Memorandum

Subject: 87-CA-03. Chlorothalonil (Bravo® 500, EPA Reg. No. 50534-8) on Mushrooms. Section 18 Request. No Acc. Number RCB #1718

From: Michael S. Metzger, Chemist Hazard Evaluation Division (TS-769)

Thru: Edward Zager, Section Head, SRS 2 Residue Chemistry Branch Hazard Evaluation Division (TS-769)

To: Emergency Response and Minor Use Section Registration Division (TS-767C)

The California Department of Food and Agriculture requests a Section 18 specific exemption authorizing the use of chlorothalonil on mushrooms to control Verticillium fungicola. The formulation to be used is Bravo® 500, a dispersible suspension containing 4.17 lbs.a.i./gallon (40.4% a.i.). Applications will be made to approximately 25 million ft² of mushrooms.

Tolerances are established for combined residues of chlorothalonil (tetrachloroisophthalonitrile) and its metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) in or on numerous commodities ranging from 0.05 ppm for bananas (edible pulp) to 15 ppm for celery and papayas. Several tolerances are pending (40 CFR 180.275; 21 CFR 193.84). A Registration Standard has been completed for chlorothalonil (Residue Chemistry Chapter, 11/4/83).

The proposed use includes a maximum of 6 applications to the soil surface as follows:

1. 8 fl oz (0.26 lbs.a.i.)/1000 ft² as soon as possible after casing.
2. 4 fl oz (0.13 lbs.a.i.)/1000 ft² at pinning (emergence).
3. 4 fl oz (0.13 lbs.a.i.)/1000 ft², 2-4 applications at breaks.
A maximum of 28 fl oz (0.91 lbs a.i.)/1000 ft²/crop cycle could be applied. Applications would be made in a minimum of 20 gallons of water per 1000 ft² of bed, and a 48 hour PHI would be imposed. Applications to mature mushrooms would be prohibited.

The Chlorothalonil Registration Standard identified several data gaps in the area of plant metabolism including the need for translocation studies involving ring-labeled [¹⁴C]-chlorothalonil, and identification of water-soluble compounds which constitute a major portion of the [¹⁴C]-chlorothalonil residues taken up from treated soils by plants. These have not yet been received. For the purposes of this Section 18 only, we consider the residue of concern to consist of parent chlorothalonil, SDS-3701, and 2 impurities found in technical chlorothalonil, hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN).

No new residue data were submitted with this Section 18.

Residue data were submitted with PP#6E3410 (Acc. No. 262766). Two analytical methods were used to generate these data, Methods #702-3CR-84-0074-000 and #632-3CR-83-0043-000.

Both methods quantify residues of chlorothalonil per se, SDS-3701, HCB and PCBN. The first method involves extraction with H₂SO₄-acidified acetone followed by partitioning with petroleum ether affecting separation of SDS-3701 from the other 3 compounds. Following additional clean-up steps and derivitization of SDS-3701 to the methyl ether, analysis is accomplished by GLC using an electron capture detector. Recoveries of the 4 components ranged from 70-130% at fortification levels of 0.01-10.0 ppm. Reported sensitivities are 0.01 ppm for chlorothalonil and SDS-3701, 0.003 for HCB and 0.005 for PCBN.

The second method utilizes various extraction solvents and clean-up procedures. Analysis is accomplished by GLC using an electron capture detector. Details can be found for both procedures in PP#6E3410 (Acc. No. 262766). Recoveries for the 4 components ranged from 60-112% at fortification levels of 0.01-10.0 ppm. Reported sensitivities are 0.03 ppm for chlorothalonil and SDS-3701, 0.004 ppm for HCB and 0.008 ppm for PCBN.

Residue data submitted with PP#6E3410 were reviewed previously (N. Dodd, 11/12/86). This review is repeated in part below.
West Winfield, PA

Bravo® 500 was applied at 0.26 lbs a.i./1000 ft² at casing, and at 0.13 lbs a.i./1000 ft² at pinning and after breaks. Applications were made in 19-31 gallons of water per 1000 ft². PHI values are given in the summary tables in parentheses. Residues in these tables are given in ppm.

<table>
<thead>
<tr>
<th></th>
<th>1'st Break (120 hrs) (2 apps.)</th>
<th>2'nd Break (72 hrs) (3 apps.)</th>
<th>2'nd Break (96 hrs)</th>
<th>3'rd Break (48 hrs) (4 apps.)</th>
<th>4'th Break (72 hrs) (5 apps.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorothalonil</td>
<td>0.05-0.17</td>
<td>0.14-0.58</td>
<td>0.16-0.24</td>
<td>1.57-1.91</td>
<td>0.64-1.15</td>
</tr>
<tr>
<td>SDS-3701</td>
<td>ND -0.03</td>
<td>0.01-0.06</td>
<td>0.02-0.03</td>
<td>0.03-0.04</td>
<td>0.06-0.11</td>
</tr>
<tr>
<td>HCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PCBN</td>
<td>ND-0.006</td>
<td>ND-0.016</td>
<td>ND-0.005</td>
<td>0.014-0.017</td>
<td>0.006-0.015</td>
</tr>
</tbody>
</table>

Avondale, PA

Bravo® 500 was applied at the same rate as in West Winfield, PA (above) in 25 gallons of water per 1000 ft².

<table>
<thead>
<tr>
<th></th>
<th>1'st Break (48 hrs) (2 apps.)</th>
<th>2'nd Break (48 hrs) (3 apps.)</th>
<th>3'rd Break (48 hrs) (4 apps.)</th>
<th>4'th Break (48 hrs) (5 apps.)</th>
<th>5'th Break (48 hrs) (6 apps.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorothalonil</td>
<td>1.31-1.94</td>
<td>1.86-2.55</td>
<td>2.66-3.07</td>
<td>3.05-3.28</td>
<td></td>
</tr>
<tr>
<td>SDS-3701</td>
<td>0.06-0.07</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03-0.04</td>
<td></td>
</tr>
<tr>
<td>HCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>PCBN</td>
<td>0.013-0.015</td>
<td>0.019-0.021</td>
<td>0.026-0.030</td>
<td>0.019-0.022</td>
<td></td>
</tr>
</tbody>
</table>

State College, PA

Bravo® 500 was applied at the same rates as discussed above in 19-31 gallons of water per 1000 ft².

<table>
<thead>
<tr>
<th></th>
<th>1'st Break (48 hrs) (2 apps.)</th>
<th>2'nd Break (48 hrs) (3 apps.)</th>
<th>3'rd Break (48 hrs) (4 apps.)</th>
<th>4'th Break (48 hrs) (5 apps.)</th>
<th>5'th Break (48 hrs) (6 apps.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorothalonil</td>
<td>0.21-0.44</td>
<td>0.26-0.71</td>
<td>0.31-0.75</td>
<td>0.35-0.50</td>
<td>0.70-1.79</td>
</tr>
<tr>
<td>SDS-3701</td>
<td>ND</td>
<td>0.02</td>
<td>0.01-0.02</td>
<td>0.01-0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>HCB</td>
<td>ND</td>
<td>ND</td>
<td>ND-0.003</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PCBN</td>
<td>ND-0.007</td>
<td>ND-0.012</td>
<td>0.006-0.012</td>
<td>ND-0.008</td>
<td>0.008-0.015</td>
</tr>
</tbody>
</table>
Bravo® 500 was also applied at 0.15-0.24 lbs. a.i./1000 ft² at casing and 0.07-0.12 lbs. a.i./1000 ft² at pinning and at breaks.

<table>
<thead>
<tr>
<th>Break</th>
<th>1'st Break</th>
<th>2'nd Break</th>
<th>3'rd Break</th>
<th>4'th Break</th>
<th>5'th Break</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(48 hrs)</td>
<td>(48 hrs)</td>
<td>(48 hrs)</td>
<td>(48 hrs)</td>
<td>(48 hrs)</td>
</tr>
<tr>
<td></td>
<td>(2 apps.)</td>
<td>(3 apps.)</td>
<td>(4 apps.)</td>
<td>(5 apps.)</td>
<td>(6 apps.)</td>
</tr>
<tr>
<td>Chlorothalonil</td>
<td>0.40-0.54</td>
<td>0.51-0.85</td>
<td>0.56-1.00</td>
<td>0.47-1.03</td>
<td>0.70-1.73</td>
</tr>
<tr>
<td>SDS-3701</td>
<td>ND -0.01</td>
<td>ND-0.02</td>
<td>0.02</td>
<td>0.01-0.02</td>
<td>0.03-0.05</td>
</tr>
<tr>
<td>HCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND -0.003</td>
</tr>
<tr>
<td>PCBN</td>
<td>0.005-0.007</td>
<td>0.007-0.013</td>
<td>ND-0.006</td>
<td>0.006-0.011</td>
<td>0.011-0.029</td>
</tr>
</tbody>
</table>

**Connecticut**

Bravo® 500 was applied at a rate of 0.14 or 0.28 lbs. a.i./1000 ft². Four scenarios were followed: One application at 0.14 lbs. a.i./1000 ft² and a PHI of 5 days (1'st break); 2 applications at 0.14 lbs. a.i./1000 ft² and a PHI of 6 days (2'nd break); 2 applications at rates of 0.14 lbs. a.i./1000 ft² and 1 application at 0.28 lbs. a.i./1000 ft² and a PHI of 4 days (3'rd break); and 2 applications at 0.14 lbs. a.i./1000 ft² and 2 applications at 0.28 lbs. a.i./1000 ft² and a PHI of 3 days (4'th break). Applications were made at pinning and prior to formation of caps. The only detectable residues found were at the two highest application rates (i.e. 4 apps.) in which chlorothalonil only was found at <0.03-0.08 ppm.

**Oregon**

Bravo® 75W was applied at 0.23 lbs. a.i./1000 ft² followed by 1-5 applications at 0.12 lbs. a.i./1000 ft². Applications were made in 19 or 31 gallons of water per 1000/ft².

<table>
<thead>
<tr>
<th></th>
<th>(38 hrs.)</th>
<th>(48 hrs.)</th>
<th>(36 hrs.)**</th>
<th>(38 hrs.)</th>
<th>(48 hrs.)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorothalonil</td>
<td>5.88-6.68</td>
<td>3.64-6.20</td>
<td>6.74-7.38</td>
<td>2.04-6.00</td>
<td>4.16-5.52</td>
</tr>
<tr>
<td>SDS-3701</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>HCB</td>
<td>ND-0.005</td>
<td>ND -0.04</td>
<td>0.005</td>
<td>ND-0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>PCBN</td>
<td>0.069-0.092</td>
<td>0.046-0.079</td>
<td>0.086-0.105</td>
<td>0.046-0.066</td>
<td>0.041-0.061</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>(38 hrs.)</th>
<th>(48 hrs.)*</th>
<th>(48 hrs.)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorothalonil</td>
<td>1.62-3.10</td>
<td>2.98-3.22</td>
<td>2.80</td>
</tr>
<tr>
<td>SDS-3701</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>HCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PCBN</td>
<td>0.017-0.041</td>
<td>0.032-0.039</td>
<td>0.025-0.030</td>
</tr>
</tbody>
</table>

*Data for 31 gallons water per 1000 ft² only
**Data for 19 gallons water per 1000 ft² only
Based on these data, and for the purposes of this Section 18 only, we conclude that residues are not likely to exceed the following values in or on mushrooms as a result of the proposed use:

- Chlorothalonil + SDS-3701: 8 ppm
- PCBN: 0.1 ppm
- HCB: 0.005 ppm

**Meat, Milk, Poultry and Eggs**

No animal feed items are involved with this use. Therefore, secondary residues in eggs, milk, and in the meat, fat and meat by-products of cattle, goats, hogs, horses, poultry and sheep are not likely to occur as a result of the proposed use.

**Conclusions**

(1) For the purposes of this Section 18 only, we will consider the residue of concern for chlorothalonil use on mushrooms to consist of parent chlorothalonil, SDS-3701, HCB and PCBN.

(2) For the purposes of this Section 18 only, we estimate that residues are not likely to exceed the following values in mushrooms as a result of the proposed use:

- Chlorothalonil + SDS-3701: 8 ppm
- PCBN: 0.1 ppm
- HCB: 0.005 ppm

(3) No animal feed items are involved in this use. Therefore, secondary residues are not expected in milk, eggs or in the meat, fat and meat by-products of cattle, goats, hogs, horses, poultry and sheep as a result of the proposed use.

(4) For the purposes of this Section 18 only, we consider Method #702-3CR-84-0074-000 to be adequate for enforcement purposes (see PP#6E3410, Acc. No. 262766).

(5) Analytical reference standards are available from the Pesticides and Industrial Chemicals Repository.
Recommendations

TOX considerations permitting, RCB has no objections to this Section 18. An agreement should be made with the FDA regarding the legal status of the treated commodities in commerce.

cc: Chlorothalonil (Bravo®) S.F., R.F., Section 18 S.F., Circu, M. Metzger, PMSD/ISB
RDI: E. Zager: EZ: 12/22/86: RDS: 12/22/86
TS-769: RCB: M. Metzger: MM: Rm803a: CM#2: 12/22/86