expression. This position was reaffirmed by TOX in a memo from E. Doyle to R. Schmitt and E. Zager (4/1/91), which stated that "TOX Branch has no toxicological concerns regarding exclusion of TCP from the tolerance statements for chlorpyrifos. Chlorpyrifos is regulated on the basis of cholinesterase inhibition. TCP is inactive with respect to anticholinesterase activity." Thus, the only residue of concern in plants is the parent compound, chlorpyrifos.

Animals

As outlined in the SRR, and amended as described above, the nature of the residue in ruminants and poultry is adequately understood. The residue of concern is the parent compound, chlorpyrifos.

ANALYTICAL METHODOLOGY

The analytical method used to detect chlorpyrifos residues is a modified version of the method described in Dow Chemical Company Method ACR 84.4 "Determination of Chlorpyrifos and 3,5,6-trichloro-2-pyridinol in Stone Fruits by Gas Chromatography", MRID# 00155580. The modifications made were in the use of glassware, standard solution concentrations, and a change in the extracting solvent for sugarcane bagasse (replacing acetone with methanol). Briefly, residues are extracted from samples with acetone (methanol if bagasse is going to be analyzed). The extracts are centrifuged, reduced in volume, cleaned up on a Sep-Pak C_{18} cartridge, and eluted with methanol. The residues in the eluate are partitioned with hexane and analyzed using gas liquid chromatography with a flame photometric detector (recovery data on sugarcane is discussed under Residue Data, on page 7). The detection limit is 0.01 ppm.

Enforcement methods for chlorpyrifos (parent only) determination in plant matrices (bananas, peaches, and cottonseed) are outlined in PAM II as methods I, II, and VI. In method I, chlorpyrifos is extracted with acetone, filtered, partitioned into hexane and cleaned up on a silica gel column. The residue is dissolved in acetone and determined by GLC, using a phosphorus-specific flame detector. The limit of detection is 0.01 ppm. In method II, chlorpyrifos is extracted with acetone, filtered, and the filtrate is extracted with methylene chloride. This extract is dried with sodium sulfate and evaporated to dryness. The dry residue is dissolved in hexane, partitioned into acetonitrile, evaporated to dryness, and dissolved in acetone for GLC determination using a phosphorus-specific flame photometric detector. The limit of detection is 0.01 ppm. In method VI, chlorpyrifos is extracted from the sample with acetone, evaporated to dryness, and hexane is added to obtain an azeotropic solution. The residue is dissolved in methanol and chromatographed on acidic alumina. The eluate is diluted with water and partitioned with hexane. The extract is further cleaned up with acetonitrile partitioning and florisil chromatography. Chlorpyrifos is determined by GLC using a phosphorus-specific flame detector. The limit of detection is 0.01 ppm.

An enforcement method for chlorpyrifos (parent only) determination in animal matrices (animal tissues and milk) is outlined in PAM II as method IV. Briefly, samples are extracted with hexane/acetonitrile solution, concentrated, diluted with sodium sulfate, and cleaned on a silicic acid column. Chlorpyrifos is eluted with 7.5% methylene chloride in hexane, evaporated to dryness, and dissolved in hexane for determination by GLC with an electron capture detector. The limit of detection is 0.1 ppm.

CBTS concludes that adequate methodology is available for enforcement purposes and for analysis of parent chlorpyrifos in sugarcane.

MULTIRESIDUE TESTING

The FDA Pestrack data base (PAM Vol. I, Appendix, date 11/6/90) indicates that complete recovery has been obtained for chlorpyrifos under FDA multiresidue methods A, C, and E.

RESIDUE DATA

Residue data reflecting the application of chlorpyrifos to sugarcane appear in the following report:

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"Chlorpyrifos: Magnitude of the Residue on Sugarcane"; W.L. Biehn; 1/25/93; Laboratory Project ID IR-4 PR No. 3239, Dow Protocol No. 87124, HSPA Study No. 16-5258. Performing laboratory was Hawaiian Sugar Planters Assoc., Aiea, Hawaii (MRID# 426454-01).

Six trials were conducted during 1987 in Florida (3) and Hawaii (3). According to Census of Agriculture, 1988, these states accounted for at least 74% of the sugarcane production in the United States. Band application of Lorsban® 4E plus Lorsban® 15G was made at a rate of 2 lbs. ai/A each (for a total of 4 lbs. ai/A) and 4 lbs. ai/A each (for a total of 8 lbs. ai/A). After pesticide application samples of sugarcane were harvested within 7 to 8 months in Florida and 12 months in Hawaii. After pesticide application, the Hawaii cane samples were processed in the Hawaiian Sugar Planters Association, Environmental Science Department, and after processing they were shipped to the Hawaiian Sugar Planters Association Analytical Laboratory, Aiea, Hawaii. The Florida cane samples were processed by the United States Sugar Corporation Research Department, and after processing they were shipped to Dow Chemical Company, Midland, Michigan and from there to Hawaii to be analyzed for chlorpyrifos residues.

No residue data were sent from Louisiana. Although there are differences between Louisiana, Florida, and Hawaii in the soil where sugar cane is grown, climate, sugar cane varieties, and harvest interval (9 to 12 months in Louisiana vs. 12 to 24 months in Hawaii and Florida); we conclude that residues from the proposed use should not be different from one place to the other. Also, considering the fact that a 8 month PHI is being proposed, CBTS concludes that geographical representation of residue data is adequate for the proposed use on sugarcane.

Samples of sugarcane stalks were analyzed for chlorpyrifos residues up to almost 24 months after sampling. Maximum interval between extraction and analysis was 26 days. Samples of bagasse, refined sugar, and molasses were analyzed for chlorpyrifos residues up to almost 22 months after sugarcane processing. Maximum interval between extraction and analysis was 6 days for bagasse and refined sugar, 4 days for molasses.

Studies examining the stability of chlorpyrifos in frozen sugarcane and sugarcane processed fractions were not conducted. Residues of chlorpyrifos were shown to be stable in sorghum grain, forage, and fodder stored for 61 - 85 days at -18°C; fresh mint hay, spent mint hay, and mint oil stored at -20°C for 10 months; alfalfa forage, and hay stored at -18°C for 327 - 346 days; corn grain, forage, and fodder stored at -18°C for 27 months; sweet corn fodder stored at -18°C for 2.75 years; sugar beet roots and tops stored at -18°C for 3.75 years (Second Round Review (SRR), Residue Chemistry Chapter dated 11/18/88).

CBTS will translate the available storage stability data of chlorpyrifos in sorghum, mint, alfalfa, corn, and sugar beets to support the subject tolerance petition.

Recovery data were obtained from untreated samples of sugarcane stalks, bagasse, refined sugar, and molasses fortified with chlorpyrifos at the level of 0.01 ppm and 0.10 ppm prior to extraction. Recovery values ranging from 70% to 89% were obtained for sugarcane stalks; 80% to 110% for sugarcane bagasse; 70% to 85% for refined sugar; and 77% to 104% for molasses. Submitted chromatograms show well resolved peaks in support of these data.

Residue data on sugarcane stalks, "A" molasses, bagasse, and refined sugar show that nondetectable residues (<0.01 ppm) were obtained after chlorpyrifos treatment. No residue data were sent for sugarcane forage. In the absence of residue data for this feed item, the

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registrant should impose a label restriction against feed use of forage. A revised Section B is needed. Alternatively, the petitioner may submit residue data on sugarcane forage in order to support the subject tolerance petition.

CBTS has previously requested that sugarcane processing studies (GLN 171-4(1)) include the production of blackstrap molasses. Blackstrap is an animal feed commodity (about 10% of diet), and minor amounts enter the human diet. Previous processing studies had produced only A molasses. In commercial processing, A molasses is further concentrated to recover more sugar. The viscous liquid fraction from which crystalline sugar cannot be further obtained by the repeated crystallization of syrup is blackstrap. The submitted processing studies show that only A sugar and molasses were produced in Hawaii and A and B sugars and molasses and refinery sugar and molasses were produced in Florida. Refinery sugar and molasses are the product of re-melting the A and B sugars and purifying these sugars by calcium carbonate precipitation, filtering, treating with activated charcoal and a final recrystallization. The resulting product of this process is refinery sugar and molasses. The refinery molasses are used for animal feed and as an edible molasses. The petitioner indicated that refinery molasses is very pure because the A and B crystallizations (to obtain A and B sugars) remove most of the impurities. The Florida molasses fractions analyzed included the B molasses and refinery molasses. No residue data were sent for blackstrap molasses from Florida and Hawaii. Considering that a 8 month PHI is proposed, that chlorpyrifos is translocated only to a limited degree from soil or from treated leaves, that under prolonged exposure to UV chlorpyrifos undergoes extensive degradation, and that nondetectable residues were obtained in cane and "A" molasses, CBTS will not require blackstrap molasses data in support of this petition. Concentration of residues above the rac tolerance is not expected.

MEAT, MILK, POULTRY AND EGGS

Since residues of chlorpyrifos per se are below the detection limit, we expect no significant increase in the dietary burden of poultry and ruminants.

OTHER CONSIDERATIONS

An International Residue Limit (IRL) Status Sheet is appended to this review. There are no Codex, Canadian or Mexican limits established for chlorpyrifos per se on sugarcane. Therefore, no compatibility problems exist.

Attachment: International Residue Limit Status Sheet

cc: RF, Circu., José J. Morales, M. Flood, E. Haeberer, PP#3E4192
H7509C: Reviewer (JJM): CM#2: Rm 804-Q: 305-5010: typist (JJM): 6/29/93
RDI: E. Haeberer (6/29/93): M. Flood (6/29/93): R. Loranger (6/29/93)