Memorandum

SUBJECT: PPA41ZP723. Chlorothalonil on mint. Evaluation of residue data and analytical method.

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TO: Clinton Fletcher, Product Manager No. 43
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and
Toxicology Branch
Hazard Evaluation Division (TS-769)

THRU: Charles L. Trichilo, Chief
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

The IR-4 Technical Committee and the Agricultural Experiment Stations of Indiana, Michigan and Wisconsin propose a tolerance of 0.1 ppm for the combined residues of chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) and its hydroxy metabolite (4-hydroxy-2,5,6-trichloroisophthalonitrile) in or on mint hay.

There are several chlorothalonil tolerances established on various RAC’s ranging from 0.05 ppm for the edible pulp of bananas to 15 ppm for celery and papayas. Tolerances are pending for cherries (0.1 ppm), peaches (25 ppm), soybeans (0.2 ppm), grapefruit (0.1 ppm) and oranges (0.1 ppm). Submitted with this petition is a letter of authorization (1/14/81, R.P. Burton to C. Fletcher, Minor Use Officer, RD) from the Diamond Shamrock Corporation.

Conclusions:

1a. The nature of the residue is adequately understood. The residue is expected to consist primarily of the parent and metabolite, 4-hydroxy-2,5,6-trichloroisophthalonitrile.

1b. An impurity in the technical material that may present a residue problem is hexachlorobenzene (HCB). We defer to TOX as to their concern over residues of HCB in mint oil that, by our estimate, may reach 0.1 ppm.

1c. A second impurity that may present a residue problem is pentachlorobenzonitrile (PCBN). We have recently asked the manufacturer to analyze the technical material for this impurity. Until this data is submitted we can make no conclusion as to the significance of PCBN in mint.
2. Adequate analytical methods are available for enforcement of the proposed tolerance.

3a. Before we can make a conclusion as to an appropriate tolerance the petitioner should explain the disparity between results of residue tests incorporating the 1X rate, which showed residues in fresh mint hay of <0.1 ppm, and the results of tests incorporating the 2X rate from which combined residues of up to 3.0 ppm were realized.

3b. No detectable residues of the parent and its hydroxy metabolite are expected in mint oil. However, HCB may be present (see conclusion 1b).

3c. Since the residue data is from one state only (Indiana) the use of chlorothalonil must be limited to the mint producing states of the midwest (Michigan, Wisconsin and Indiana). Wilder use will require representative residue data.

3d. The proposed use (Section B) is for spearmint; the tolerance is proposed for mint (Section F). Sections B and/or F should be revised in such a way that the use is consistent with the tolerance. We have no objection to a use that would include peppermint as well as spearmint.

4. Since the proposed use includes a label feeding restriction there will be no problem with secondary residues in meat, milk, poultry and eggs.

5. An International Residue Limit Status sheet is attached. No chlorothalonil in mint tolerances are established outside the United States.

Recommendations:

We recommend against the proposed tolerance; for further consideration we require:

1. Analyses (by the manufacturer) of the technical material for PCBN. This request was made earlier in conjunction with PPRF2405.

2. A determination by TOX as to whether low levels of HCB in mint oil would be of concern. If TOX has concern over our estimate of the 0.1 ppm level, actual HCB analysis of mint oil derived from treated mint will be needed.

3. The petitioner should explain the disparity between residues found as a result of the 1X rate and the high residues that result from the 2X rate.

4. Section B or Section F should be revised in such a way that the proposed use is consistent with the proposed tolerance.

The petitioner should be advised of the geographic limitations imposed on this use (conclusion 3c) (see attachment).
DETAILED CONSIDERATIONS

Manufacture

The manufacturing process for technical chlorothalonil was discussed in our review of PP#4E1502 (memo of 1/27/74, R. Schmitt).

Hexachlorobenzene (HCB) was reported to be a contaminant in 8% of 306 batches of technical chlorothalonil that were analyzed (PP#8E2065, memo of 11/20/78, T. McLaughlin).

A second impurity in the technical material is pentachlorobenzonitrile (PCBN). We have recently requested the manufacturer to submit data that shows the level of PCBN in the technical material (PP#0F2405, memo of 1/30/81, L. Bradley). When this data is submitted we will make a conclusion as to the significance of potential residues of PCBN in mint.

Formulation

The formulation proposed for use on mint is Bravo 500 which contains 4.17 lb a.i./gallon (500g/L). This formulation was described in our review of an amendment to PP#6F1799 (see memo of 3/13/80, P.V. Errico). All inert are cleared under Section 180.1101.

Another registered formulation, which was used for the residue experiments submitted with this petition, is Bravo 6F. This formulation contains 5 lb a.i./gallon.

Proposed Use

For control of Rust and Septoria leaf spot on spearmint the rate is 2 pints (ca 1 lb a.i.) of Bravo 500/A in sufficient water to obtain adequate coverage. The first application is to be made when the emerging plants are 4 to 8 inches high. Repeat applications are to be made at 5-10 day intervals or as necessary to maintain control but no more than 3 applications are allowed each season. No applications are to be made within 80 days of harvest.

A label restriction prohibits the feeding of treated fresh or extracted mint hay to livestock.

If the petitioner wishes we would have no objection to the use being made more general, i.e., for mint (which would include peppermint) rather than for spearmint.
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 (PPGs 7F0599, 1F1024, 2F1230, 4E1502, 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 and can be translated to spearmint.

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 it is of concern because of its transfer potential to meat and milk.

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 impurities HCB and PNCB may also constitute a portion of the residue.

Analytical Method:

The method of enforcement for determination of residues 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 GC or EC-GLC.

Recovery of chlorothalonil from fresh mint hay ranged from 86 to 110% (avg. 98%, fortification, 0.02 to 0.2 ppm); the two recovery values submitted for the hydroxy metabolite were 75 and 84%, both at fortifications of 0.2 ppm. No recovery data for spearmint oil are submitted but chromatograms of control samples show no interfering peaks. (The oil, which is isolated by steam distillation, would contain no bound residues). We conclude that adequate analytical methods are available for enforcement of the proposed tolerance.

Residue Data:

Residue experiments were carried out in Indiana during 1976 and 1977 seasons. This limited geographic representation will support the use of chlorothalonil on mint in the states of Michigan, Wisconsin and Indiana. Wider usage will require representative residue data. (As mentioned in the "Proposed Use" section of this review we would have no objection if the use was extended to include peppermint).
The formulation used for the residue experiments was Bravo 6F. We expect that residues from this formulation would be essentially the same as those from the Bravo 500 formulation.

From the highest proposed rate (3 applications of ca. 1 lb a.i./A, PHI=ca. 80 days) the combined residues in fresh mint hay ranged from undetectable (<0.01 ppm for either compound) to 0.06 ppm.

Residues as a result of the 2X rate (3 applications PHI=ca. 80 days) ranged up to 2.2 ppm for the parent and up to 0.01 ppm for the metabolite. Of 8 residue values at the 2X rate, six gave combined residues greater than 2 ppm.

Residues in/on the spent hay were similar to those in fresh hay at both application rates.

Mint oil produced from mint hay that had been treated at either 1X or 2X rate carried no detectable residue (0.01 ppm).

The submitted data raise some questions as to the adequacy of the proposed tolerance. The data generated using the 2X rate suggest that the proposed tolerance is too low. Before we can make a favorable recommendation the petitioner should explain the great disparity between the 1X and 2X residue data; i.e., data at the 1X rate show residues of <0.01 ppm on fresh hay whereas residues at the 2X rate approach 3 ppm.

No residue data for HCB are submitted. If chlorothalonil containing HCB were applied at the maximum rate and if all of the HCB from these applications were incorporated into mint oil (assuming a 50 Tb/A yield) the resulting concentration would be 30 ppm. For several reasons this is an exaggerated figure:

1. Not all of the HCB would contact mint
2. Distillation of HCB into the oil would probably not be quantitative, though it may be efficient.
3. Most significantly the dissipation of HCB from mint is expected to be quite fast. HCB applied to grass at an initial level of 1060 ppm was reduced to 15.6 ppm at 15 days and to less than 1 ppm (0.08% of the applied dose) at 93 days (N.J. Beall, J. Environmental Quality 5 (4) 367 (1976)). We expect the rate of dissipation from mint (over the 80 day PHI) to be similar.

Taking these matters into consideration we estimate that the maximum amount of HCB that would be present in mint oil would be ca. 0.1 ppm. If TOX expresses concern over this level we will require analysis of mint and mint oil that has been treated with chlorothalonil containing HCB.
Another impurity in the technical material that may present a residue problem is pentachlorobenzonitrile (PCBN). We have recently requested that the manufacturer analyze the technical material for this impurity (PP#OF2405, memo of 1/30/81, L. Bradley). We can make no conclusion about the significance of PCBN levels in mint until the requested analyses are submitted.

(Since mint oil is diluted by a factor of 1,000 to 10,000 when incorporated into feed the amount of HCB or PCBN reaching the consumer would be small).

Meat, Milk, Poultry and Eggs:

Since the proposed use includes a label restriction that prohibits the feeding of fresh or spent mint hay to livestock, there will be no problem of secondary residues in meat, milk, poultry and eggs.
Minor Use Tolerances

Mr. Edwin L. Johnson, Office of Pesticide Programs, Deputy Assistant Administration, has issued a minor use policy dated 9/30/80. One of the issues addressed in the statement is the setting of minor use tolerances based on the submission of residue data from specific geographical areas. A tolerance is normally set on a national basis and is supported by residue data from the major growing areas for the individual crops.

In order to enable users of 40 CFR Section 180. to be able to distinguish these minor use tolerances for specific areas from other tolerances which are supported by the full complement of residue data, we recommend that these tolerances be identified in the CFR.

We suggest a system whereby the minor use tolerances be asterisked in the CFR and be accompanied by an explanatory footnote. An appropriate footnote would be, "This minor use tolerance is based on residue data from specific geographical areas. In order to expand the area of usage on this crop, additional residue chemistry data for these areas will need to be submitted."
# INTERNATIONAL RESIDUE LIMIT STATUS

**CHEMICAL**: Chlorothalonil

**PETITION NO.**: IE2373

**CCPR NO.**: 81

**Codex Status**

- **No Codex Proposal Step 6 or above**

**Residue (if Step 9): Sum of chlorothanil and 4-hydroxy-2,5,6-trichloro-1,3-benzene dicarbonitrile expressed as chlorothalonil**

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<th>Crop(s)</th>
<th>Limit (mg/kg)</th>
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**Residue**: (1) 2,4,5,6-tetrachloroisophthalonitrile

(2) 4-hydroxy-2,5,6-trichloroisophthalonitrile

<table>
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<th>Crop(s)</th>
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**CANADIAN LIMIT**

**Residue**: Chlorothalonil

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**MEXICAN TOLERANCIA**

**Residue**: Chlorothalonil

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**Notes:**