PP#6E1761

PP#6E1761. Chlorothalonil on papayas.
Evaluation of Analytical methods and residue data

MAY 11 1976

William S. Cox, Chemistry Branch, RD (WH-567)

PM No. 21 (Dr. E. Wilson)
and Toxicology Branch

THRU: Chief, Chemistry Branch, RD

Dr. C. C. Compton, on behalf of the IR-4 Technical Committee and the Agricultural Experiment Station of Hawaii, is proposing the establishment of a tolerance for residues of the fungicide chlorothalonil (tetrachloroisophthalonitrile) and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile in or on papayas at 5 ppm.

Tolerances have been established for residues of chlorothalonil (Sec. 180.275) on a number of commodities at levels of 0.1-15 ppm. Co-pending PP#6F1749 proposes tolerances of 15 ppm and 25 ppm for cherries (sweet and tart) and peaches, respectively.

Conclusions

1. By translation of data from other commodities, we consider the fate of chlorothalonil on papayas to be adequately understood.

2. Adequate methods are available to enforce the proposed tolerance.

3. Residues from the proposed use may exceed the proposed tolerance levels. A tolerance of 15 ppm will be adequate to cover residues resulting from the proposed use.

4. Residues in any edible byproduct of papayas will be below the level in the whole fruit and no food additive tolerance is needed.

5. Since no feed items are involved from this use, Sec. 180.6(a)(3) applies.

Recommendation:

Contingent upon ~~the revision of Section B to limit the proposed use to papayas grown in Hawaii only and~~ the amending of Section F to propose a tolerance level of 15 ppm, and if TOX and EEE considerations permit, we recommend for the establishment of the tolerance of 15 ppm for residues of chlorothalonil and its 4-hydroxy metabolite in or on papayas.

IMPURITY INFO NOT INCLUDED

INERT INGREDIENT INFORMATION IS NOT INCLUDED

Detailed Considerations

Chlorothalonil is formulated as Bravo 6F containing 6 lbs. of chlorothalonil/gal. In PPs#4E1502 and 5E1569, it was noted that one of the inerts was identified only as [redacted] By telecon between W. S. Cox/J. Lucietta, Diamond Shamrock, we have learned that [redacted] and is listed under 180.1001(c) as [redacted] All other inerts are cleared under 180.1001(c) or (d).

Technical chlorothalonil is 95.6-98.5% pure. Impurities consist of [redacted] A description of the manufacturing process was submitted in connection with PP# 4E1502 and discussed in the Dr. R. Schmitt memo of 11/27/74.

The possibility of HCB in the technical product and as a residue was discussed in the Dr. R. Schmitt, 10/27/74 review of PP# 4E1502. It was concluded at that time, and we concur, that no residue problem of HCB residues existed from the use of chlorothalonil.

Proposed Use

Chlorothalonil is to be applied to papayas in Hawaii only at the rate of 3 lbs. act/A by ground. Multiple applications (up to 12) may be made at fourteen day intervals with a PHI of 14 days. The proposed labeling contains restrictions against grazing treated areas of feeding byproducts after processing to livestock used for food. While the restriction against feed use of byproducts is not usually considered practical, the peel or seeds from processing of papayas are not likely to be used as an animal feed. Therefore, we are not objecting to this restriction.

Nature of the Residue

The metabolism of chlorothalonil has been discussed most recently in connection with PP# 4E1502 (Dr. R. Schmitt review dated 7/22/74). No additional metabolism data have been submited with this petition.

The parent compound and small amounts of the 4-hydroxy metabolite constitute the residue of concern in plants. This conclusion is based on 14C studies on corn and tomatoes and cold studies on potatoes in which other possible metabolites were not detected. The 4-hydroxy metabolite is the principal component of the residue in soils (70%) but on plants the 4-hydroxy metabolite is at most 10% of the residue. Data in this petition show that there are only trace residues (<0.1 ppm) of the 4-hydroxy metabolite.

Foliar deposits of chlorothalonil do not translocate and there is no uptake from roots to aerial plant parts. Residues on fruit are almost entirely surface deposits.

We consider the fate of chlorothalonil on papayas to be adequately understood.

Analytical Method

The data submitted were obtained by a slightly modified version of the analytical procedure submitted in appendix II to the amended Section D of PP# 9F0743. This same modified method was used in connection with PP# 5E1569 (chlorothalonil on passion fruit).*

The method consists of an acidified-acetone extraction, separation of the parent from the 4-hydroxy metabolite on a florisil column, methylation of the 4-hydroxy metabolite using diazomethane and separate GLC detection of parent and metabolite with an electron capture detector.

This method underwent a successful tryout in our (AMS) laboratory on peanuts (0.3 and 0.6 ppm) and broccoli (2.5 and 5 ppm) for both parent and the 4-hydroxy metabolite.

Papaya fruit (whole) were fortified with chlorothalonil or the 4-hydroxy metabolite at levels of 0.1 to 1.0 or 0.1 ppm, respectively. Chlorothalonil recoveries ranged overall from 82-103% with most in the range of 85-96%. Recoveries of the 4-hydroxy metabolite ranged overall from 77-104% with most in the range of 92-100%. Control samples contained essentially N.D. residues ($\leq$0.01 ppm) of chlorothalonil and the 4-hydroxy metabolite.

We consider the available methodology adequate for enforcement and appropriately validated with respect to the residue data.

*Confirmed by telecon D. H. Baker, Jr./E. Harkel (IR-4 Technical Committee), 4/19/76.

Residue Data

Storage stability data for residues of the parent compound and its 4-hydroxy metabolite were not presented in this petition. However, adequate storage stability data for such residues were presented most recently in connection with PP#5E1569 (see memo of A. Rathman, 3/4/75).

The available residue studies are quite limited; these are comprised of two studies conducted at two different sites in Hawaii. In each study, papayas were treated at 1.5, 3.0 and 6.0 lbs. act./A (representing 0.5, 1 and 2X the maximum recommended rate on papayas). A total of three applications were made in each study with the recommended 14-day interval being observed between each application. Following the first spray, samples were taken at 0, 1, 2, 3, 7 and 14 days; samplings were made at 14 days after each of the second and third sprayings. It should be noted that the proposed use pattern would permit up to twelve applications per season versus the three made in the residue studies.

At zero day after the first spray, maximum combined residues of parent and metabolite from the recommended (1X) maximum rate were 2.4 ppm. From the 0.5 X rate, the maximum found was 1.2 ppm (which converts to 2.4 ppm when adjusted to the 1X rate). From the 2X rate, the maximum reported was 5.2 ppm (which converts to 2.6 ppm when adjusted to the 1X rate). As indicated under Nature of the Residue, residues of the 4-hydroxy metabolite were essentially negligible (≤0.1 ppm), regardless of the number of treatments or the rates of treatment involved.

At the end of the studies (3 applications at 14-day intervals), the following maximum residues were noted at a 14 day PHI (after adjusting the 0.5 and 2.0X rate to 1X): 2.4 ppm, 3.2 ppm and about 4.0 ppm for the 0.5, 1 and 2X application rates respectively.

Due to the limited number of studies and residue values reported, there is no clearcut indication of buildup of residues from replicate applications at biweekly intervals. In some cases, there appears to be a decline of residues from the second application to the third; in other cases, there appears to be a slight buildup from the first to the second to the third. Overall, a conservative interpretation of the data indicates that there may be a slight but continuing accumulation of residues following replicated applications. Despite the meagerness of the data and the absence of any study reflecting the permitted 12 applications, we conclude that residues, at harvest from 12 applications at the recommended rate would fall into the range of 10 to 15 ppm. There is further assurance that a tolerance of 15 ppm would be adequate in that growth dilution was not considered in estimating that 15 ppm would be adequate. For this minor crop it is not necessary that additional residue studies be conducted to determine with more precision the actual level necessary to cover residues resulting from the proposed use.

In this connection, it should be noted that neither lengthening the proposed PHI nor reducing the number of applications per year would be practical. Papayas bear blossoms and fruit the year round (as in the case of some varieties of lemons); thus, the developing fruit must be protected the year round and the regular treatments at 14-day intervals are necessary to control the various fungi in Hawaii.

Overall, we conclude that the proposed tolerance of 5 ppm is not adequate, but that one of 15 ppm would be adequate.

Byproducts of Papaya

Most papaya is consumed as a fresh fruit. Some papaya is converted into papaya juice (by pressing the pulp after peeling) or papaya nectar (papaya juice plus added pulp). Small amounts of the rind may be processed into preserves as in the case of watermelon rind preserves.

In all the cases of processed byproducts, the papayas are washed prior to processing; since chlorothalonil residues are surface residues, most of the residues would be removed during the washing process (see data discussed in PP#5E1569, memo of 3/4/75, re processing of passion fruit). Based on the available data, we conclude that a food additive tolerance is not necessary for any byproduct of treated papayas.

Residue in Meat, Milk, Poultry and Eggs

Because there are no livestock or poultry feed items involved in this petition, the proposed use can be placed into Section 180.6(a)(3).

W. S. Cox

cc: TOX, EEE, HFO-130 (FDA), CHM(5)
WH-567:CHM:W.S. Cox:rl:5/7/76:WSME RM-117
RDI:RSQuick 5/2/76, JGCummings: 5/4/76