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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
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OFFICE OF  
PESTICIDES AND TOXIC  
SUBSTANCES

MEMORANDUM

Subject: Captan on Raspberries. Request for Review of Residue Data in Anticipation of Forthcoming 24(C) SLN Registration.  
No Accession Number / No MRID Number  
CB No. 8292. DP Barcode D165932.

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**CBRS has been asked to expedite review of this Action by Anne Lindsay, Director, Registration Division (memo to Penelope A. Fenner-Crisp, 7/19/91).**

The Department of Agriculture of Washington State has submitted captan residue data for raspberries in advance of submission of a 24(C) Special Local Needs registration request. The reason for submission of these data prior to the formal 24(C) request is that quick review is requested due to an urgent need for authorization to use captan as soon as possible (see A. Lindsay memo). The formulation to be used is Captan 50-WP, a 50% a.i. wettable powder (EPA Reg. No. 10182-145).

Tolerances are established for residues of the fungicide captan (N-trichlormethylthio-4-cyclohexene-1,2-dicarboximide) on numerous raw agricultural commodities ranging from 0.05 ppm (meat, fat, and meat by-products of cattle and hogs) to 100 ppm (spinach), and include a 25 ppm tolerance for raspberries (40 CFR 180.103). A Registration Standard has been completed for Captan (Residue Chemistry Chapter, 8/15/85).

There are currently no registered uses of captan on raspberries.

The proposed 24(C) use is as follows:

RASPBERRIES, BLACKBERRIES

For the control of Anthracose, Botrytis, and Spur Blight -- Apply 4 pounds of Captan 50-WP (2.0 lbs.a.i.) per acre when blossoms are in bud (young canes are 8-10" long). Make a second application two weeks later. Apply a fall spray after old canes are removed.

For the control of fruit rot -- Apply 4 pounds of Captan 50-WP per acre 3-5 days before harvest, at mid-harvest and 8-10 days after the mid-harvest application. Do not apply within three days of harvest.

Apply in sufficient water to apply thorough coverage of foliage and/or fruit.

Data for raspberries were discussed in the Residue Chemistry Chapter of the Registration Standard. It was concluded that the available residue data did not support the established tolerance "since the data are meager, and do not reflect multiple (more than two) applications, sampling on the day of harvest, the use of WP or FlC formulations or the maximum lb ai/100 gal rate". Residue data were available from a single Washington State test site in which raspberry plants were treated once or twice with the 5% D formulation at 2.5 lbs.a.i./A. Raspberries harvested 7 days after the latter of 2 applications bore residues of 0.7 and 0.9 ppm. Raspberries harvested 12 days after the latter of 2 treatments bore 1 ppm residues (1 sample). Raspberries harvested 1 day after a single treatment contained 1.2 ppm captan.

The results of field trials carried out by IR-4 in OR and WA in 1990 were submitted in this report. The analytical method used to generate these data was "Determination by Gas Chromatography of Captan and Tetrahydrophthalimide Residues in Raw and Processed Agricultural Crops" (No MRID Number). Briefly, captan and THPI are extracted from the sample with ethyl acetate in the presence of phosphoric acid and anhydrous sodium sulfate. The extract is filtered, and the filtrate is washed with 1% aqueous phosphoric acid solution followed by solvent removal. The sample is cleaned up on a nuchar/silica gel column. The residue is quantified by GC/ECD. Several modifications to the method made by the performing laboratory are detailed in the report.

The reported LODs are 0.025 ppm for captan and 0.1 ppm for THPI. The reported residue levels in untreated control samples were <0.025, 0.055, and 0.12 ppm for captan, and <0.10 ppm for THPI. Chromatograms were submitted for the <0.025 ppm and 0.12 ppm captan samples and a single THPI untreated control sample. These data indicate that the reported LOD for captan residues in raspberries of 0.025 ppm using this method is incorrect.

However, this is not a significant issue in determining the appropriateness of the method to enforce the raspberry tolerance which is much higher than the reported LOD (tolerance = 25 ppm).

Fortification/recovery data have not been provided. Storage stability data have been provided and are summarized in Table 1. For **Captan**, it is not possible to determine the storage stability in raspberries based on these data. The range of captan recoveries is large (56-156%) and variable (mean = 110%, s.d. = 32%), and it is not possible to determine if these results are due completely to problems with the analytical methodology or are partly due to residue decline on storage. The data do indicate the unacceptability of the method for collection of captan residue data and for enforcement due to the variable recovery. Two chromatograms of spiked samples (1.0 and 30 ppm) were provided. For **THPI**, recoveries ranged from 54-90% (mean = 71%, s.d. = 11%). Again it is not possible to determine whether the results are due to the analytical method or whether they are due to residue decline on storage. Fortification/recovery data are required to allow isolation of these variables. Chromatographs of samples spiked at 0.05 and 30 ppm were provided.

We note that the performing laboratory (New York Agricultural Experimental Station, Analytical Chemical Laboratories, Geneva, NY) modified the analytical method in several ways. Therefore, we cannot judge the adequacy of the method as written. However,

Table 1: Storage Stability Data for Captan and THPI in Raspberries

Compound	Fort. Level (ppm)	% Recovery	Storage time (mos.)
Captan	0.05	156	3
	0.1	128, 130	3.5, 3
	1.0	56, 93	2.5, 3.5
	5.0	102	NP*
	30	109	NP*
THPI	0.05	< LOD	5.5, 6.5
	0.1	< LOD	5.5 - 6.5
	1.0	54, 71	5.5, 6.5
	5.0	60, 76	NP*
	30	69, 79	NP*

NP = information Not Provided

the method incorporating the changes made by the performing laboratory is inadequate for collection of residue data or for enforcement for captan residues in raspberries. The method may be adequate for determination of THPI in raspberries. However, additional fortification/recovery data must be submitted.

Samples were shipped on dry ice and stored frozen between sampling from the field (-19°C or -29°C) and between chopping and analysis (-40° or -10°C). Lengths of time between harvest and analysis ranged from 4-5 months. Extraction dates and storage conditions of the extracts were not provided.

Residue data are summarized in Table 2. Field trials were carried out in the states of Oregon and Washington. A 50 WP formulation was used in both states. In Oregon, raspberries were treated with either 9 applications at 1.63 lbs.a.i./A or 8 applications at 1.63 lbs.a.i./A and the final application at 0.98 lbs.a.i./A. In Washington, the application rates stated throughout the submission were either 10 applications at 5.0 lbs.a.i./A or 9 applications at 5.0 lbs.a.i./A and the final application at 3.0 lbs.a.i./A. However, CBRS recalculated the stated application rates for the Washington studies using the weight of formulation which the report states was used for each application, together with the site description. The report states that 1.5 lbs. of the 50% formulation was applied per application (= 0.75 lbs.a.i./application). The site description shows that 3 100-ft lengths of row, 9 ft between rows, were treated with captan (corresponds to ca. 2700 ft<sup>2</sup> or 0.062 acre).

Table 2: Residues of Captan and THPI in Captan-Treated Raspberries

Loc	App. Rate (lbs ai/ A)	# Apps	Days Between Apps	PHI (days)	Residue (ppm)	
					Captan	THPI
OR	1.63	9	9-19	0	5.7	0.37
				7	1.1	0.12
	1.63+0.98	9	9-19	0	5.6	0.49
				7	2.1	0.16
WA	5	10	9-11	0	38	1.7
				7	23	1.2
	5+3	10	9-11	0	36	2.1
				7	16	0.89

This results in a calculated treatment rate of 12.1 lbs.a.i./A rather than the 5.0 lbs.a.i./A stated throughout the submission. Similarly, the 3.0 lbs.a.i./A rate is recalculated as 7.3 lbs.a.i./A. This discrepancy must be reconciled by the submitter.

CBRS cannot determine whether the established tolerance for captan residues on raspberries will be exceeded until issues discussed above related to analytical methodology and application rates used in the field trials are resolved.

### Conclusions and Recommendations

The residue data discussed in this report do not adequately show whether the 25 ppm tolerance for residues of captan on raspberries will be exceeded as a result of the proposed use. The analytical method used to generate residue data is not adequate for purposes of generating residue data nor for enforcement because of the large variability in recoveries demonstrated.

If samples obtained in this study are to be reanalyzed using alternate methodology, information addressing the apparent discrepancy in the application rate in the Washington state field trials must be submitted. Additionally, fortification/recovery data must be submitted for the method used and appropriate storage stability data must be provided. A complete sample history including storage times and conditions must be provided. Furthermore, the proposed use should be reflected by the residue data. We refer the submitter to the Pesticides Assessment Guidelines, Subdivision O, Residue Chemistry for additional information.

CBRS recommends against issuance of any 24(C) registration supported by these residue data.

cc: M. Metzger (CBRS), Captan S.F., Captan Reg. Std. File, RF, Circu (7), C. Furlow (PIB/FOD, H7506C)  
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H7509C:CBRS:M.Metzger:MM:Rm810f:CM#2:7/31/91