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WASHINGTON, D.C. 20460

Hand
9-16-94

SEP 16 1994

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

MORAND

SUBJECT: PP#4324: Mancozeb on Almonds (MRID # 43018401, CBRS Nos. 13536 and 14204, Barcode Nos.: D201278 and D206514). 203

FROM: R. M. Perfetti, Ph.D., Chemist R. Perfetti
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THRU: W. J. Hazel, Ph.D., Section Head W. J. Hazel
Reregistration Section 2
Chemistry Branch II: Reregistration Support
Health Effects Division (7509C)

TO: PM #21/C. Grable
Herbicide/Fungicide Branch
Registration Division (7505C)

Attached is a review of a petition requesting the establishment of a tolerance for residues of mancozeb in/on almonds. CBRS recommends against the establishment of the proposed tolerances for the residues of mancozeb in/on almond nutmeats and hulls at 0.1 and 10 ppm, respectively, because of the deficiencies cited in Conclusions 1, 2, 3a, and 4 below. The registrant should adequately address each of these issues before the present petition can be favorably granted.

1. No storage stability data were submitted with this petition. Supporting storage stability data reflecting the stability of residues of mancozeb and ETU in/on almond nutmeats and hulls stored frozen up to 285 days must be submitted. In addition, the registrant must provide additional information regarding dates of sample shipment and the temperature of sample storage at the laboratory.
2. No minimum retreatment interval was specified in the proposed use pattern. The registrant must submit a revised section B specifying a minimum retreatment interval.



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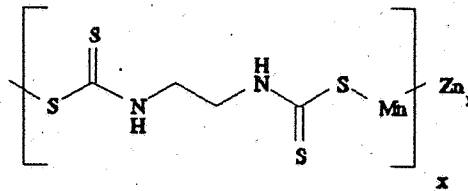
- 3a. The submitted field trial data are inadequate to support the tolerance petition because insufficient field trials were conducted, and no raw data pertaining to the field portion of the study were submitted. A minimum of 5 additional trials must be conducted with the FLC formulation. Concurrent storage stability studies should be performed with these trials. The raw data associated with the field portions of the submitted study (e.g., notes on locations of plots, plot maintenance, calibration of application equipment, stage of crop growth at each application and at time of sampling, and methods of sampling) must be submitted for each of the field trials. For guidance on number and location of field trials, the registrant should consult "EPA Guidance on Number and Location of Domestic Crop Field Trials for Establishment of Pesticide Residue Tolerances" (E. Saito and E. Zager, 6/2/94). For guidance on which raw data should be submitted, the registrant should consult "Guidance on Submission of Raw Data" (D. Edwards and E. Zager, 7/14/93).
- 3b. The submitted field trial data indicate that the uncorrected combined residues of mancozeb and ETU were 4.83-6.45 ppm in/on almond hulls and nondetectable (<0.06 ppm) in/on almond nutmeats harvested 136-161 days following the last of 3 applications of the 80% WP or 75% DF formulation at 4.8 lb ai/A/application (1x the proposed maximum seasonal rate).
4. When the deficiencies discussed above have been adequately fulfilled, the registrant should submit a revised Section F to reflect proposals for tolerances for the combined residues of mancozeb and ETU in/on "almonds, nutmeats" and "almonds, hulls."

If you need additional input please advise.

Attachment 1: Mancozeb Petition Review

cc (With Attachment 1): RBP, Mancozeb Reregistration
Standard File, Mancozeb Subject File, RF, Circ., E. Saito RB/SRRD
and Dynamac.

MANCOZEB



Shaughnessy No. 014504; Case 0643

(CBRS No. 13536; DP Barcode No. D201278)

PP#4F04324

REGISTRANT'S PETITION IN SUPPORT OF TOLERANCE ESTABLISHMENT

BACKGROUND

Rohm and Haas Co. proposes the establishment of tolerances for residues of mancozeb in/on almond nutmeats at 0.1 ppm and almond hulls at 10 ppm. To support these tolerance proposals, the registrant cited previously submitted field residue data for almonds (1990; MRID 43018401). These data have not been reviewed and are reviewed here for adequacy in supporting the proposed tolerances.

Tolerances for residues of mancozeb in/on raw agricultural and processed commodities are currently expressed in terms of residues of a fungicide which is a coordination product of zinc ion and maneb (manganous ethylene bisdithiocarbamate) containing 20 percent manganese, 2.5 percent zinc, and 77.5 percent ethylene-bisdithiocarbamate (the whole product calculated as zinc ethylenebisdithiocarbamate) [40 CFR §180.176, §180.319, §185.6300, and §186.6300].

Mancozeb is a List A chemical. A Mancozeb Reregistration Standard (Guidance Document) was issued 3/87, and a Reregistration Standard Update was issued 8/11/92. The EBDC PD 4 (57 FR 7484, 3/2/92) concluded that uses of mancozeb on the following food/feed crops would be eligible for reregistration: apples, asparagus, bananas, barley, corn (field, pop, and sweet), cotton, crabapples, cranberries, cucumbers, fennel, grapes, melons (cantaloupe, casaba, crenshaw, honeydew, and watermelon), oats, onions (dry bulb only), papaya, peanuts, pineapples, potatoes, quince, rye, sugar beets, squash (summer only), tomatoes, and wheat.

CONCLUSIONS

1. No storage stability data were submitted with this petition. Supporting storage stability data reflecting the stability of residues of mancozeb and ETU in/on almond nutmeats and hulls stored frozen up to 285 days must be submitted. In addition, the registrant must provide additional information regarding dates of sample shipment and the temperature of sample storage at the laboratory.
2. No minimum retreatment interval was specified in the proposed use pattern. The registrant must submit a revised section B specifying a minimum retreatment interval.
- 3a. The submitted field trial data are inadequate to support the tolerance petition because insufficient field trials were conducted, and no raw data pertaining to the field portion of the study were submitted. A minimum of 5 additional trials must be conducted with the FIC formulation. Concurrent storage stability studies should be performed with these trials. The raw data associated with the field portions of the submitted study (e.g., notes on locations of plots, plot maintenance, calibration of application equipment, stage of crop growth at each application and at time of sampling, and methods of sampling) must be submitted for each of the field trials. For guidance on number and location of field trials, the registrant should consult "EPA Guidance on Number and Location of Domestic Crop Field Trials for Establishment of Pesticide Residue Tolerances" (E. Saito and E. Zager, 6/2/94). For guidance on which raw data should be submitted, the registrant should consult "Guidance on Submission of Raw Data" (D. Edwards and E. Zager, 7/14/93).
- 3b. The submitted field trial data indicate that the uncorrected combined residues of mancozeb and ETU were 4.83-6.45 ppm in/on almond hulls and nondetectable (<0.06 ppm) in/on almond nutmeats harvested 136-161 days following the last of 3 applications of the 80% WP or 75% DF formulation at 4.8 lb ai/A/application (1x the proposed maximum seasonal rate).
4. When the deficiencies discussed above have been adequately fulfilled, the registrant should submit a revised Section F to reflect proposals for tolerances for the combined residues of mancozeb and ETU in/on "almonds, nutmeats" and "almonds, hulls."

RECOMMENDATIONS

CBRS recommends against the establishment of the proposed tolerances for the residues of mancozeb in/on almond nutmeats and hulls at 0.1 and 10 ppm, respectively, because of the deficiencies cited in Conclusions 1, 2, 3a, and 4 above. The registrant should adequately address each of these issues before the present petition can be favorably granted.

DETAILED CONSIDERATIONS

Plant and Animal Metabolism

The qualitative nature of mancozeb residues in plants and livestock is adequately understood. Mancozeb and ETU are the residues of concern (refer to the discussion in CBRS No. 12268, DP Barcode D193431, R. Perfetti, 10/4/93). The Agency has recommended that the tolerance expression for mancozeb be revised to include residues of ETU.

Residue Analytical Methods

Adequate methods are available for mancozeb data collection and tolerance enforcement. The Pesticide Analytical Manual (PAM), Vol. II lists a colorimetric method (designated as Method III), based on the Keppel method (JAOAC, 54:528-532) for the enforcement of tolerances for residues of mancozeb. The Mancozeb Reregistration Standard Update, dated 8/11/92, concluded that analytical methods converting EBDCs and some metabolites to carbon disulfide will be considered adequate for enforcement, along with a specific method for ETU.

Samples of almonds and almond hulls from the submitted field trials were analyzed for residues of mancozeb and ETU by Enviro-Bio-Tech Ltd. (Bernville, PA) using colorimetric (EBT-201.00) and GC (EBT-200.02) methods, respectively. The colorimetric method for determination of mancozeb residues is based on the Keppel method (PAM Vol. II, Method III). Briefly, samples are refluxed in dilute acid and the evolved CS₂ is trapped and reacted with a copper complex to form a yellow compound, which is measured colorimetrically at 435 nm. The limit of detection was 0.05 ppm.

The GC method for determination of ETU residues is based on the method of Onley and Yip and is similar to the ETU methods discussed in the Mancozeb Reregistration Standard Update, dated 8/11/92. Briefly, residues in samples are extracted with methanol. The methanol extract is concentrated by rotary evaporation and cleaned up on an aluminum oxide column by elution with methanol. The extract is then derivatized with 1-bromobutane to form butyl-ETU, which is extracted with chloroform, partitioned into toluene, and analyzed by GC using flame photometric detection (FPD) in the sulfur mode. The limit of detection was 0.01 ppm.

Concurrent method recoveries of mancozeb and ETU from samples of untreated almond nutmeats and hulls were determined; these data are presented in Table 1 and were corrected for apparent residues in untreated, unfortified samples. The submitted method recovery data indicate that the colorimetric and GC/FPD methods are adequate for data collection of mancozeb and ETU residues, respectively, in/on almond nutmeats and hulls.

Table 1. Concurrent method recoveries of mancozeb and ETU from samples of almond nutmeats and almond hulls fortified separately with mancozeb and ETU.

Commodity	Mancozeb		ETU	
	Fortification level, ppm	Recovery, % ^a	Fortification level, ppm	Recovery, % ^a
Nutmeats	0.05	89.0-94.4 (5)	0.01	75.5-115.0 (5)
	0.10	89.2-94.4 (5)	0.10	73.0-100.0 (5)
Hulls	0.05	84.0-94.6 (5)	0.01	81.5-97.5 (5)
	5.00	91.5 (1)	0.10	77.0-107.0 (5)
	6.00	93.2-95.2 (4)	--	--

^a Number of samples in parentheses.

Storage Stability Data

Samples from the submitted field trials were shipped frozen to Rohm and Haas (Spring House, PA) by overnight delivery and stored frozen at ca. -10 C for an unspecified period prior to shipment to Enviro-Bio-Tech for analysis. At Enviro-Bio-Tech, samples were stored frozen (temperature unspecified) prior to analysis. Total storage intervals between harvest and analysis were 238-285 days.

No storage stability data were submitted to support the field trial data. Supporting storage stability data reflecting the stability of residues of mancozeb and ETU in/on almond nutmeats and hulls stored up to 285 days must be submitted. In addition, the registrant must provide additional information regarding dates of sample shipment and the temperature of sample storage at the laboratory.

Proposed Use Patterns

Rohm and Haas proposes to add uses of mancozeb on almonds to the following product labels:

Product Name	Formulation	EPA Reg. No.
Dithane M-45 Agricultural Fungicide	80% WP	EPA Reg. No. 707-78
Dithane F-45 Flowable Mancozeb Agricultural Fungicide	37% FIC	EPA Reg. No. 707-156
Dithane M-45 Flowable M Agricultural Fungicide	32% FIC	EPA Reg. No. 707-162
Dithane DF/70 Agricultural Fungicide	70% DF	EPA Reg. No. 707-179
Dithane DF Agricultural Fungicide	75% DF	EPA Reg. No. 707-180

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The registrant proposes a use pattern of a maximum of 3 applications at 4.8 lb ai/A/application with a PHI of 5 weeks after petal fall. No minimum retreatment interval was specified. The registrant must submit a revised section B specifying a minimum retreatment interval. The maneb use pattern for almonds, as specified in the EBDC PD, is a maximum of 4 applications per season at 6.4 lb ai/A/application, with a minimum retreatment interval of 7 days and a PHI of 5 weeks after petal fall.

The registrant proposes tolerances for residues of mancozeb in/on almond nuts and hulls of 0.1 and 10 ppm, respectively. The Agency has recommended that the current tolerance expression for mancozeb be revised to include residues of ETU. Therefore, the registrant should submit a revised Section F to reflect proposals for tolerances for the combined residues of mancozeb and ETU in/on "almonds, nutmeats" and "almonds, hulls."

Magnitude of the Residue in Almond Nutmeats and Hulls

To support these tolerance proposals, the registrant cited previously submitted field residue data for almonds (1990; MRID 43018401). Five field trials were conducted in CA in 1988; at each trial, almonds were treated with 3 applications of the 80% WP or 75% DF formulation at 4.8 lb ai/A/application, with retreatment intervals of 8-19 days, for a total seasonal rate of 14.4 lb ai/A (1x the proposed maximum seasonal rate). Samples were harvested 136-161 days following the final application and were stored frozen for 238-285 days prior to analysis. No field reports were provided in the submission.

The results of the field trials are presented in Table 2. Both corrected and uncorrected (for concurrent method recovery) residue values are reported. Apparent residues of mancozeb and ETU were nondetectable (<0.05 and <0.01 ppm, respectively) in/on 5 samples each of untreated almond nutmeats and hulls.

Table 2. Residues of mancozeb and ETU in/on almond nutmeats and hulls, grown in CA, following 3 applications of the 80% WP or 75% DF formulation at 4.8 lb ai/A/application (1x the proposed maximum seasonal rate).

Commodity	Form.	PTI ^a	Residues, ppm ^b					
			Mancozeb		ETU		Combined	
			Corr. ^c	Uncorr.	Corr. ^d	Uncorr.	Corr.	Uncorr.
Nutmeats	WP	136	<0.05	<0.05	<0.01	<0.01	<0.06	<0.06
			<0.05	<0.05	<0.01	<0.01	<0.06	<0.06
	WP	160	<0.05	<0.05	<0.01	<0.01	<0.06	<0.06
			<0.05	<0.05	<0.01	<0.01	<0.06	<0.06
	WP	161	<0.05	<0.05	<0.01	<0.01	<0.06	<0.06
DF	160	<0.05	<0.05	<0.01	<0.01	<0.06	<0.06	
		<0.05	<0.05	<0.01	<0.01	<0.06	<0.06	
DF	161	<0.05	<0.05	<0.01	<0.01	<0.06	<0.06	
		<0.05	<0.05	<0.01	<0.01	<0.06	<0.06	
Hulls	WP	136	4.94	4.64	0.206	0.183	5.15	4.83
			5.47	5.14	0.178	0.158	5.65	5.30
	WP	160	5.55	5.22	0.439	0.391	5.99	5.61
			6.36	5.98	0.529	0.471	6.89	6.45
	WP	161	5.05	4.75	0.223	0.198	5.27	4.95
			5.74	5.40	0.257	0.229	6.00	5.63
	DF	160	5.97	5.61	0.349	0.311	6.32	5.92
			6.26	5.88	0.512	0.456	6.77	6.34
	DF	161	5.16	4.85	0.120	0.107	5.28	4.96
			5.89	5.54	0.192	0.171	6.08	5.71

^a Posttreatment interval.

^b Each residue value represents one sample.

^c Residues were corrected for average concurrent method recovery of 94%.

^d Residues were corrected for average concurrent method recovery of 89%.

The submitted field trial data are inadequate to support the tolerance petition because insufficient field trials were conducted, and no raw data pertaining to the field portion of the study were submitted. A minimum of 5 trials with each of the proposed formulations is required to establish a tolerance for almonds; data for a WP formulation can be translated to a DF formulation. Therefore, 5 additional trials must be conducted with the FIC formulation. Concurrent storage stability studies should be performed with these trials. The raw data associated with the field portions of the study (e.g., notes on locations of plots, plot maintenance, calibration of application equipment, stage of crop growth at each application and at time of sampling, and methods of sampling,) must be submitted for each of the field trials. For guidance on number and location of field trials, the registrant should consult "EPA Guidance on Number and Location of Domestic Crop Field Trials for Establishment of Pesticide Residue Tolerances" (E. Saito and E. Zager, 6/2/94). For guidance on which raw

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The submitted field trial data indicate that the uncorrected combined residues of mancozeb and ETU were 4.83-6.45 ppm in/on almond hulls and nondetectable (<0.06 ppm) in/on almond nutmeats harvested 136-161 days following the last of 3 applications of the 80% WP or 75% DF formulation at 4.8 lb ai/A/application (1x the proposed maximum seasonal rate).

EPA MEMORANDA CITED IN THIS REVIEW

CBRS No.: 12268
DP Barcode: D193431
Subject: Response to Mancozeb Reregistration Standard: Plant and Livestock
Metabolism Upgrades
From: R. Perfetti
To: L. Rossi and E. Saito
Dated: 10/4/93
MRID(s): 42840501

MASTER RECORD IDENTIFICATION NUMBERS

The citation for the MRID document reviewed in this document is presented below.

43018401 Satterthwaite, S. (1990) Mancozeb and ETU Residues in Almonds: Lab Project
Number: 34A-90-12. Unpublished study prepared by Enviro-Bio-Tech, Ltd. 206 p.