MEMORANDUM

SUBJECT: Residue Data Reflecting Aerial Versus Ground Spray Applications of Captan on Foliar Crops.

DEB No.: 4203
MRID Nos.: 407454-01 through -09

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The Captan Task Force, whose members include Chevron Chemical Company, Makhteshim Chemical Works, Ltd., and ICI Americas, Inc., has submitted field residue data reflecting the application of captan by air or ground concentrate or ground dilute application methods. These field residue trials were conducted to compare residue levels resulting from the different application methods.

Field trials were conducted on almonds, apples, cantaloupes, grapes, peaches, strawberries, and tomatoes.

Background

DEB recommended (See Nan S. Gray memorandum dated April 22, 1988) that tolerances to cover residues of captan on certain raw agricultural commodities be lowered providing the registered use on each crop be limited to that specified in the April 22, 1988 memorandum and that final conclusions concerning appropriate tolerance levels depend on the final results of the storage stability studies. Also, an adequate enforcement method to detect secondary residues in meat,
enforcement method to detect secondary residues in meat, milk, poultry, and eggs that could result from the feeding of certain crops to livestock must be made available before several of the other tolerances can be established.

DEB reiterates that the following conclusions concerning appropriate tolerance levels depend upon the outcome of the storage stability studies and that an adequate enforcement method to detect secondary residues in meat and milk must be made available to retain certain other tolerances.

Conclusions and Recommendations

1. The analytical methods used to generate the crop residue data are adequate.

2. The recommended tolerances of 0.5 ppm for almonds and 75 ppm for almond hulls will not be exceeded as a result of aerial applications or concentrate ground application of Captan 50 WP.

3. DEB concludes that total residues of captan in or on apples will not exceed the established tolerance of 25 ppm when Captan 50 WP is applied aerially.

4. DEB concludes that total residues of captan occurring on cantaloupes as a result of aerial application will be no higher than those resulting from dilute ground applications of Captan 50 WP and will not exceed the established tolerance of 25 ppm. However, the 25 ppm tolerance to cover residues of captan on cantaloupes has been cancelled with a PD 4 Notice dated February 24, 1989.

5. Residues of captan occurring on grapes as a result of aerial applications will be equal to or less than those occurring from dilute ground application of Captan 50 WP.

6. Aerial applications or concentrate ground applications of Captan 50 WP will not result in higher residues in or on peaches than those resulting from dilute ground applications.

7. Residues of captan occurring in or on strawberries as a result of the aerial applications were higher than those occurring as a result of ground applications. However, residues resulting from the aerial applications did not exceed the established tolerance of 25 ppm.
8. Total residues of captan occurring on tomatoes as a result of aerial applications of Captan 50 WP are generally lower than those resulting from ground application methods.

Analytical Method

The analytical method used to quantitate captan residues in crops was "Determination of Captan Residues and its Primary Metabolite, tetrahydrophthalimide (THPI) in Crops," Chevron Method No. RM-K-2 (December 29, 1982). Morse Laboratories, Inc. modified the method by using packed-column gas chromatography with Coulson electrolytic conductivity detection. This method determines captan and THPI residues in crops at levels of 0.05 ppm or greater for each analyte.

A brief general description of the method for oily crops (almond nut meat and corn grain) follows: A representative aliquot of a macerated sample is extracted three times with ethyl acetate by using an Omni mixer. Each extract is filtered to separate the solids from the ethyl acetate extract solution. The ethyl acetate from the combined extract is then evaporated. The residual oil phase is subjected to acetonitrile-hexane partitioning cleanup. The acetonitrile extract is evaporated to dryness and the residue is dissolved in a suitable solvent for nuchar-silica gel column cleanup. The nuchar-silica gel separation subjects the extract to further cleanup and also serves to separate the captan from the THPI. Each of two fractions from the column cleanup is concentrated (evaporated) to a suitable volume for gas chromatography analysis. The captan fraction is analyzed by using the halogen mode of the detector and the THPI fraction is analyzed by using the nitrogen mode.

For non-oily crops (all matrices other than almond nut meat and corn grain), a representative aliquot of a ground sample is acidified, then extracted three times with ethyl acetate by using an Omni mixer. Each extract is filtered to separate the solids from the ethyl acetate extraction solution. The combined ethyl acetate extract is then subjected to aqueous 1% phosphoric acid/ethyl acetate cleanup. The nuchar-silica gel separation subjects the extract to further cleanup and also serves to separate the captan from the THPI. Each of two fractions from the column cleanup is concentrated (evaporated) to a suitable volume from gas chromatographic analysis. The captan fraction is analyzed by using the halogen mode of the detector and the THPI fraction is analyzed by using the nitrogen mode.
DEB reiterates its previous conclusion (L. Bradley, July 22, 1986; N. Gray, April 22, 1988) that the analytical methods used to obtain the crop residue data are adequate.

**Storage Stability**

Storage stability data are discussed in a separate memorandum (see L. Propst, December 19, 1989). In general, crops analyzed here were done in a timeframe to be considered acceptable.

**Almonds**

Tolerances have been established for residues of the fungicide captan (N-trichloromethylthio-4-cyclohexane-1,2-dicarboximide) on almonds at 2 ppm and on almond hulls at 100 ppm. DEB recommended (See Nan S. Gray memorandum dated April 22, 1988) that tolerances of 0.5 ppm be established for almonds and 75 ppm for almond hulls when an adequate enforcement method for meat and milk is available. The registered use should be limited to a maximum application of 1.5 lb/100 gal of spray with a maximum of 350 gal spray/A, ground application only and a 30-day PHI.

Almonds grown in California received four applications of Captan 50 WP using the maximum label rate of 4.5 lb ai/A (18 pounds total active per season) as a foliar treatment by air or concentrate and dilute ground application methods. PHIs ranged from 139 to 142 days. Maximum residues found in each commodity from the different treatments are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Captan (ppm)</th>
<th>THPI (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hull - Air</td>
<td>4.48</td>
<td>0.17</td>
</tr>
<tr>
<td>Hull - Concentrate</td>
<td>6.76</td>
<td>0.17</td>
</tr>
<tr>
<td>Hull - Dilute</td>
<td>7.72</td>
<td>0.22</td>
</tr>
<tr>
<td>Shell - Air</td>
<td>0.15</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Shell - Concentrate</td>
<td>0.17</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Shell - Dilute</td>
<td>0.19</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Meat - Air</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Meat - Concentrate</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Meat - Dilute</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

Recovery from almond nut fortified at 0.1 ppm of captan was 90 percent. Recovery from almond shell fortified at 2.0 ppm of captan was 96 percent. Recovery from almond hulls fortified at 10.0 ppm of captan was 73 percent.
Recovery from almond nut fortified with THPI at 0.1 ppm was 118 percent. Recovery from almond shell fortified at 0.5 ppm of THPI was 82 percent. Recovery from almond hulls fortified at 1.0 ppm of THPI was 68 percent.

The longest that any of the unmacerated samples were stored from harvest to extraction was 74 days.

The recommended tolerances of 0.5 ppm for almonds and 75 ppm for almond hulls will not be exceeded as a result of aerial applications or concentrate ground application of Captan 50 WP.

**Apples**

A tolerance of 25 ppm has been established for residues of the captan in or on apples.

Apples grown in the State of Washington received six foliar applications of Captan 50 WP using the maximum label rate of 4.0 lb ai/A (24 pounds total active ingredient per season) by air or dilute ground application methods. Maximum residues found in mature fruit from air applications were 0.86 ppm captan and < 0.05 ppm THPI. Maximum residues found in mature fruit from dilute ground applications were 2.84 ppm captan and < 0.05 ppm THPI.

Recovery from whole mature apples fortified at 5.0 ppm of captan was 85 percent. Recovery from whole mature apples fortified at 1.0 ppm THPI was 70 percent.

The longest that any of the unmacerated samples were stored from harvest to extractions was 42 days.

DEB concludes that residues of captan in or on apples will not exceed the established tolerance when Captan 50 WP is applied aerially at the currently registered rates.

**Cantaloupe**

The 25 ppm tolerance established to cover residues of captan on cantaloupes has been cancelled with a PD 4 Notice dated February 24, 1989.

Seven foliar treatments using Captan 50 WP at the rate of 2.0 lb ai/A were made both by air and dilute ground application methods to cantaloupes grown in California. A 0-day PHI was observed. Maximum residues resulting from air applications in mature fruit were 1.81 ppm of captan < 0.05 ppm of THPI. Maximum residues resulting from dilute
ground applications were 6.72 ppm of captan and 0.17 ppm THPI.

Recovery from whole mature cantaloupes fortified at 2.0 ppm of captan was 92 percent. Recovery from whole mature cantaloupes fortified at 0.5 ppm THPI was 81 percent.

The longest that any of the unmacerated samples were stored from harvest to extraction was 34 days.

DEB concludes that total residues of captan occurring on cantaloupes as a result of aerial application will be no higher than those resulting from dilute ground applications of Captan 50 WP.

Grape

A tolerance of 50 ppm has been established to cover residues of captan on grapes. DEB recommended (See Nan S. Gray memorandum dated April 22, 1989) that the tolerance of 50 ppm be lowered to 25 ppm on grapes providing an adequate enforcement method is available to detect secondary residues in meat and milk that could result from feeding grapes or processed commodities derived from them. The registered use should allow for a maximum rate of 2 lb ai/A, ground applications only with a 0-day PHI.

Six foliar treatments using both air and dilute ground applications at the rate of 2.0 lb ai/A (12 lbs active total) were made to grapes grown in New York. A 0-day PHI was observed. Maximum residues occurring in mature fruit from aerial applications were 3.92 ppm captan and 0.08 ppm THPI. Maximum residues occurring in mature fruit from dilute ground applications were 8.36 ppm captan and 0.25 ppm THPI.

Recovery from whole mature grapes fortified at 10.0 ppm of captan was 76 percent. Recovery from whole mature grapes fortified at 1.0 ppm of THPI was 80 percent.

The longest that any of the unmacerated samples were stored from harvest to extraction was 46 days.

Residues of captan occurring on grapes as a result of aerial applications will be equal to or less than those occurring from dilute ground applications.

Peach

A tolerance of 50 ppm has been established to cover residues of captan in peaches. DEB recommended (Nan S. Gray, April 22, 1988) that the established tolerance be lowered to
25 ppm and the registered uses be limited to a maximum of 1 lb active/100 gal spray with a maximum for 400 gal/spray/A ground applications only with a 0-day PHI.

Peaches grown in California received eight applications using 4.0 lb ai/A (32 pounds active total) of Captan 50 WP applied by air, ground concentrate, and ground dilute application methods. A 0-day PHI was observed. Maximum residues reported in mature fruit for captan were 4.28 ppm from air application, 8.30 ppm from concentrated ground application, and 12.30 ppm from dilute ground application. Maximum residues reported in mature fruit for THPI were 0.07 ppm from air application, 0.16 ppm from concentrated ground application, and 0.50 ppm from dilute ground application.

Peaches grown in Washington received six applications using 4.0 lb ai/A (24 pounds total active) of Captan 50 WP applied by air and ground dilute application methods. A 0-day PHI was observed. Maximum residues of captan reported from air applications were 4.34 ppm and < 0.05 ppm for THPI. Maximum residues found in mature fruit resulting from dilute ground applications were 5.84 ppm for captan and 0.08 ppm THPI.

Recoveries from whole mature peaches at 1.0, 5.0, and 10.0 ppm of captan ranged from 72 to 95 percent. Recoveries from whole mature peaches fortified at 0.2 and 1.0 ppm THPI ranged from 81 to 86 percent.

The longest that any of the unmacerated samples were stored from harvest to extraction was 83 days.

Residue levels on peaches resulting from aerial applications of Captan 50 WP will be no higher than those occurring from ground application.

**Strawberry**

A tolerance of 25 ppm has been established to cover residues of captan on strawberries. DEB recommended (See Nan S. Gray memorandum dated April 22, 1988) that the registered use pattern be restricted to a maximum of 3 lb ai/A, ground equipment only, 0-day PHI.

Field trials were conducted on strawberries grown in California comparing residue levels resulting from six foliar treatments using 4.0 lb ai/A (24 lb total active) applied by air versus ground concentrate versus ground dilute application methods. Maximum residues reported on mature fruit receiving air applications were 15.0 ppm of captan and 0.69 ppm for THPI. Maximum residues reported on strawberries
receiving concentrate ground applications were 1.04 ppm of captan and 0.09 ppm THPI. Maximum residues reported on strawberries receiving dilute ground applications were 8.90 ppm of captan and 0.54 ppm for THPI.

Recoveries from whole mature strawberries fortified with 2.0 and 10.0 ppm of captan ranged from 86 to 94 percent. Recoveries from whole mature strawberries fortified at 0.5 and 1.0 ppm of THPI ranged from 76 to 94 percent.

The longest that any of the unmacerated samples were stored from harvest to extraction was 127 days.

Residues of captan occurring in or on strawberries as a result of the aerial applications were higher than those occurring as a result of ground applications. However, residues resulting from the aerial applications did not exceed the established tolerance.

**Tomatoes**

A tolerance of 25 ppm has been established to cover residues of captan on tomatoes. Providing that an adequate enforcement method is available to detect secondary residues in meat and milk, DEB recommended (See Nan S. Gray memorandum dated April 22, 1988) that the tolerance be lowered to 15 ppm and the registered use be limited to 3.75 lb ai/A, ground applications only, and a 0-day PHI.

Tomatoes grown in Texas received four treatments using 3.75 lb ai/A (15 lb total active) of Captan 50 WP applied by air or dilute ground application methods. A 0-day PHI was observed. Maximum residues reported for tomatoes receiving air applications were 0.53 ppm captan and 0.11 ppm THPI. Maximum residues reported for tomatoes treated with dilute ground applications were 2.10 ppm captan and 0.32 ppm THPI.

Recoveries from whole mature tomatoes fortified at 2.0 ppm of captan were 93 percent. Recoveries from whole mature tomatoes fortified at 0.5 ppm of THPI were 85 percent.

The longest that any of the unmacerated samples were stored from harvest to extraction was 55 days.

Residues of captan occurring on tomatoes as a result of aerial applications tended to be lower than those occurring from dilute ground application methods.