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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
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OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Residue Data Review for Soybean and Wheat Seed Treatments with Captan, Record No. 256461; ID No. 10182-293; DEB No. 6142; MRID Nos. 413061-01 and -02

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These data are 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). Data from other crops were reviewed recently (C. Olinger, 10/06/89). Soybean data were previously found deficient due to a lack of forage data from some sites.

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."

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### 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.
- 3a. Storage stability data covering the samples analyzed here are sufficient for the soybean forage.
- 3b. Insufficient information regarding the wheat forage stability study was provided to conclusively determine the maximum stability interval. No THPI stability data are available.
- 3c. No stability data are available for wheat grain. The registrant's intention to translate corn grain data is not appropriate.
- 4a. No residues were detected in soybean forage when seeds were treated at the maximum application rate. The data are not adequate since the interval between treatment and planting was unacceptably long.
- 4b. Residue data indicate no residues were detected on any of the wheat grain, forage and straw analyzed when seeds were treated at the maximum application rate. The data may not be accepted until the storage stability deficiencies are resolved.

### Recommendations

The soybean forage data are not adequate because of the deficiency cited in item 4b above. The wheat data are not adequate because of the lack of sufficient storage stability data as described in items 3b and 3c above. The registrant must submit a new soybean forage residue study with a time interval between seed treatment and planting which would better reflect the maximum potential for exposure. Clarification of the experimental details from the wheat forage stability study must be provided. THPI stability data must be submitted. Stability data from wheat grain for captan and THPI must be submitted reflecting storage conditions of the seed treatment residue data. If the storage stability is less than the storage intervals of the wheat grain residue data submitted, then a new residue study must be submitted. The previous deficiencies regarding storage stability studies of beet tops and corn grain still exist. No further recommendations may be made on captan seed treatments until the additional data required are 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 the maximum application rates of the active ingredient for the crops reviewed here.

<u>RAC</u>	<u>Amount A.I.</u>
Soybeans	0.75-0.8 oz/bushel
Wheat	0.125 lb/100 lb seed

#### Nature of the Residue

Data describing 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 plants, 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-1K-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. Oily crops may undergo further clean-up by GPC prior to the Nuchar/silica column clean-up. 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 wheat 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. DEB recommends in any future data (using this method) submitted that the standards should be run at levels close to the expected concentration. Since no residues at or above 0.05 ppm were detected in any of the samples these data will be accepted.

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

<u>Crop</u>	<u>RAC</u>	<u>Captan</u>		<u>THPI</u>	
		<u>Spiking Level*</u>	<u>Percent Recovery</u>	<u>Spiking Level*</u>	<u>Percent Recovery</u>
Wheat	Forage	0.05	84-116	0.05	84-114
	Grain	0.05	84-102	0.05	74- 92
	Straw	0.05	80-104	0.05	72- 90
Soybeans	Forage	0.05	116-118	0.05	72-112*

\*All spiking levels are in ppm.

\*Corrected for background as determined by analysis of a control sample.

### Storage Stability

Storage stability results for soybean forage were reported previously in MRID No. 40752301 (L. Propst 12/19/89). Additional stability data was provided with the subject studies for wheat forage. Previously submitted studies indicated degradation of captan to THPI, but the rate of degradation depends upon the RAC, and the extent to which it has been processed.

### Soybeans

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. L. Propst previously concluded that residues were stable in/on soybean forage for 15 months. Treated samples were extracted within 27 days of sampling.

### Wheat

Storage stability data for wheat forage is presented below. Untreated wheat forage was fortified with 0.5 ppm captan only. A description of sample preparation/maceration techniques was not provided. No information regarding storage conditions was provided, so it could not be determined if storage conditions were similar to those of the treated samples, or even if they were stored frozen.

<u>Time Interval</u>	<u>ppm Found Captan</u>	<u>ppm Found THPI</u>	<u>Total Recovery ppm</u>	<u>Total Percent Recovery</u>
0 Day	0.414	0.000	0.414	83
1 Month	0.386	0.146	0.532	106
3 Month	0.366	0.080	0.446	89
6 Month	0.097	0.350	0.447	89

Previous stability data submitted calculated the total residue concentrations (expressed as captan), from levels of captan and THPI by adding twice the concentration of THPI to that of captan. This procedure was followed because a given amount of THPI requires as precursor twice this amount of captan, on a weight/weight basis. However the total residue data listed above was not calculated in this manner. The THPI data may have been calculated as captan equivalents, but it cannot be determined from the minimal data presented. If the THPI has not been calculated as captan equivalent, then it is inappropriate to simply add the captan and THPI data to determine the total recovery.

Additional information is required to fully assess the applicability of this storage stability study. Sample maceration procedures should be described since previously submitted studies

demonstrated that the stability of captan on some RAC's depends on the extent of maceration. Details regarding the sample storage must be provided. The calculation technique for determining the THPI and total recoveries must be described. A preliminary estimate of the stability of captan on wheat forage is 3 months. Stability data for THPI per se must be provided.

The registrant intends to translate previously submitted corn grain stability data to wheat grain. The reviewer (L. Propst 12/19/89) concluded that captan residues are stable for only one month in/on corn grain. (The registrant claims a two month stability.) Regardless wheat grain samples were stored up to 97 days after sampling prior to sample extraction.

Accordingly, the corn grain stability data do not support the storage for the wheat grain sample data reviewed herein. DEB strongly recommends that the registrant submit stability data from wheat grain for both captan and THPI reflecting the storage conditions of this study. Previous storage stability studies have shown considerable variation in stability among the RAC's and the extent to which they have been macerated. If the wheat grain does not demonstrate stability up to 97 days then a new residue study must be submitted with the samples analyzed within the appropriate storage period determined.

### Magnitude of Residue Data

#### Soybean Forage

Soybean residue from seed treatments had been submitted previously (C. Olinger 10/6/89). However forage had not been sampled at all of the trial sites, so additional data were required.

Soybean trials were conducted in Illinois and North Carolina. 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 NC. The seed was planted 6/13/89 in IL and 5/19/89 in NC. The soybean forage was sampled 8/09/89 in IL and 8/21/89.

Upon reviewing the previous soybean residue data submitted (C. Olinger, 10/6/89), it appears the same batch of seed was used for both the 1988 and 1989 soybean residue trials. Analyses of the seed were identical in both 1988 and 1989 trials. No dates of analysis are provided. Given the nature of captan, degradation of captan to THPI would have been expected.

The samples were extracted within 27 days of harvest. No

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residues were detected in any of the control or treated samples. However due to the extended period of time between treatment of the seed and the planting, in the absence of degradation or stability data, DEB is not confident the level of captan in the seed at planting reflects the maximum application date. Accordingly this deficiency has not been resolved and the registrant should submit new soybean forage residue data.

### Wheat

Three varieties of wheat were treated with 4 fl. oz. Captan 400 per 100 lb. seed, the maximum application rate, equivalent to 1250 ppm. The seeds were analyzed and the results are presented below.

<u>Site</u>	<u>Captan</u> <u>(ppm)</u>	<u>THPI</u> <u>(ppm)</u>	<u>Treatment</u> <u>Date</u>	<u>Planting</u> <u>Date</u>
California	1117	34	8/29/88	12/15/88
Illinois	1058	33	8/29/88	9/15/88
Mississippi	1198	26	8/29/88	9/21/88
South Carolina	1198	26	8/29/88	11/29/88

Forage samples were collected within 27-209 days after planting. Grain and straw were sampled within 189-288 days after planting. Forage samples were stored 14-56 days after sampling prior to extraction, grain samples 79-97 days, and straw samples, 75-98 days. It is noted that several of the sample extracts were not analyzed until 4-6 weeks after extraction. This is a much longer time than is normally desirable. Since fortification samples with acceptable recoveries were subjected to the same extraction and analysis conditions, DEB will not reject the data merely on the extended time interval.

No residues were detected in any of the wheat forage, grain, or straw samples from any of the sites, with the exception of forage from Mississippi. There was an apparent THPI residue of approximately 0.05 ppm. The residue was not confirmed when the extract was analyzed by capillary-GC/MSD.

The residue data are adequate to meet the data requested in the DCI. However deficiencies regarding the storage stability studies must be resolved before the data can be accepted.

cc: CLOlinger, Circulate, RF, SF, Reg. Std. File, RDSchmitt, E. Eldredge (PMSD/ISB)

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