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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#6E3439 (RCB No. 1290). Chlorpyrifos on Dates.
Evaluation of Analytical Method and Residue
Data (Accession No. 264129).

FROM: Nancy Dodd, Chemist *Nancy Dodd*
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

THRU: John H. Onley, Ph.D., Section Head *John H. Onley*
Tolerance Petition Section II
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

TO: Hoyt Jamerson, PM #43
Registration Support and
Emergency Response Branch
Registration Division (TS-767C)

and

Toxicology Branch
Hazard Evaluation Division (TS-769C)

The petitioner, IR-4, on behalf of the IR-4 National Director, Dr. R.H. Kupelian, and the Agricultural Experiment Station of California requests the establishment of a tolerance for the combined residues of the pesticide chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in or on the raw agricultural commodity dates at 0.5 ppm (of which no more than 0.3 ppm is chlorpyrifos). The proposed tolerance with regional registration is for use in California (CA) only.

Tolerances are 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

(TCP) in or on a variety of commodities at levels ranging from 0.05 ppm on banana pulp, nectarines, peaches, pears, and plums (fresh prunes) to 25 ppm (food additive tolerance) on citrus oil (40 CFR 180.342; 21 CFR 123.85, 193.85, and 561.98).

Residue Chemistry Branch (RCB) has recommended (PP#3F2884/FAP#3H5396, K. Arne, January 24, 1984) for proposed revisions of several established tolerances in which the amount of chlorpyrifos per se is specified but the combined residue level of parent plus TCP would not change. Dow Chemical Company proposed the revisions to lower the effect of existing tolerances on the acceptable daily intake (ADI).

A Registration Standard for chlorpyrifos was completed on September 30, 1984.

A letter of authorization dated July 15, 1986 has been sent by Robert Bischoff of Dow Chemical Company to Hoyt Jamerson, RD, OPP, to authorize use of all relevant Dow data concerning chlorpyrifos in support of the IR-4 petition on dates.

Conclusions

1. The nature of the residue in dates is adequately defined for the purposes of this IR-4 petition on the minor crop dates. The residues of concern on dates are chlorpyrifos per se and its metabolite 3,5,6-trichloro-2-pyridinol (TCP) (see also Nature of the Residue section of this review).
 2. Adequate analytical methods are available for enforcement of the proposed tolerance on dates.
 3. Adequate storage stability data are available.
 4. The proposed tolerance of 0.5 ppm (of which no more than 0.3 ppm is chlorpyrifos) is adequate to cover the residues resulting from the proposed use on dates.
 5. No feed items are involved in this proposed use of chlorpyrifos on dates. Therefore, RCB concludes that this use falls in category 3 of section 180.6(a) with respect to residues in meat, milk, poultry, and eggs.
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6. An International Residue Limits (IRL) Status sheet is attached. There are no Codex, Canadian, or Mexican tolerances for chlorpyrifos on dates. Therefore, no compatibility questions exist with respect to Codex.

Recommendation

Providing that the proposed label contains a use restriction for CA only (see Note to PM below) and TB and EAB considerations permitting, RCB will recommend for the proposed use of chlorpyrifos on dates.

Since the proposed use is restricted to dates grown in CA only, any future tolerance for chlorpyrifos on dates should be included in a separate subsection under 40 CFR 180.342 to avoid confusion regarding future 24(c) registrations and crop-grouping eligibility. The "tolerances with regional registration" would be referenced along with future regional registration tolerances in a new subsection (n) under 40 CFR 180.1 which would define the Agency's interpretation of "tolerances with regional registration." An appropriate interpretation for 40 CFR 180.1, subsection "n," would be:

Certain tolerances are based on geographically limited residue data. These "tolerances with regional registration" are included in separate subsections under 40 CFR 180.101 through 180.999. In order to expand the area of usage on these crops, additional residue data generated in these areas will be required. Persons seeking geographically broader registration on these crops should contact the appropriate EPA product manager concerning whether additional residue data are required.

Note to PM: The present Dow label for Polyethylene-D contains the statement "polyethylene containing chlorpyrifos insecticide for the manufacture of banana fruit bags (shrouds)." The statement should be revised to include dates: "polyethylene containing chlorpyrifos insecticide for the manufacture of banana and date fruit bags (shrouds)." The label should also contain the statement that use on dates is restricted to CA; this is in agreement with Section F and the residue data.

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DETAILED CONSIDERATIONS

Manufacture and Formulation

The chlorpyrifos manufacturing process is described in Confidential Appendix A of the Registration Standard. Technical chlorpyrifos is at least 94% pure.

Product chemistry data gaps were cited in the Registration Standard (see Chlorpyrifos Registration Standard and Dow's response to product chemistry data gaps in S. Malak's memorandums dated September 11, 1985 (five different memorandums), September 25, 1985 (two different memorandums), and September 27, 1985; in G. Makhijani's memorandums dated July 30, 1985 and September 19, 1985; in G. Makhijani's and K. Arne's memorandum dated September 27, 1985; in C. Deyrup's memorandum dated February 19, 1986; and in B. Suhre's memorandum dated July 15, 1986.

The formulation proposed for use on dates is Polyethylene-D. The polyethylene contains chlorpyrifos at a concentration of 1% chlorpyrifos and 99% inerts. The Polyethylene-D is used in the manufacture of fruit bags (shrouds). The inerts are cleared under 40 CFR 180.1001 [REDACTED]

[REDACTED] We do not foresee any residue problems involving the subject use on dates with respect to impurities in the formulation.

Proposed Use

Dates in CA: Place bag of Polyethylene-D® over date bunches during the Kimri or Khalal stage of growth. Secure the top of the bag around the bunch stalk and leave the bottom open. (Young, green-colored dates are in the "Kimri" stage. The "Khalal" stage begins when the dates begin to change from green to another color (yellow, pink, red, scarlet, or yellow spotted with red, depending on the cultivar.)

Note to PM: The present Dow label for Polyethylene-D contains the statement "polyethylene containing chlorpyrifos insecticide for the manufacture of banana fruit bags (shrouds)." The statement should be revised to include dates: "polyethylene containing chlorpyrifos insecticide for the manufacture of banana and date fruit bags." The label should also contain the statement that use on dates is restricted to CA.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

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Nature of the Residue

Plants

The nature of the residue in plants has been discussed in RCB's review of FAP#1H5295 on tomato pomace (K. Arne, November 20, 1981) and in the Chlorpyrifos Registration Standard (September 30, 1984). To resolve legume, corn, and root crop metabolism data gaps cited in the Chlorpyrifos Registration Standard, Dow intends to conduct corn and sugar beet metabolism studies. RCB has previously concluded (memorandum of R. Loranger, March 25, 1985) that a legume metabolism study will not be required provided that corn and root crop metabolism studies are provided which identify most of the residue. RCB also concluded that the residue should be identified by GC or HPLC and confirmed by mass spectroscopy (see N. Dodd memorandum of July 15, 1985 re: EPA Registration No. 464-523).

Plant metabolism was recently summarized in connection with PP#6F3358 (S. Malak, September 30, 1986). Radioactive residues in apple peel were 35 percent chlorpyrifos per se, 5.1 to 5.6 percent 3,5,6-trichloro-2-pyridinol (TCP), and 60 percent unidentified. Three additional metabolites have been tentatively identified in corn, soybeans, and beans: 3,5,6-trichloro-2-pyridyl phosphate, O-ethyl O-(3,5,6-trichloro-2-pyridyl)phosphate, and O-ethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate. These three metabolites would probably be determined by an enforcement method which hydrolyzes chlorpyrifos to TCP and determines TCP (such as Method VII in PAM II).

TB has previously indicated that unidentified metabolites and degradates in soybean and apple metabolism studies are not of toxicological significance (see memorandum of K. Arne, PP#1F2620/FAP 2H5331, March 24, 1982 concerning TB memorandums).

RCB previously concluded (PP#6F3358, S. Malak, September 30, 1986) that the metabolism was adequately understood in pears but not for future uses on other than fruit crops. The residues of concern on pears are considered to be chlorpyrifos per se and its metabolite TCP.

Dates are a minor crop.

RCB concludes that the nature of the residue in dates is adequately defined for the purposes of this IR-4 petition on the minor crop dates. The residues of concern on dates (a fruit crop) are chlorpyrifos per se and its metabolite 3,5,6-trichloro-2-pyridinol (TCP).

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For future uses on other than fruit crops, metabolism studies on those crops may be needed. The plant metabolism studies are requested in connection with the Chlorpyrifos Registration Standard (January 25, 1984).

Analytical Methods

The analytical method used to obtain residue data on fresh and processed dates was "Method for Chlorpyrifos and its Metabolite 3,5,6-Trichloro-2-pyridinol (TCP) on Fresh and Processed Dates." The unpublished method, developed by the Trace Analytical Laboratory of the University of California at Davis, determines chlorpyrifos and its metabolite TCP separately. The dates (including seeds) are extracted with acetone/water. The extract is partitioned between a solvent mixture of hexane-benzene and 0.1 M NaHCO₃ solutions to obtain chlorpyrifos in the hexane-benzene layers and TCP in the 0.1 M NaHCO₃ solution. Chlorpyrifos residue in the hexane-benzene solution is cleaned up using a Florisil column eluted with 5% ethyl ether in hexane. Chlorpyrifos is then analyzed by GLC using a N/P detector. The 0.1 M NaHCO₃ solution containing TCP is acidified to pH > 3 and TCP residue is partitioned into benzene. TCP is derivatized with bis(trimethylsilyl) acetamide. TCP is analyzed by GLC using a Hall conductivity detector. The claimed sensitivity of the method is 0.02 ppm for chlorpyrifos and 0.05 ppm for TCP. Recoveries of chlorpyrifos from processed and unprocessed dates fortified at levels of 0.05 to 0.10 ppm were 88 to 110 percent. Recoveries of TCP from processed and unprocessed dates fortified at levels of 0.10 to 0.20 ppm were 79 to 99 percent.

Five enforcement methods for chlorpyrifos in plant commodities are available in PAM II (Methods I, II, III, VI, and VII). EPA has conducted a method try-out on Method II for chlorpyrifos per se in peaches. The present method used to obtain residue data on dates is most similar but not identical to a combination of Method I for analysis of chlorpyrifos and Method III for analysis of TCP.

RCB concludes that adequate analytical methods are available for enforcement of the proposed tolerance on dates.

Residue Data

Storage Stability

The storage stability of chlorpyrifos is discussed in the Chlorpyrifos Registration Standard. Various fruits, vegetables, and nuts were fortified at levels ranging from 0.1 to 1.0 ppm and stored at -18 °C (0 °F) for 5 to 27 months. Residues of chlorpyrifos or TCP ranged from 66 to 109 percent (average 85%)

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of the initial fortification levels. Residues in apples and walnuts stored 4 years were 61 to 105 percent and 82 to 100 percent, respectively, of the initial fortification levels. Residues of chlorpyrifos and TCP in tomatoes stored 29 months at -18 °C were 82 to 88 percent and 89 to 109 percent, respectively, of the initial fortification levels.

Samples of dates were fortified with 0.05 or 0.10 ppm chlorpyrifos or with 0.10 or 0.20 ppm TCP on January 6, 1986 and stored frozen until February 6, 1986. Recoveries for processed and unprocessed dates were 73 to 98 percent chlorpyrifos and 72 to 96 percent TCP.

RCB concludes that adequate storage stability data are available.

Dates

One study was conducted in the Coachella Valley of CA. Plastic bags impregnated with 1% or 2% chlorpyrifos were placed on date bunches when the dates were in the "Kimri" or "Khalal" stages. The bags were 4 ml thick, 20 inches in diameter, and 60 inches long. The open top was wrapped around the bunch stalk and taped with duck tape. Dates were harvested 106 days later, when dates were in the "Tamar" stage (the last stage of development). Samples were stored at -15 °C until shipment to the lab in dry ice. Samples were stored in the lab at -30 °C. Dates were sampled on November 14, 1985 and analyzed in December 1985. Control samples registered < 0.02 ppm chlorpyrifos and < 0.05 ppm TCP. Residues in dates covered for 106 days with the impregnated plastic bags were as follows:

	<u>Residues (ppm)</u>		
	<u>Chlorpyrifos</u>	<u>TCP</u>	<u>Total</u>
1% bag	0.09-0.10*	0.10-0.12*	0.19-0.21
	0.06-0.18**	0.03-0.07**	0.09-0.25
2% bag	0.27-0.37*	0.16-0.24*	0.43-0.61
	0.26-0.59**	0.05-0.08**	0.31-0.66

* Processed

** Field (unprocessed)

RCB concludes that the proposed tolerance of 0.5 ppm (of which no more than 0.3 ppm is chlorpyrifos) is adequate to cover the residues resulting from the proposed use on dates.

Meat, Milk, Poultry, and Eggs

No feed items are involved in this proposed use of chlorpyrifos on dates. Therefore, RCB concludes that this use falls in category 3 of section 180.6(a) with respect to residues in meat, milk, poultry, and eggs.

Other Considerations

An International Residue Limits (IRL) Status sheet is attached. There are no Codex, Canadian, or Mexican tolerances for chlorpyrifos on dates. Therefore, no compatibility questions exist with respect to Codex.

Attachment 1: International Residue Limit Status sheet

cc: RF, Circu, Reviewer-N. Dodd, EAB, EEB, F. Boyd-RCB, PP#6E3439,
FDA, PMSD/ISB-Eldredge

RDI:JH Onley:11/18/86:RD Schmitt: 11/18/86

TS-769:RCB:CM#2:RM 810:X1681:N. Dodd:Kendrick & Co.:11/21/86

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