5-3-82

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

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MAY 3 1982

Memorandum

Subject: PP#2F2602 Chlorothalonil on stone fruits. Evaluation of analytical method and residue data including 3/26/82 amendment.

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and

Toxicology Branch
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Diamond Shamrock Corporation proposed a tolerance for residues of chlorothalonil (which include the parent plus a metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile) on stone fruits at 0.2 ppm when the petition was submitted. With the 2/26/82 amendment, tolerances were revised and proposed for the individual fruits as follows:

Apricots	0.2 ppm
Cherries (sweet and sour)	0.5 ppm
Nectarines	0.2 ppm
Peaches	0.3 ppm
Plums	0.2 ppm
Prunes	0.2 ppm

Chlorothalonil tolerances are established for several commodities ranging from 0.05 ppm for the edible pulp of bananas to 15 ppm for celery and payayas (40 CFR 180.275). Tolerances are pending for peaches (25 ppm) and cherries (15 ppm) from late season uses.

Conclusions

1. The nature of the residue is adequately understood. The residue of concern consists of parent plus the metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile.

2. Hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN) are impurities in the technical material at levels of up to 0.05 and 2.5%, respectively. Because these impurities would be applied at a low rate and since the proposed PHI is relatively long we do not expect them to present a residue problem. Furthermore, neither of these compounds were detected (HCB <0.004 ppm and PCBN <0.008 ppm) in residue experiments reflective of the proposed use.

3. The proposed application rates are expressed in terms of lb a.i./A. Applications to orchard crops are more meaningfully expressed in terms of lb a.i./100 gallons of spray applied to runoff; the petitioner should submit a revised Section B in which this is done.

4. Adequate analytical methods are available for enforcement purposes.

5a. The proposed use on plums is a bloom use and will not cause the proposed 0.2 ppm tolerance to be exceeded.

5b. The proposed use on fresh prunes is a bloom use and will not cause the proposed 0.2 ppm tolerance to be exceeded. (No detectable residues of chlorothalonil, the 4-hydroxy metabolite, HCB or PCBN resulted on either plums or fresh prunes from the proposed use). Since this use did not result in any detectable residues in fresh prunes we do not expect any residue in dried prunes. No food additive tolerance is needed.

5c For peaches, nectarines and apricots the highest residue found as a result of the shuck split application was 0.82 ppm from a 3.3x rate. Based on this study we conclude that a tolerance of 0.5 ppm is needed for peaches, nectarines, and apricots. The petitioner should submit a revised Section F in which these tolerances are proposed.

5d. From a slightly exaggerated application to cherries at the shuck split stage residues as high as 0.46 ppm were found. Based on this study we conclude that a tolerance of 0.5 ppm is needed.

6. Since the proposed use does not invlove any items normally used for livestock feed there will be no problem of secondary residues in meat, milk, poultry, and eggs.

7. An International Residue Limit Status sheet is attached. There ia a temporary Codex MRL for chlorothalonil on cherries at 10 ppm. Since we do not expect residues greater than 0.5 ppm on cherries as a result of the proposed use these tolerances cannot be made compatible.

Recommendation

Toxicological considerations permitting, we recommend for the tolerances proposed for prunes, plums and cherries. For the other fruits under consideration, a revised Section F in which the following tolerances are proposed should be submitted.

Apricots	0.5 ppm
Peaches	0.5 ppm
Nectarines	0.5 ppm

The petioner should also submit a revised Section B in which the application rate is expressed as lb a.i./100 gallons spray applied to runoff or an equivalent amount applied as a low volume spray.

Detailed Considerations

Manufacture and Formulation

The manufacturing process for technical chlorothalonil was discussed in our review of PP#4E1502 (memo of 11/27/74, R. Schmitt).

Hexachlorobenzene (HCB) was reported to be a contaminant (at an average level of [redacted] in 8% of 308 batches of technical chlorothalonil that were analyzed (PP#8E2025, memo of 12/28/78, T. McLaughlin). A second impurity in the technical material is pentachlorobenzonitrile (PCBN) which may be present at levels of up to 2.5% (see PP#1E2473, memo of 3/4/82, K. Arne). Because these compounds would be applied at low rates and since the proposed PHI is relatively long we do not expect them to present a residue problem. HCB and PCBN were not detected in residue experiments reflective of the proposed use for any of the fruits involved.

IMPURITY INFO IS NOT INCLUDED

The formulation proposed for use on stone fruits is Bravo 500 which contains 4.17 lb a.i./gallon (500 g/L). This formulation was described in our review to an amendment to PP#6F1799 (see memo of 3/13/80, P.V. Errico). All inerts are cleared under 180.1001.g

Proposed Use

For control of leaf curl and coryneum blight on peaches, nectarines and apples, 4 1/2 to 6 pints (2.3 to 3.1 lb a.i)/A Bravo 500 are applied in late autumn. One to two additional applications are made in mid to late winter before the buds begin to swell. Where coryneum blight occurs one application is to be made at petal fall and one at the shuck split stage.

For control of brown rot, blossom blight and scab on peaches, nectarines, and appricots, applications (at the rate indicated above) are to be made at popcorn (pink or red bud) and at full bloom. If weather conditions favor disease development, an additional application is to be made at petal fall. An application is to be made at such split to control peach/nectarine scab. No application is to be made after shuck split and before harvest.

For control of brown rot and blossom blight in cherries, plums and prunes, 4 1/2 to 8 pts (2.3-4.2 lb a.i.)/A (6 to 8 pt/A for sweet cherries Bravo 500 are to be applied at the popcorn early white bud) stage. (If weather conditions favor disease development, another application is to be made at the popcorn (early white bud) stage.) In addition to these, one 4 1/2 to 6 pt/A application is to be made at shuck split to cherries for control of cherry leaf spot. For control of cherry leafspot after harvest, one application is to be made within 7 days after fruit removal. In orchards with a history of high leafspot incidence, a second application is made 10-14 days later.

Applications to orchard corps are more meaningfully expressed as lb a.i./100 gallons spray applied to runoff. The petitioner should submit a revised Section B in which the above directions are expressed in these terms.

Nature of the Residue

No new metabolism studies were submitted with this petition. The metabolism of chlorothalonil in plants and animals has been reviewed in detailed in conjunction with earlier petitions (PP#s 7F0599, 1F1024, 2F1230, 4F1502, 6F1799 and 6G1871). Based on the available studies for several species of plants (corn, tomatoes, potatoes) and animals (dogs, rats, cows) we conclude that the nature of the residue is adequately understood.

The residue in plants is mainly surface in nature. Foliar deposits of chlorothalonil do not translocate and there is no uptake from roots to aerial plant parts.

The parent compound and the 4-hydroxy metabolite constitute the residue of concern in plants and animals. The 4-hydroxy metabolite is a minor component of the residue but is of concern because of its transfer potential to meat and milk.

Analytical Method:

The method of enforcement for determination of residue of chlorothalonil and its 4-hydroxy metabolite is outlined in PAM II; in essence it entails the simultaneous extraction of parent and metabolite from the crop using acidified acetone, separation of the two on a florisil column, conversion of the metabolite to its methyl ether and determination of the derivative and parent compound via MC-or EC-GLC.

Most of the residue data submited with this petition include analyses for HCB and PCBN; these compounds are isolated by varying the eluants used for column chromatography and are then determined by GC.

The following check and recovery values are submitted for peaches:

Compound analyzed	Check (ppm)	Recovery Fort.(ppm)	Range(%)	Avg.(%)
Parent	<0.03	0.8-9.3	69-101	83
Metabolite	<0.03	0.03-0.35	58-75	69
HCB	<0.004	0.006-0.036	60-90	71
PCBN	<0.0005	0.011-0.077	58-86	71

Acceptable check and recovery values are also submitted for cherries, nectarines, plums, and apricots. Adequate analytical techniques are available for enforcement purposes.

We consider sensitivity of the method to be about 0.03 ppm for parent and the 4-hydroxy metabolite, 0.004 ppm for HCB and 0.008 ppm for PCBN.

Residue data

The petitioner originally proposed a tolerance for the crop group stone fruits but with the 3/26/82 amendment revised Section B to propose tolerances for each fruit. This is appropriate because 1) non-neglibible residues are expected (a group tolerance for stone fruits is allowable only when expected residues are negligible) and 2) because of different use patterns higher residues are expected on cherries, peaches, nectarines, and apricots than on plums and prunes.

In several of the submitted residue experiments, HCB and PCBN levels were determined. In no instance was HCB detected (<0.004 ppm). In one experiment, PCBN was found at a level of 0.009 ppm as the result of a 3.3x application to peaches at the shuck split stage. We do not expect detectable levels of these compounds as a result of the proposed use.

In no experiments representative of the proposed use were detectable levels of the 4-hydroxy metabolite found. In the following discussions, the residue referred to is that of the parent compound.

Peaches

Residue experiments were carried out in California, Washington, Louisiana, Oregon and Missouri. The highest residue found from experiments approximating the proposed use (in terms of time of application) was 0.82 ppm which resulted from 3 applications of 20 pts (10.4 lb a.i.)/A (3.3x), the last at the shuck split stage (1-2 weeks after petal fall).

In three other experiments, mature peaches from trees that had been treated with 1-3 applications of 3.75 to 8 pints (1.95 to 4.17 lb a.i.)/A, the last at or shortly after shuck split, were found to contain no detectable levels of parent or metabolites. A total of 12 samples were analyzed.

In experiments where the last of three applications of 10 pts (5.21 lb a.i.)/A (1.7x) was made at petal fall, the highest residue found in mature fruit (PHI = 17 days) was 0.12 ppm.

Several experiments in which peaches were treated with up to three applications of 8.5-16 pts (4.4-8.3 lb a.i.)/A, the last at full blossom, resulted in no detectable residues except for one sample that carried residues at the level of detection (0.03 ppm).

Based on the 0.82 ppm value found as a result of a 3.3x application we conclude that a tolerance of 0.5 ppm is needed for peaches. The proposed tolerance (0.3 ppm) is inadequate. This level would be the same as we are recommending for apricots, cherries and nectarines.

Nectarines

Three experiments (including two submitted with 3/26/82 amendment) to determine residues of chlorothalonil in nectarines were carried out in California. In one experiment, 2 applications of 16 pts (8.3 lb a.i.)/A (2.7x) were made, the second at petal fall. No detectable residue was found in the mature fruit 141 days later.

Two experiments involved application up to the time of 60-85% bloom. This resulted in no detectable residues at harvest. Based on the data submitted for peaches (for which the use is the same), we conclude that a tolerance of 0.5 ppm is needed for nectarines.

Apricots

Four residue experiments for apricots are available, two in the 3/26/82 amendment. One to three applications of 2 to 4 pts (1.05 - 2.1 lb a.i.)/A were made, the latest at petal fall. No residues were detected at harvest, 109 to 121 days later. No data representative of shuck split application to apricots is available. Based on the peach residue data we conclude that a tolerance of 0.5 ppm is needed for apricots.

Cherries

Residue experiments were carried out in Oregon and New York. Two to four application of 6 to 10 pints (3.1 to 5.2 lb a.i.)/A were made, the last at either shuck split (7 experiments) or full bloom (1 experiment). Treatments involving shuck split applications resulted in residues of up to 0.46 ppm as the result of a slightly exaggerated rate (8 pts/A; the label limits the shuck split application to 6 pts/A.) (The PHI varied from 55-76 days.) Most residues found were low (<0.1 ppm). Based on the 0.46 ppm value, we conclude that a 0.5 ppm tolerance is needed for cherries.

Plums

Residue experiments for plums were carried out in California and Washington. Applications of 6 to 20 pts (3.1-10.4 lb a.i.)/A were made up to petal fall. In one study, 3 applications of 20 pints/A, the last at petal fall (no application beyond petal fall is proposed for plums), resulted in no detectable residues at harvest, 96 days later. We conclude that the proposed tolerance of 0.2 ppm is adequate for plums.

Prunes

Residue experiments for fresh prunes were carried out in Oregon. Prunes were treated with 1-2 applications of 4 1/2 to 6 pints (2.3 to 3.1 lb a.i.)/A, the last at petal fall (as proposed in Section B). No residues were detected at harvest, 113 days later. Based on this data and the above plum data, we conclude that the proposed tolerance of 0.2 ppm for prunes is adequate. Since we expect no detectable residues in prunes, we expect none in dried prunes and a food additive tolerance isn't needed.

Meat, Milk, Poultry and Eggs

Since no feed items are involved here, there will be no problem of secondary residues in meat, milk, poultry, and eggs.

TS-769:RCB:KArne:vg:CM#2:Rm810:X77324:4/27/82
cc: RF, Circ, Arne, Thompson, FDA, TOX, EEB, EFB, PP#2F2602
RDI: Quick, 3/14/82 Schmitt, 4/14/82

INTERNATIONAL RESIDUE LIMIT STATUS

K. Arne

CHEMICAL Chlorothalonil

PETITION NO. 2F2602

CCPR NO. 81

CODEX STATUS

/ / No Codex Proposal
Step 6 or above

RESIDUE (If Step 9): sum of chlorothalonil and 4-hydroxy-2,5,6-trichloro-1,3-benzenedicarbonitrile, expressed as chlorothalonil

Crop(s)	Limit (mg/kg)
cherries	10 1/

PROPOSED U.S. TOLERANCES

RESIDUE: Parent plus 4-hydroxy-2,5,6-Trichloroisophthalonitrile

Crop(s)	Tol. (ppm)
apricots	0.2 ppm
cherries (sweet and sour)	0.5 ppm
nectarines	0.2 ppm
peaches	0.3 ppm
plums	0.2 ppm
prunes	0.2 ppm

CANADIAN LIMIT

RESIDUE: _____

Crop	Limit (ppm)
none	(on stone fruits)

MEXICAN TOLERANCIA

RESIDUE: presumably parent

Crop	Tolerancia (ppm)
peaches	25

NOTES: 1/ Temporary Codex limit pending submission of additional acceptable TOX studies.