

US EPA ARCHIVE DOCUMENT

*Petition*

*6/2/76*

PP #6F1749. Chlorothalonil on cherries and peaches.  
Evaluation of analytical methods and residue data.

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

PM No. 21 (Dr. E. Wilson)  
and TB

THRU: Chief, Chemistry Branch, RD

Diamond Shamrock Chemical Company, a unit of Diamond Shamrock Corporation is proposing the establishment of tolerances for residues of the fungicide chlorothalonil (tetrachloroisophthalonitrile) and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile in or on cherries (sweet and tart) at 15 ppm and in or on peaches at 25 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 #6E1761 is proposing a tolerance of 5 ppm for papayas.

#### Conclusions

1. By translation of data from other commodities, we consider the fate of chlorothalonil on cherries and peaches to be adequately understood.
2. Adequate methods are available to enforce the proposed tolerance.
3. (a) Residues from the proposed use on peaches will not exceed the proposed tolerance of 25 ppm.  
(b) Residues from the proposed use on cherries may exceed the proposed tolerance of 15 ppm. A tolerance of 25 ppm for cherries will be needed to cover such residues.  
(c) Conclusions 3(a) and (b) pertain to peaches and cherries grown in states east of the Mississippi River. The data for fruit (peaches and cherries) grown in the Mountain and West Coast States are too meager to allow us to make any conclusions as to an adequate tolerance level for the proposed uses in these areas. Consequently, the label must be amended to prohibit the use of chlorothalonil in the Mountain and West Coast States except when used for control of peach leaf curd (dormant applications only).
4. The proposed uses do not involve any feed items and Section 180.6(a)(3) applies. This conclusion is contingent upon the petitioner amending the label to include a restriction against the grazing of treated orchards.

Recommendation

Because of Conclusions 3(b), 3(c) and 4, we recommend that the proposed tolerances not be established. For further consideration of the proposed tolerances, the following should be submitted:

(1) An amended Section F increasing the proposed tolerance for cherries to 25 ppm.

(2) An amended Section B (label) reflecting the following restrictions:

"Do not allow livestock to graze treated areas."

"Do not use on cherries (or peaches) grown in either the Mountain States or the West Coast States" except for use on peaches to control peach leaf curl. Alternatively, adequate residue data for peaches and cherries grown in those states should be submitted to support the proposed post-petal fall uses.

Detailed Considerations

Chlorothalonil is formulated as Bravo 6F containing 6 lbs. of chlorothalonil/gal. All the inerts are cleared except for [REDACTED]. As in the case of PP# 4E1502 (chlorothalonil on onions), we would expect no residue problems from this low level of surfactant.

Technical chlorothalonil is 95.6-98.5% pure. Impurities consist of [REDACTED]

[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 Uses

Cherries: For the control of various fungi, Bravo 6F is to be applied by diluting up to 1.5 pints (1.1 lbs. act) in 100 gallons of water and spraying cherry trees with the following limitations:

Do not apply within 7 days of harvest. Do not exceed 15 pts (11.25 lbs. active) per acre per application. Apply by ground application only.

After petal fall, applications are to be made at 10 to 14 day intervals.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

IMPURITY INFO IS NOT INCLUDED

**Peaches:** For all uses on fungi except peach leaf curl (West Coast only), Bravo 6F is applied as directed for cherries and with the same limitations as to PHI and as to ground equipment only. However, the maximum number of pts per application is limited to 7.5 (equivalent to 5.6 lbs. active) per acre. After petal fall, applications are to be made at 10 to 14 day intervals.

**Note:** As to the use against peach leaf curl (West Coast only), this use involves application of the same rates as indicated above but during the dormant season; the label does permit a followup application 14 to 21 days after the "dormant" application. We would expect essentially no residues from this type of use.

In this connection (and as noted below under Residue Data), the residue data reflecting use in the growing areas in the Mountain and West Coast States (most of which are arid and require irrigation) is very meager for cherries and non-existent for peaches. The few available studies are inadequate for us to make any conclusions as to the adequacy of the proposed tolerances with respect to use of chlorothalonil on peaches and cherries grown in such areas. Consequently, in the absence of such data, the label must be amended to prohibit the use of Bravo 6F on cherries and peaches grown in the Mountain and West Coast States except for the use against peach leaf curl (dormant application only). Alternatively, the petitioner should present adequate residue data reflecting the proposed post-petal fall applications to cherries and peaches grown in the Mountain and West Coast States.

Finally, the label does not bear any restriction against the grazing of treated orchards. While not common, some orchards are planted to cover crops and in the absence of any tolerances for meat and milk, a grazing restriction will be needed for our favorable consideration of the proposed <sup>tolerances.</sup>

#### 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 submitted with this petitions.

The parent compound and small amounts of the 4-hydroxy metabolite constitute the residue of concern in plants. This conclusion is based on <sup>14</sup>C 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. Foliar deposits of chlorthalonil do not translocate and there is no uptake from roots to aerial plant parts. By translation of the available studies for several species of plants and animals, we conclude that the fate of chlorthalonil on cherries and peaches is adequately understood. The parent compound and the 4-hydroxy metabolite are the only components of concern in plant and animal residues.

Analytical Method

The data submitted were obtained by essentially the same procedure outlined in PAM II.

The PAM II 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.

The major modification in the currently submitted procedure is the substitution of n-propyl-3-p-tolyltriazene for diazomethane as the reagent used in the conversion of the 4-hydroxy metabolite to the corresponding (volatile) ether. Since the 4-hydroxy metabolite comprises an insignificant portion of the residue on cherries and peaches, we are not questioning the modified method.

In addition, the petitioner presents comparative studies reflecting surface extraction versus extraction after maceration; these studies show that, for cherries and peaches, recoveries via surface extraction (stripping) are generally higher than those generated via extraction after maceration.

The petitioner reports the following validation data for the modified method:

<u>Substrate</u>	<u>Fortification and level</u>	<u>Recovered</u>	<u>Blank (apparent ppm in controls)</u>
Cherries	0.13 to 1.0 ppm chloro-thalonil	107% (average for surface ext.)  89.4% (average for ext. of macerate)	0.21 ppm or less (see note)
"	0.13 ppm 4-hydroxy metabolite	92.9% (average for ext. of macerate)  No data for surface extraction.	0.03 ppm or less

<u>Substrate</u>	<u>Fortification and level</u>	<u>Recovered</u>	<u>Blank (apparent ppm in controls)</u>
Peaches	0.1 to 0.74 ppm chloro-thalonil	101.4% (average for surface ext.)  93.7% (average for ext of macerate)	0.13 ppm or less
"	0.1 to 0.2 ppm 4-hydroxy metabolite	95.4% (average for ext. of macerate)  No data for surface extraction	0.09 ppm or less

While these fortifications used are well below the proposed tolerance levels, we find the validation data to be adequate as we would expect recoveries at higher levels to be more consistent than those generated at levels of 1 ppm or less.

#### Residue Data

**Cherries:** Except for some limited (and essentially non-pertinent) studies from Oregon and Washington, all the data for cherries reflect studies conducted in Michigan and Wisconsin. Even the data from Wisconsin are limited and only one study from that state reflects the proposed use with respect to the number of applications and PHI. However, for purposes of estimating residues on cherries grown in the states east of Mississippi only, we conclude that studies from Michigan and Wisconsin are adequate. On the other hand, the available data for states west of the Mississippi are too meager for us to make any conclusions with respect to residues which might occur in cherries grown in such major producing areas as California, Washington and Oregon.

After adjusting the dose rates used in the various studies to the proposed rate (1.5 pts. Bravo 6F/100 gallons), and considering the fact that some studies (on peaches) show essentially no losses between the day of the last of seven applications and the proposed 7-day PHI, the data support a conclusion that residues on cherries from the proposed use on cherries could approach but not exceed a level of 25 ppm versus the proposed tolerance of 15 ppm. While it is true that most of the adjusted residue data reflect levels much lower than the 25 ppm level, the data are too limited and too erratic to support a tolerance level lower than 25 ppm.

Overall, we conclude that the proposed tolerance level of 15 ppm for cherries is not adequate; one of 25 ppm would be adequate. Furthermore, in the absence of adequate data for cherries grown in the arid areas of the Mountain States and the West Coast States, the label should restrict the proposed use to cherries grown in the states east of the Mississippi

River. According to R. E. Michell, EEE, RD, the fungal diseases of cherries and peaches are not a serious problem in the western part of the United States. Thus, we are not depriving the petitioner of a valuable use by prohibiting the proposed uses in the Mountain and Pacific Coast States.

Peaches: The data for peaches <sup>are</sup> much more adequate than ~~that~~ <sup>those</sup> for cherries in that there is an appreciably larger number of studies and there is a broad geographical representation of states east of the Mississippi River. However, there are no data whatsoever for peaches grown in the states west of the Mississippi.

Except for one calculated value of 27.0 ppm on zero day (after adjustment to 1X) all the residue data support a conclusion that the proposed tolerance of 25 ppm is adequate. These studies were run at 2/3X, 1X and 1.17X the proposed application rate. These were run concurrently with the 2X application rate study which produced the one value of 27 ppm. This one calculated value is one of three replicates which had a calculated average of 22.6 ppm (after adjustment to the 1X rate).

Overall, we conclude that the proposed tolerance of 25 ppm for peaches is adequate. However, since there are no data at all for the peaches grown in areas west of the Mississippi River, the label must be amended to prohibit the use of chlorothalonil on peaches grown in the Mountain States on the West Coast States. (Since some peaches are grown commercially in Missouri and Arkansas, we cannot restrict the use to states east of the Mississippi.

#### Residues in Meat, Milk, Poultry and Eggs

Cherries and peaches are not considered to be animal or poultry feed items; thus, as far as the fruit are concerned the proposed uses fall into Section 180.6(a)(3). However, the label does not bear any restriction against the grazing of treated orchards; while not common, some orchards are interplanted to cover crops which may be grazed by cattle. In the absence of a grazing restriction or a tolerance proposal for grasses, we are unable to categorize the feed uses of such cover crops.

A restriction against the grazing of animals in treated areas will allow us to place the proposed uses in category 3 of Section 180.6(a).

#### Other Considerations

Except for dried peaches, none of the edible processed byproducts of cherries and peaches involve items which could bear concentrated residues of chlorothalonil. As we do not set food additive tolerances for dried peaches (on the basis that they are reconstituted with water prior to consumption), there is no need for a food additive tolerance in connection with the proposed uses.

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cc: TOX, EEE, HFO-130(FDA), CHM(5)