US EPA ARCHIVE DOCUMENT

PIRSD/ISB
1894

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

OCT 29 1987

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

Memorandum

Subject: Chlorpyrifos (Lorsban® 4E, EPA Reg No. 464-448) on Tobacco. Amended Registration for Increased Application Rate.
Acc. No. 402652-01

From: Michael S. Metzger, Chemist
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

Thru: Edward Zager, Section Head, SRS 2
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

To: Dennis Edwards, PM 12 Team
Registration Division (TS-767C)

Dow Chemical Company requests Amended Registration for Lorsban® 4E (4 lbs. chlorpyrifos/gallon, emulsifiable concentrate) applications to tobacco. The proposed use would allow an increase in the application rate from 3 to 5 lbs.a.i./A.

Tolerances are established for residues of the pesticide chlorpyrifos (O,O-diethlyl O-(3,5,6-trichloropyridyl) phosphorothioate) and its metabolite 3,5,6-trichloro-2-pyridinol on numerous commodities ranging from 0.05 ppm in or on lima and snap beans to 25 FA ppm in citrus oil. Numerous tolerances are pending (40 CFR 180.342, 180.3(e)(5); 21 CFR 123.85, 193.85, 561.98). A Registration Standard has been completed for chlorpyrifos (Residue Chemistry Chapter, 1/25/84).

Lorsban® 4E is currently labelled for a single application at 2-3 quarts (2-3 lbs.a.i.)/A one week prior to transplanting in a minimum of 10 gallons of water per acre as a broadcast (overall) spray to the soil surface. The insecticide would be incorporated into the soil immediately following application to a depth of 2-4 inches. Lorsban® 4E could also be applied in a tank mix with Nemacur® 3 to control nematode infestations.

The proposed use would increase the maximum application rate to 5 qts. product (5 lbs.a.i.)/A for control of all insects

on the label as well as nematodes. Additionally, tank mix applications with Nemacur® 3 would be made at the same rates as previously (2 lbs.a.i. Lorsban® 4E/A plus 4 quarts Nemacur® 3 /A) but would be made 24-48 hours (rather than 1 week) prior to transplanting. Finally, the proposed label indicates that Telone II Soil Fumigant should be applied at the recommended label rates for infestations of M. arenaria, M. javanica or high populations of M. incognita rather than the directions of the current label which indicate increasing the Nemacur® 3 application rate to 6.67 quarts/A to control the first 2 of these 3 species.

When this amendment ws previously submitted (see review of L. Cheng, 1/9/85), the restriction "do not make more than one application per season" was deleted on the proposed label. In the current submission, this restriction was maintained on the proposed label as indicated by RCB in that review. Therefore, we consider this deficiency resolved.

Residue data for soil applications of Lorsban® 4E and Lorsban® 15G to tobacco fields utilized intervals between application and transplanting of 0-7 days. Therefore, we expect no increase in residues due to the decrease in the interval between application and transplanting from 1 week to 24-48 hours included on the proposed label.

The label modifications indicating that Telone II should be applied for certain insect infestations is not germane to this Lorsban® 4E Amended Registration request and will not be further addressed here.

RCB previously reviewed the available residue data for pre-transplant soil applications of Lorsban® 4E to tobacco fields and estimated that combined residues of chlorpyrifos plus its pyridinol metabolite could be as high as 0.22 - 0.25 ppm in treated tobacco as a result of the proposed use (see L. Cheng, 1/9/85; C. Frick, 7/21/86). RCB, therefore, indicated that pyrolysis studies must be conducted on the pyridinol metabolite of chlorpyrifos (major residue found in tobacco).

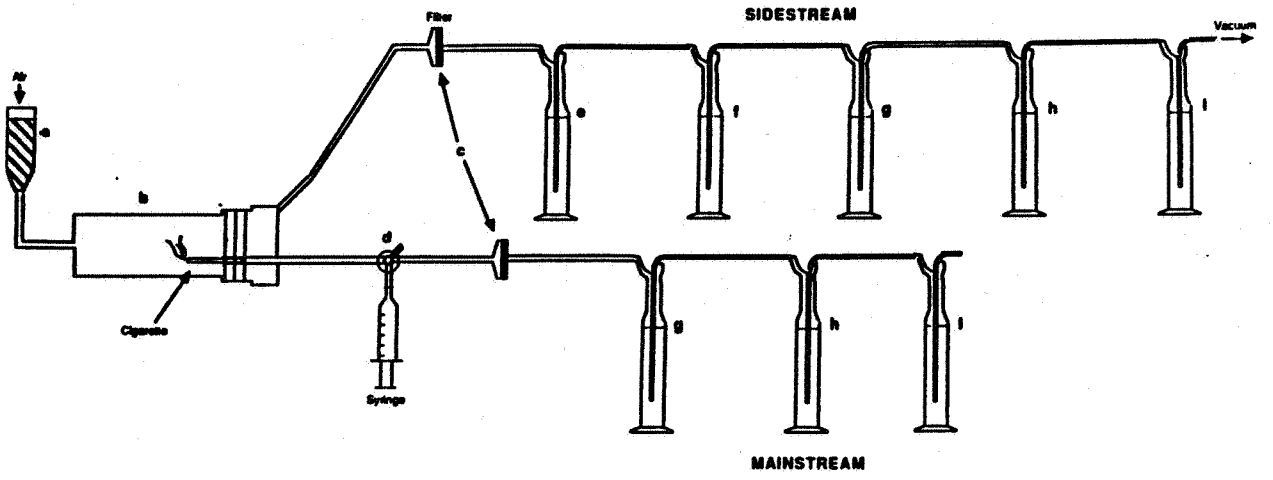
In response, Dow Chemical Company U.S.A. now submits a study titled, "A Study of Pyrolysis of 3,5,6-Trichloro-2-pyridinol in Cigarette Tobacco" (Leon W. Levan, Hazelton Laboratories America, Inc.; P. J. McCall, Agricultural Chemistry R&D Laboratory; 7/1/87).

Five standard reference research cigarettes (Code 2R1, Kentucky Tobacco Institute) were spiked with 117,500 dpm (0.90 ug.) of ^{14}-C-3,5,6-trichloro-2-pyridinol (labelled at C_2 and C_6 positions, 11.6 mCi/mmol, 96.9% radiochemical purity) in acetone solution. The cigarettes were stored in a refrigerator for 24 hours prior to being smoked.

2

Three additional cigarettes were fortified with ^{14}-C pyridinol and stored in the same manner, and were cut into 6 approximately equal sections. Each section was then combusted in a sample oxidizer and total radioactivity was determined. Recovery of radioactivity from these cigarettes was 92.9%.

Cigarettes were smoked in the glass apparatus shown below (copied from report submitted). Each trap shown contained 160 ml. of the specified solvent, and cold baths consisted of 95% ethanol and dry ice.



a. Drying tube
b. Smoking chamber
c. Cambridge filter
d. Three-way stopcock
e. Methanol trap (room temperature)
f. Cold trap
g. Methanol trap (cold)
h. Ethanol trap (cold)
i. CarboSorb trap (only one shown)

Smoking of cigarettes was accomplished in the following manner. A cigarette was placed in the holder, and the system was sealed. Air flow was adjusted to 500 ml. per minute through the system, the smoking chamber was opened, the cigarette was lit, and the smoking chamber was immediately sealed again. The 3-way valve (d) was opened at 1 minute intervals to permit approximately 35 ml. portions of smoke to be pulled into the syringe, and the smoke was then injected through the mainstream traps. Side stream smoke was pulled through the traps in that line by the vacuum pump. Five cigarettes were smoked in this manner. The Cambridge filters were used to collect the tar and paticulate matter from the smoke; the methanol and ethanol traps were used to collect the volatile organic compounds; and the Carbo-Sorb traps were used to collect CO_2.

The Cambridge filters were extracted with methanol, a process which was said to quantitatively remove the radioactivity. This extract was combined with a methanol rinse from the filter holder, and the solution was cleaned up on a silica gel column (see Table 2). The smoking chamber and connecting lines were rinsed with methanol. A list of all fractions collected is shown in Table 1 together with the total radioactivity found in each fraction. Total radioactivity in each fraction was determined by LSC using either a Perma Fluor V cocktail (for Carbo-Sorb) or an Insta-Gel cocktail (for all other solutions). Cigarette butts were combusted in a sample oxidizer and the radioactivity determined by LSC.

Analytical TLC was used to characterize the radioactivity in the smoke fractions. Solvent systems used were chloroform:acetone:glacial acetic acid (3:15:0.5 or 12:6:0.1). Preparative TLC was used to separate radioactive components in the major silica gel column fractions (see Table 2). Major radioactive zones were scraped from the plates and eluted with acetone:methanol (3:2), concentrated, and an aliquot was analyzed by reverse phase HPLC. A second aliquot was reacted with N,O-bis(trimethylsilyl)acetamide (BSA) and analyzed by GC using a flame ionization detector and a radioactivity counter (1:1 split between GC column and detector).

Table 1: Percent Radioactivity in Smoke Fractions

Fraction	Percent of Applied ^{14}C
Mainstream	
Filter extract and line rinse	27.1
Methanol trap	2.75
Ethanol trap	1.54
Carbo-Sorb trap	0.01
Sidestream	
Filter extract	5.89
Line rinse	4.10
Cold trap number 1	0.14
Methanol trap number 1 (room temp.)	1.64
Methanol trap number 2 (cold)	3.35
Absolute ethanol trap	2.27
Carbo-Sorb trap number 1	25.5
Carbo-Sorb trap number 2	0.01
Ashes	1.57
Butts	2.73
Total	78.6

Recovery of radioactivity from the silica gel fractions is shown in table 2 (both Table 1 and Table 2 taken from report from Dow). The presence of significant amounts of radioactivity in the various fractions suggests the presence of multiple radioactive species. However, this is attributed to matrix effects in the report since analysis of some fractions showed TLC migration, HPLC elution volumes and GC retention times for only a single chemical which corresponded to those for unreacted 3,5,6-trichloro-2-pyridinol.

Table 2: Recovery of Radioactivity from Silica Gel Column Fractions (%)

Eluate	Mainstream Filter Fraction	Sidestream Filter Fraction	Sidestream Line Rinse
Hexane	5.8	0.2	0.0
Hexane:chloroform (50:50)	28.3	32.4	51.8
Acetone:chloroform (75:25)	25.5	38.3	36.6
Methanol	31.1	34.7	14.9
Total	90.7	105.6	103.3

Radioactivity from the carbo-Sorb traps was not characterized but was assumed to consist of only $^{14}CO_2$ since these streams were downstream from the solvent traps which would collect volatile organic chemicals.

In summary, the major pyrolysis product of 3,5,6-trichloro-2-pyridinol is the unreacted compound (ca. 51%). CO_2 is also found in significant amounts (ca. 25%). 51% of the radioactivity was characterized (trichloropyridinol), 25% was not characterized but assumed to be CO_2, 4.3% (from the ashes and butts) was not characterized and approximately 20% was not recovered. This corresponds to approximately 0.13 ppm 3,5,6-trichloro-2-pyridinol and 0.06 ppm CO_2 in cigarettes containing 0.25 ppm pyridinol, with 0.06 ppm uncharacterized residue.

Conclusions and Recommendations

The above study adequately characterizes and quantitates the pyrolysis products of 3,5,6-trichloro-2-pyridinol. Additionally, the Lorsban® 4E label has been modified to allow only 1 application per season to tobacco. Therefore, RCB has no objection to this Amended Registration.

cc:Chlorpyrifos (Lorsban®) S.F., R.F., Amended Use S.F., Circu, M. Metzger, PMSD/ISB
RDI:E.Zager:EZ:10/28/87:RDS:10/28/87
TS-769C:RCB:M.Metzger:MM:Rm803a:CM#2:10/28/87