RF

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

OCT 6 1989

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Residue Data Review for Corn, Soybean, Beet, and Spinach Seed Treatments with Captan, DEB No. 5589, EPA No. 239-1246, MRID Nos. 411491-01 through -04

FROM: Christine L. Olinger, Chemist
Special Registration Section I
Dietary Exposure Branch
Health Effects Division (H7509C)

THRU: Andrew Rathman, Section Chief
Special Registration Section I
Dietary Exposure Branch
Health Effects Division (H7509C)

TO: Eugene Wilson, PM-23
Fungicide-Herbicide Branch
Registration Division (H7505C)

This data is being submitted to support registration of seed treatments with Captan. Data had been submitted previously and found deficient due to contaminated controls (N. Gray 4/22/88). The studies were repeated and are presented here.

Residue data regarding seed treatment uses were required to be submitted by July 6, 1989 as outlined in the Data Call-In Notice (April 29, 1985) and the Special Review Position Document #4. The requirements, as specified in the DCI are as follows:

> "EPA requires residue data for captan and THPI for representative crops to support low level tolerances covering seed treatments. Residue data for crops grown from treated seed must be submitted for corn, soybeans, potatoes, rice or a small grain, and two of the vegetables having seed treatments."

Conclusions

1. The nature of the residue in plants is adequately understood. The residues of concern are captan and its primary metabolite, tetrahydrophthalimide (THPI).

2. An analytical method is available which is appropriate for enforcement purposes.

3. Storage stability data covering the samples analyzed here are sufficient for most crops. However additional information is needed for corn grain and beet tops.

4. Residue data indicates no residues were detected on any of the crops analyzed. However until the storage stability information is finalized for the corn grain and beet tops no final conclusions can be drawn. Additional soybean forage data is required, since data from only one site was provided. According to a letter submitted with the data (A. Mueller to L. Schnaubelt, 6/27/89), additional forage studies are in progress.

5. No data regarding residues on rice or a small grain were provided as outlined in the DCI notice. Data submitted previously were inconclusive due to contaminated controls. According to a letter submitted with the data (A. Mueller to L. Schnaubelt, 6/27/89), studies with winter wheat are forthcoming.

Recommendations

Data is available which supports the registration for captan seed treatments on spinach. Additional information is required regarding storage stability studies of beet tops and corn grain. Insufficient soybean forage data was provided. No further recommendations may be made on captan seed treatments until the additional data required is submitted.

Since no residues were detected, tolerances should be proposed at the combined method sensitivity limits of captan and its metabolite tetrahydrophthalimide for those crops which do not have existing tolerances.

Detailed Considerations

Use

Captan formulations are registered for use as a slurry, dry, and/or planter box seed treatments at a variety of rates and formulations. According to the registration standard, the following crops have registered uses of captan seed treatments: alfalfa, avocado, barley, beans, beets, broccoli, Brussel sprouts, cabbage, cantaloupe, carrots, cauliflower, clover, sweet corn, field corn, collards, cotton, cucumber, eggplant, flax, grasses, kale, lentils, lespedeza, millet, muskmelons, mustard greens, oats, okra, onions, peanuts, peas, pepper, potato (seed piece), pumpkins,

radishes, rape, rice, rutabagas, rye, safflower, sesame, sorghum, soybeans, spinach, squash, sugar beets, sunflower, Swiss chard, tomatoes, trefoil, turnips, watermelons, and wheat. Listed below are examples of application rates of the active ingredient for the crops reviewed here.

RAC	Amount A.I.
Soybeans	0.75-0.8 oz/bushel
Spinach	3 oz ai/100 lb
Sugar Beets	
West	3 oz/100 lb
East	6 oz/100 lb
Corn-Sweet	1.8-2.0 oz/bushel
Corn-Field	0.5 oz/bushel

Nature of the Residue

Data depicting the identity of metabolites of captan are available for apples (following foliar or postharvest treatment) and oranges (postharvest treatment only). Since captan and captafol have common metabolites in plant, captafol metabolism studies with tomatoes and corn (which were submitted in the Captafol Registration Standard) were compared and evaluated with the captan apple and orange studies.

The following metabolites have been identified in apple fruit, apple foliage and orange fruit: 4-tetrahydrophthalimide (THPI), 4-tetrahydrophthalamic acid (THPAM), 4,5-epoxyhexahydrophthalimide (THPI-epoxide), 5-hydroxy- 3-tetrahydrophthalimide (5-OH-THPI), 3-hydroxy- 4-tetrahydrophthalimide (3-OH-THPI), and N-trichloromethylthio)-4,5-epoxyhexahydrophthalimide (captan-epoxide). The major residue are the parent, THPI, and THPAM; THPI-epoxide, captan-epoxide, and 3- and 5-OH THPI are minor residues in plants.

Additional studies were required, and were reviewed in a memorandum by N. Gray (8/18/88). The residues of concern are captan and its primary metabolite, THPI.

Analytical Method

The method used for these studies was Chevron Method RM-IK-2, with modifications by Morse Laboratories. The sample is macerated and acidified with phosphoric acid. Water is added to dry crops; ethyl acetate and sodium sulfate are added and the entire mixture is blended, followed by filtration through sodium sulfate. The ethyl acetate extraction is repeated twice. Oily crops undergo an acetonitrile/hexane partition, while non-oily crops are partitioned with ethyl acetate/water. According to the summary in the report submitted, the oily crop extract is cleaned-up by gel permeation

chromatography (GPC). However handwritten in the analytical method (submitted as an appendix) is the statement that the GPC can be omitted. No description of the actual techniques used could be found on the raw data sheets included. The dried residue remaining from any crop used is reconstituted in dichloromethane and the extract is applied to a Nuchar/silica column. Captan and THPI are eluted in separate fractions. The method then states the fraction containing captan is further cleaned-up on a Florisil column; however no procedure is outlined in the method for application and elution.

The captan fraction is analyzed by gas chromatography (GC) with a Coulson electrolytic conductivity detector (CECD) in the halogen mode and the THPI by GC/CECD in the nitrogen mode. Some soybean forage samples were subjected to further confirmation by capillary GC with mass selective detection.

Quantitation of the captan is determined by comparison with a standard curve. According to the method linearity of the THPI is checked, but quantitation is based on a single standard. Fortification samples were all done at the 0.05 ppm level, the detection limit. However quantitation of the THPI was done by comparing the sample response to a standard equivalent to a sample at the 0.4 ppm level. No proof of THPI linearity was demonstrated in the data submitted. DEB recommends in any future data (using this method) submitted that the standards should be run at levels close to the expected concentration, and that proof of linearity is shown. Since no residues at or above 0.05 ppm were detected in any of the samples this data will be accepted.

Fortification samples were analyzed with each set of treated samples. Results are shown below.

		Captan		THPI*	
Crop	RAC	Spiking Level*	Percent Recovery	Spiking Level*	Percent Recovery
Beets	Roots	0.05	72-104	0.05	82-88
	Tops	0.05	76-104	0.05	80-104
Soybeans	Seed	0.05	84-88	0.05	70-108
	Hay	0.05	84	0.05	80-112
	Forage	0.05	80	0.05	72
Spinach	Leaves	0.05	84-92	0.05	78-86
Corn	Grain	0.05	96-116	0.05	70-98
	Forage	0.05	96-108	0.05	80-90

*All spiking levels are in ppm.
*Some THPI values were corrected for interferences detected in the controls.

Storage Stability

Most of the storage stability results were reported previously in MRID No. 40752301 (L. Propst review in progress). Additional stability data was provided with these studies for beet tops and corn grain. All studies indicate degradation of captan to THPI, but the rate of degradation depends upon the RAC, and the extent to which it has been processed.

Spinach

Captan degrades rapidly to THPI in spinach, whether or not the sample has been chopped prior to storage. The rate of degradation is increased when the sample is chopped more finely. L. Propst concluded that the maximum acceptable storage time for total residues of captan + THPI is three months, based on the data submitted. All samples analyzed in the study submitted were analyzed within 97 days.

Soybeans

Captan degrades rapidly to THPI in soybean grain. The data in MRID No. 40752301 indicate a maximum storage stability of three months. The treated soybean grain samples were analyzed within 105 days of harvest.

Forage samples were spiked separately with captan and THPI in the previous studies submitted. After fifteen months 69% of the captan was recovered, and 74% of the THPI. Treated samples were analyzed within 105 days.

Corn

The soybean forage and wheat forage data were used to support stability in the corn forage. The wheat studies indicate that captan and THPI are stable through three months of storage. The forage was stored for a maximum of 187 days, which is covered by the aforementioned soybean data.

Captan degrades very quickly to THPI in corn grain, even when the grain is not processed prior to storage. L. Propst had concluded the maximum storage time was 1 month. Additional stability data was submitted with the residue data; however no information regarding study conduct other than a summary of results was provided. The body of the report contained a statement that the detailed information was provided in an appendix, but it was not included. A summary table is provided below.

	Fortified with 0.5 ppm Captan[1]					Fortified with 0.5 ppm THPI	
Month	Captan PPM	Captan Recovery	THPI PPM	Total PPM	Total Recovery	THPI PPM	THPI Recovery
0	0.40	81%	(2)	(2)	(2)	0.46	92%
2	0.15	30%	0.20	0.56	112%	(3)	(3)
8	0.19	37%	0.15	0.33	67%	0.40	80%

1. Samples were separately fortified with captan and THPI. At the 2 and 8 month intervals the samples were analyzed for both captan and THPI. Total residue concentrations expressed as captan are calculated from levels of captan and THPI by adding twice the concentration of THPI to that of captan. This procedure is followed because a given amount of THPI requires as precursor twice this amount of captan, on a weight/weight basis.

2. The 0 day captan fortified samples were not analyzed for THPI.

3. THPI-fortified samples were not analyzed at this interval.

THPI appears to be stable over the eight month period covered in the study. However there seems to be an error for the total captan + THPI recovery at the eight month period. The THPI residue found is supposed to be doubled and added to the captan residue to calculate the total residue found and the percent recovery. The THPI value listed above was not doubled prior to adding it to the captan value, therefore yielding a total recovery of 67%. If the total recovery is calculated from the individual captan and THPI values listed above, the recovery is 96%. In the absence of study information, no conclusion can be drawn as to whether the individual THPI value or the total recovery value is correct. Previous stability data did not indicate total residue stability at 2 months, which conflicts with the new data. The new stability data cannot be accepted until additional information regarding the stability study can be provided.

Beets

Previous stability data submitted for sugar beet tops proved inconclusive. THPI-fortified samples indicated stability through 15 months; however captan-fortified samples were not analyzed for THPI, and, at all time intervals past study initiation, less than 40% of the captan was recovered. Additional stability data was submitted with the report and is summarized below. Sugar beet tops were fortified at a level of 0.5 ppm. No information regarding

sample processing prior to storage is provided.

Interval (Month)	Captan PPM	Captan Recovery	THPI PPM	Total[1] PPM	Total Recovery
1	0.42	86%	0.03	0.46	90%
3	0.45	91%	0.10	0.55	111%

1. The samples were analyzed for both captan and THPI. Total residue concentrations expressed as captan are calculated from levels of captan and THPI by adding twice the concentration of THPI to that of captan. This procedure is followed because a given amount of THPI requires as precursor twice this amount of captan, on a weight/weight basis.

Additional information regarding stability study conduct was not provided. This data seems to conflict with the previous study, which did not indicate stability of the captan even after 1 month of storage. No conclusions may be drawn until complete details of the new data are provided.

Sugar beet stability is represented by the potato tuber studies. Data presented in MRID no. 40752301 indicate stability for up to six months. The beet samples analyzed were stored for a maximum of 80 days prior to analysis.

Magnitude of Residue Data

Spinach

Spinach trials were conducted in North Carolina, Mississippi, California, and Illinois. Captan 400 was applied to the seed on August 5, 1988 at a rate of 6 oz./100 lb. seed, for a theoretical rate of 1875 mg/kg seed. Actual analysis of the seed yielded 1725 ppm captan and 30 ppm THPI. The seed was planted between 9/2/88 and 9/21/88 and the spinach harvested from 10/28/88 to 12/12/88.

The samples were analyzed within 18-97 days of harvest. No residues were detected in any of the control or treated samples.

Soybeans

Soybean trials were conducted in Illinois and Alabama. Captan 400 was applied to the seed on June 22, 1988 at a rate of 2.5 oz./100 lb. seed, for a theoretical rate of 780 mg/kg seed. Actual analysis of the seed yielded 694 ppm captan and 27 ppm THPI for the variety grown in IL and 632 ppm captan and 20 ppm THPI for the variety grown in AL. The seed was planted between 6/23/88 and 8/2/88. The soybeans were harvested 11/7-8/88, and the forage was

sampled 8/31/88 in Alabama. Due to a field error no forage was sampled in Illinois.

The samples were analyzed within 36-105 days of harvest. No residues were detected in any of the control or treated samples.

Corn

Corn trials were conducted in North Carolina, California, and Illinois. Captan 400 was applied to the seed on June 22, 1988 at a rate of 4 oz./100 lb. seed, for a theoretical rate of 1250 mg/kg seed. Actual analysis of the seed yielded 2000 ppm captan and 300 ppm THPI for the variety grown in NC and CA, and 1200 ppm captan and 33 ppm THPI for the variety grown in IL. The seed was planted between 6/27/88 and 7/14/88; the forage was sampled between 8/11/88 and 9/6/88, and the corn harvested between 8/24/88 and 10/3/88.

The samples were analyzed within 99-187 days of harvest. No residues were detected in any of the control or treated samples.

Beets

Beet trials were conducted in North Carolina, California, and Illinois. Captan 400 was applied to the seed on August 5, 1988 at a rate of 12 oz./100 lb. seed, for a theoretical rate of 3750 mg/kg seed. Actual analysis of the seed yielded 3400 ppm captan and 43 ppm THPI. The seed was planted between 9/2/88 and 9/16/88 and the beets harvested from 11/7/88 to 12/12/88.

The samples were analyzed within 18-97 days of harvest. No residues were detected in any of the control or treated samples.

cc:CLOlinger, Circulate, RF, SF, E. Eldredge (PMSD/ISB), Reg. Std.
H7509C:DEB:CLOlinger:clo:CM#2:Rm 803: 10/06/89
RDI: ARRathman: 10/05/89 EZager: 10/05/89