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

JAN 9 1985

MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: EPA Reg No 464-448. Chlorpyrifos on Tobacco: Amended Registration. Accession Numbers 255341 and 255342.

FROM: Leung Cheng, Chemist
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THRU: Charles L. Trichilo, Chief
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TO: Jay Ellenberger/D. Edwards, PM Team #12
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Registration Division (TS-767)

Dow Chemical has filed an amended registration of Lorsban 4E (EPA Reg No 464-448), used as a preplant insecticide/nematicide, on tobacco. The currently registered use calls for a single preplant application of 2-3 lbs ai/A, applied broadcast and incorporated to a depth of 2-4 inches. The Company now wishes to add a use to control low to moderate infestations of nematodes. For this pest chlorpyrifos is to be used at the rate of 4-5 lbs ai/A preplant with incorporation to 4 inches or more. Nemacur® 3 is to be used in combination (tank mix) at the rate of 4 qts per acre. The sole restriction of "Do not make more than one application per season" has however been removed. No other changes are made.

Tolerances have been established for combined residues of chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in or on numerous commodities including whole milk at 0.02 ppm, eggs at 0.1 ppm and meat at 0.5-2.0 ppm [40CFR§180.342].

Included in the two reports entitled "Determination of Chlorpyrifos and 3,5,6-Trichloro-2-pyridinol in Green and Cured Tobacco Grown in Soil Treated with Lorsban Insecticides"

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and "Determination of Residues in Smoke from Tobacco Treated with Chlorpyrifos", which have previously been submitted, are residue data, analytical methods for determining chlorpyrifos and its pyridinol metabolite, and sample chromatograms (see memos of L. Bradley, 6/18/80 and E. Zager, 3/2/83, EPA Reg Nos 464-448 and 464-523).

To recapitulate, chlorpyrifos determination involves sequential extractions with acetone, hexane and acetonitrile, clean-up on a silica gel column and quantitation on GC equipped with a flame photometric detector. Recoveries of 90-100% on green tobacco and 70-90% on cured tobacco were obtained at 0.01 ppm chlorpyrifos fortification. Control values were 0.006 ppm and below. Inspection of the submitted chromatograms shows peaks corresponding to 0.006 ppm can be accurately measured.

For the pyridinol metabolite, the sample is hydrolyzed with methanolic sodium hydroxide, acidified, extracted with benzene, chromatographed on acid alumina, taken up in bicarbonate solution and isolated as the trimethylsilyl derivative. Determination is done by GC/EC. A duplicate sample is also analyzed for chlorpyrifos since the difference between the two values gives the actual amount of pyridinol metabolite. Recoveries on green tobacco were 80-96% and 78-88% at 0.05 ppm and 0.2 ppm fortifications, respectively. Those on cured tobacco were 72-100%, 83-87% and 84% at 0.05 ppm, 0.2 ppm and 1.0 ppm fortifications, respectively. Control values were 0.022 ppm and lower. Based on the sample chromatograms submitted, peaks equivalent to 0.05 ppm can unambiguously be quantitated.

Residue data on air or flue cured tobacco were collected from plots in KY and NC. Lorsban 4E was applied once at 2-3 lbs ai per acre zero or seven days prior to transplant. Burley tobacco which was harvested 89 days later and then air cured (duration not specified) contained less than 0.006 ppm parent and 0.05 ppm 3,5,6-trichloro-2-pyridinol. Flue cured tobacco which was harvested 135 days or 166 days after treatment contained less than 0.01 ppm parent and 0.09 ppm pyridinol.

Since total residues in cured tobacco approach 0.1 ppm, Dow also provided residue data in smoke from cured tobacco. Cured tobacco was fortified with 0.1, 1.0 and 10 ppm chlorpyrifos and then was made into cigarettes. These cigarettes were humidified to 12% moisture content before being smoked on a machine, each through a single cambridge filter. The filter was changed after every 5 cigarettes. Pentane traps, collected after every 40 cigarettes, were placed behind the filter to check trapping efficiency of the filter. Ashes and butts were not analyzed.

Residues in mainstream and sidestream smoke were analyzed for <u>parent only</u> by injecting a 10-microliter aliquot into a

GC using flame photometric detector in the phosphorus specific mode. Acetone was employed for extracting residues in tobacco or cigarettes while pentane trap solutions were injected "as is". For filters, hexane was the extracting solvent followed by clean-up on Florisil and acid alumina columns. Recovery values were 90-102% at 0.04 ppm fortification, 92-110% at 0.2 ppm and 110% at 20 ppm chlorpyrifos on filters. Those on tobacco were 100-110% and on cigarettes were 90-99% at 0.1-10 ppm chlorpyrifos. Control values were not detectable, the limits being approximately 0.05 ppm on tobacco and cigarettes, 0.01 ppm on filters and lower on pentane solutions in our judgement.

Residues in mainstream smoke as a result of "smoking" tobacco containing 0.1 ppm chlorpyrifos were determined to contain 0.02-0.03 ppm parent per cigarette. Corresponding values found in sidestream smoke were ca 0.01 ppm.

Tobacco treated with 1.0 ppm and 10 ppm chlorpyrifos gave proportionally higher residues in mainstream smoke. Residues detected in sidestream smoke were 0.02-0.3 ppm, about 10% of those found in the mainstream. Residues in pentane trapping solutions were all less than 0.01 ppm parent regardless of level of chlorpyrifos in the tobacco.

Despite the fact that there exists a method for analyzing the pyridinol metabolite, this was not done. Also, as can be seen, only 20-30% of the residues in smoke has been identified.

From the above data it appears that residues found in the mainstream smoke are a function of those in tobacco. Assuming a maximum of 0.25 ppm (2.5 x 0.1 ppm) chlorpyrifos in treated tobacco as a result of higher proposed use rate (2.5X maximum the current rate), this would translate to a maximum of 0.05-0.075 ppm chlorpyrifos in the mainstream smoke per cigarette. Residues in sidestream smoke would be estimated at 0.02-0.03 ppm maximum. However, in no case was the metabolite 3,5,6-trichloro-2-pyridinol analyzed and, since chlorpyrifos may be extensively converted to its pyridinol metabolite on storage and/or pyrolysis, plus the indication above that residues in cured tobacco may contain up to 10 times as much pyridinol as the parent, we believe pyrolysis studies should be performed on cured tobacco which has been fortified with appropriate levels of chlorpyrifos and metabolite. Furthermore, only 20-30% of the residue in smoke has been identified, which is not in line with what is stated in the Pesticide Assessment Guidelines: "pyrolysis products derived from the active ingredient must be characterized and the level of residue in smoke must be quantified" [Subdivision O, Residue Chemistry §171-11(3)].

CONCLUSIONS and RECOMMENDATIONS

The data for parent compound only in smoke is not acceptable since this accounts for only 20-30% of the residue

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in smoke, especially in view of the higher proposed rates.

We recommend against this amended registration. The Company must perform additional pyrolysis studies on chlorpyrifos according to the Residue Chemistry Guidelines. Additionally, the use must be limited to one application per season and the label should so be revised.

cc:Circ, RF, Amended Use File, Cheng, Tobacco File
RDI:ARRathman:1/8/85:RDSchmitt:1/8/85
TS-769:RCB:LC:RM810:CM#2:1/8/85:557-7484